TECHNICAL REQUIREMENTS

NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER: PRINCIPLES AND PRACTICES

-FINAL-

May 1999

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(RTDF)

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FOREWORD

This Principles and Practices Document was prepared by the Industrial Members of the Bioremediation of Chlorinated Solvents Consortium of the Remediation Technologies Development Forum (RTDF) to disseminate up-to-date scientific information regarding **natural attenuation** (also referred to as **intrinsic remediation**) of **chlorinated solvents**. This information was assembled from research activities of the RTDF and from the experience and knowledge of the following participating companies and organizations of the RTDF Bioconsortium: Beak International, Dow Chemical Company, DuPont Company, General Electric Company, Imperial Chemical Industries, Monsanto Company, Novartis, and Zeneca Inc.

The RTDF is a public and private sector collaboration to develop innovative solutions to complex hazardous waste problems. The mission of the RTDF Bioconsortium is to accelerate the development of cost-effective bioremediation processes for degrading chlorinated solvents and to achieve public and regulatory acceptance that these processes are safe and effective.

The industrial members of the RTDF intend for this document to be as consistent as possible with the Air Force Center for Environmental Excellence and United States Environmental Protection Agency (AFCEE/EPA) Protocol which is currently under development. However, this document is not a “how to” manual; its purpose is to provide a "framework" to evaluate natural attenuation of chlorinated volatile organic compounds (VOC), that is, how to think about natural attenuation based on science. As a scientific document, its intent is not to dispense regulatory information. A separate document that provides the industrial members of the RTDF responses to reviews of previous versions of this document, issues requiring further discussion, and planned future revisions/additions to the document, is also available to the public.

ACKNOWLEDGMENTS

The RTDF appreciates the efforts of the following individuals in preparing this document: Dr. David Major, Evan Cox, and Dr. Leo Lehmicke of Beak International; Dr. David Ellis, Dr. Ron Buchanan, Ed Lutz, and Dr. Mike Lee of DuPont; Dr. Joseph Salvo, Dr. Jay Spivak, and Dr. Mark Harkness of General Electric Company; and Dr. Gary Klecka of Dow Chemical Company.

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INTRODUCTION

Q 1: What is natural attenuation?

A 1: Natural attenuation (also known as intrinsic remediation or natural restoration) was defined by the Office of Solid Waste and Emergency Response (OSWER) of the EPA as follows:

> *The term "natural attenuation" refers to naturally-occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media. These in-situ processes include biodegradation, dispersion, dilution, adsorption, volatilization and chemical or biological stabilization or destruction of contaminants.*

Simply stated, natural attenuation would be an accepted remedy when physical, chemical, and/or biological processes act to reduce the mass, toxicity, and/or mobility of subsurface contamination in a way that reduces risk to human health and the environment to acceptable levels.

The National Contingency Plan permits the use of natural attenuation as a remedy or a portion of a remedy for Superfund sites. In addition, several states (e.g., New Jersey, South Carolina, Wisconsin) have developed regulations and/or guidance regarding the evaluation and implementation of natural attenuation.

Q 2: Is natural attenuation a "do nothing" approach?

A 2: Natural attenuation is <u>not</u> a "do nothing" approach because it involves:

- Characterizing the fate and transport of the chlorinated solvents to evaluate the nature and extent of the natural attenuation processes;
- Ensuring that these processes reduce the mass, toxicity and/or mobility of subsurface contamination in a way that reduces risk to human health and the environment to acceptable levels;
- Evaluating the factors that will affect the long-term performance of natural attenuation; and

- Monitoring of the natural processes to ensure their continued effectiveness.

Q 3: How often is natural attenuation effective?

A 3: It has been estimated by the EPA (J. Wilson, pers. comm.) that natural attenuation will be effective as the sole remedy at approximately 20% of all chlorinated solvent sites. It has also been estimated that natural attenuation may serve as a portion of the remedy at an additional 50% of all chlorinated solvent sites (Ellis et al., 1996).

Q 4: Why should natural attenuation be evaluated?

A 4: Natural attenuation should be evaluated at chlorinated solvent sites because it is:

- A common sense approach to protect human health and the environment;
- A cost-effective alternative that can be used as a stand-alone technology or in association with other remediation technologies to reduce overall remediation costs;
- Minimally intrusive and usually less disruptive of facility operations and infrastructure compared to most remediation technologies; and
- Important to understand natural geochemical processes before implementing any remedial measure.

The advantages and disadvantages of natural attenuation are listed in Table 1.

Q 5: What is the intent of this Principles and Practices Document?

A 5: The intent of this document is to:

- Distill the practical aspects of the current state of the science into a framework to efficiently and economically assess natural attenuation;
- Develop a document that describes the status and benefit of natural attenuation in layman's terms and can be continually updated as new information becomes available and as feedback from stakeholders is received;
- Guide readers on how to easily integrate natural attenuation into new and/or ongoing site characterization or groundwater monitoring programs;
- Provide guidance to the public, regulators, site managers, and practitioners on how to evaluate, interpret, and validate the contribution of natural attenuation of chlorinated solvents; and

- Reference appropriate sampling and interpretation protocols and guide readers to other relevant materials.

These goals will allow the RTDF Bioconsortium to keep pace with the rapid advances in the science and knowledge that serves as the basis of this technology and to update the document on the world wide web (http://www.rtdf.org) and in print form. In the near future, the RTDF Bioconsortium will also publish documents on two other technologies: **accelerated anaerobic bioremediation** and **co-metabolic bioventing**

Q 6: Who should read/use this Principles and Practices Document?

A 6: This document has been designed to be a valuable resource tool for the public, regulators, site managers, and practitioners

Q 7: How is the Principles and Practices Document Organized?

A 7: The Document is divided into four topic sections. The first section titled "Introduction" provides information on the intent of the document, who should read/use it, what natural attenuation is and why it should be considered. The second section titled "Background" provides information regarding the technical challenges associated with sites contaminated with chlorinated solvents and the types of chlorinated solvent attenuation processes that are known to occur. The third section titled "Evaluating Natural Attenuation" provides information on how natural attenuation studies are generally conducted and what types of information are typically required to document natural attenuation. The fourth section titled "Methods" presents a step-wise process, accompanied by a flow chart that can be used to evaluate and implement natural attenuation at sites contaminated by chlorinated solvents.

Q 8: Where can key terms and definitions be found?

A 8: Appendix A provides a glossary of key terms that are commonly used in natural attenuation of chlorinated solvents. Words that appear in bold type in this document are defined in the glossary. Appendix E contains a list of acronyms that are used throughout this document.

BACKGROUND

Q 9: Why is this document focusing on chlorinated solvents?

A 9: Chlorinated solvents such as tetrachloroethene (also known as perchloroethene, PCE), trichloroethene (TCE), trichloroethane (TCA), and carbon tetrachloride (CT) are commonly used as degreasing agents at manufacturing, maintenance and service facilities around the world. They are among the most common soil and groundwater contaminants. Some of these chlorinated compounds and some of their degradation intermediates may be toxic or carcinogenic. Chlorinated solvents are a class of chemicals that can be amenable to natural attenuation but such naturally-occurring mechanisms have not been the subject of much research in the past. Consequently, such mechanisms have been over looked by both the regulated community and the regulators.

Q 10: What are the most common misconceptions regarding chlorinated solvents and their natural attenuation?

A 10: Three of the most common misconceptions regarding chlorinated solvents and their natural attenuation are that:

- Chlorinated solvents can be easily found and remediated;
- Only biological processes are important or should be considered; and
- More toxic intermediates are likely to accumulate.

Questions 11 through 14 address the first misconception, question 15 addresses the second misconception, and question 17 addresses the third misconception.

Q 11: What are the technical challenges associated with sites contaminated with chlorinated solvents?

A 11: The physical properties of many chlorinated solvents make them extremely difficult to locate, remove or treat in the subsurface. Chlorinated solvents can exist and migrate in multiple phases depending on how they were released and site conditions. These phases include:

- Vapor phase in unsaturated soils;

- Dissolved phase in groundwater; and

- Liquid phase in the subsurface (e.g., droplets, coatings, or pools) as shown in Figure 1. Chlorinated solvents in this phase are referred to as **nonaqueous phase liquids** (NAPL), which do not mix with water (i.e., they form a separate layer from water). NAPL that are less dense than water float on the water table and are referred to as light NAPL (LNAPL). NAPL that are denser than water sink below the water table and are referred to as dense NAPL (DNAPL). Most chlorinated solvents are DNAPL.

Q 12: What are the technical challenges associated with DNAPL?

A 12: The properties of DNAPL that make their investigation and remediation difficult and, in some cases, technically impracticable include:

- Complex Distribution: The distribution of DNAPL is strongly controlled by small variations in site geology and cannot be readily simulated or predicted. A released DNAPL will generally sink below the water table, spreading until it reaches confining layers (e.g., clay lenses, **aquitards**, **bedrock**) or becomes bound to the geologic matrix. Once below the water table, DNAPL do not necessarily move in the direction of groundwater flow. As a result, all of the DNAPL mass in the subsurface cannot be accurately located with current investigation technologies or techniques. An accurate determination of location is a prerequisite for effective source removal or treatment. The movement of DNAPL into small fractures and pore spaces in the subsurface prevents the effective removal of much of the DNAPL mass. Missing even a small amount of DNAPL mass means that recontamination of the groundwater can occur. It is estimated that at most DNAPL sites, over 99.9% of the DNAPL would have to be removed in order to approach the restoration levels needed to allow use of the aquifer as a drinking water supply (Pankow and Cherry, 1996).

- Low Solubilities: The low solubility of DNAPL means that it generally takes decades to centuries for DNAPL to dissolve into the groundwater. This significantly limits the utility of groundwater extraction and treatment as a remediation technology for cleanup of DNAPL sites.

- Slow Diffusion: The rate of diffusion from the geological matrix is much slower than the rate of sorption and diffusion onto/into the geological matrix. This means that even if free-phase DNAPL are treated, the slow diffusion out of the geological matrix may cause chlorinated solvents to be present in groundwater for long periods of time.

- Potential to Exacerbate the Problem through Investigation and Attempted Treatment: Improper drilling techniques in the vicinity of a DNAPL source area may result in penetration of an aquitard or confining layer, creating a new pathway for DNAPL to move downward. Similarly, treatment techniques such as de-watering to expose free DNAPL for vapor extraction may promote DNAPL migration by reducing their buoyancy.

Q 13: Can the presence of DNAPL be determined?

A 13: Site investigations designed to find DNAPL are generally impractical and ineffective. The presence of DNAPL should be suspected at sites where chlorinated solvents were typically used and disposed of (in tanks and/or waste ponds) as immiscible phase, unless historical records can account for waste solvent volume (e.g., recycling, off-site treatment/disposal).

Visual observation of DNAPL during the site investigation is not required to infer DNAPL presence. As a general rule, detecting chlorinated solvents in groundwater at concentrations exceeding 1% of their solubility suggests the presence of DNAPL or residuals (Pankow and Cherry, 1996).

Q 14: How does the presence of DNAPL affect site remediation strategy?

A 14: Proven, safe, and cost-effective technologies to remediate DNAPL sources in most groundwater environments are currently not available. Conventional groundwater remediation technologies in place at chlorinated solvent sites (e.g., groundwater extraction and treatment) remove solvents that have dissolved in the groundwater. These technologies employ long-term, active processes that are often costly and quickly reach a point of diminishing returns. As indicated above, small amounts of DNAPL mass can re-contaminate groundwater, generally making remediation of DNAPL sources to current regulatory criteria technically impracticable. Technical impracticability (TI) waivers are an appropriate regulatory mechanism and have been recognized by the EPA as appropriate for DNAPL sources.

Remediation/management strategies for most DNAPL sites should focus on integrating innovative, cost-effective techniques that will operate over the long term to mitigate risk to human health and the environment through containment. Natural attenuation is ideally suited for integration into long-term site management programs to address chlorinated solvents dissolved in groundwater. At some point in the future, more effective source removal or destruction technologies may become available. In the interim, mass removal via natural attenuation processes should be considered.

A thorough understanding of DNAPL is essential in any discussion of chlorinated solvents in groundwater. The reader is referred to Pankow and Cherry (1996) for detailed information on DNAPL behavior and its implications on remediation.

Q 15: What processes contribute to the natural attenuation of chlorinated solvents?

A 15: The processes that contribute to natural attenuation of chlorinated solvents include:

- **Degradation**: The degradation of most chlorinated solvents in groundwater occurs by **oxidation-reduction reactions** that are predominantly carried out by bacteria in the environment. These are referred to as **biodegradation** reactions. Biodegradation is usually the predominant process of natural attenuation at chlorinated solvent sites. Because of the significant and varied contributions of biodegradation to natural attenuation, biodegradation processes are discussed further in Questions 16 through 18. Some chlorinated solvents may also degrade by chemical reactions with metals (e.g., iron and iron-complexes) or water (e.g., hydrolysis reactions). Table 2 provides a list of case studies where degradation by theses processes have been documented to occur.

- **Advection, Dispersion, and Dilution**: Advection is the transport of molecules dissolved in water. During advection, molecules will also spread along and away from the expected groundwater flow path. This process is called dispersion and results from the mixing of groundwater (the solvent) and other molecules (the solute) in individual pores and channels. The combined processes of advection and dispersion result in a reduced concentration of the molecules (dilution) in the groundwater.

- **Diffusion**: Diffusion is a dispersive process that results from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to low concentration.

- **Sorption/Desorption**: Molecules can adsorb onto and, in some cases, be absorbed by geologic materials. Over time, these molecules will desorb from the geologic materials in response to concentration gradients. Sorption affects the advective rate of molecules dissolved in groundwater

- **Volatilization**: The transfer of a molecule from a liquid phase or an aqueous solution to the vapor phase (phase transfer) is termed volatilization. Chlorinated solvents are volatile organic compounds (VOC) that partition between liquid and gas phases, with the less chlorinated compounds having a tendency towards higher volatility. Volatilization may contribute to natural attenuation through the transfer of VOC from the liquid phase in the subsurface (NAPL, groundwater) to vapors in the vadose zone or to the atmosphere.

- **Stabilization**: Stabilization is a process whereby chemical molecules become chemically bound or transformed by a stabilizing agent (e.g., clay, humic materials), reducing the mobility of the molecule in the groundwater. It is usually a more irreversible reaction than adsorption.

The processes of advection, dispersion, dilution, diffusion, sorption/desorption, volatilization and stabilization are physical processes that are included in the EPA's definition of natural attenuation and are legitimate attenuation processes. They may have only a small impact at sites with high concentrations of chlorinated solvents, but may be sufficient, in and of themselves, at some sites where concentrations are low. A search of the EPA Record of Decision (ROD) database in 1995 using the search words "natural attenuation," "intrinsic bioremediation," and "intrinsic remediation" indicated 35 RODs in which natural attenuation or intrinsic remediation was selected as all or part of the remedy (Hagemann and Gill, 1995). Of these 35 sites, 17 had chlorinated solvents as one or more of the chemicals of concern. Review of these 17 sites indicate that physical attenuation mechanisms were the predominant removal mechanism at many of them; several sites had only parent compound at low concentrations (< 200 micrograms per liter [ug/L]).

Q 16: How do chlorinated solvents biodegrade?

A 16: Chlorinated solvents biodegrade by several processes, including:

- **Direct oxidation**, whereby the chlorinated compound is directly used as a **growth substrate** (**electron donor**/food source) and broken down to inorganic molecules such as carbon dioxide, water, and chloride;
- **Reductive dehalogenation**; whereby the chlorinated compound is converted to another chemical by replacing chlorine atoms with hydrogen atoms; and
- **Co-metabolism**, whereby the chlorinated compound is converted to another chemical while microorganisms use other carbon compounds for their growth substrate (food source).

Table 3 lists common chlorinated solvents and their current known degradation pathways. Figure 2 presents common degradation pathways for common chlorinated solvents.

In contrast to the biodegradation of **petroleum hydrocarbons**, evidence suggests that only a few chlorinated solvents can be used as growth substrates. Specific chlorinated solvents that can be directly oxidized are vinyl chloride (VC); dichloroethene (DCE); dichloromethane (DCM); chloromethane (CM); 1,2-dichloroethane (1,2-DCA); and chloroethane (see Table 3 and Figure 2). In **aerobic** environments (in the presence of oxygen which serves as the **electron acceptor**), chlorinated solvents are co-metabolized (i.e., used as a secondary food source) by non-specific microbial **oxygenase enzymes** that are produced by microorganisms to metabolize other growth substrates (e.g., methane, propane, toluene, ammonia, ethene, ethane). In **anaerobic** environments (in the absence of oxygen), chlorinated solvents act as **electron acceptors** in a process called **reductive dechlorination**, where hydrogen atoms replace chlorine atoms on the chlorinated solvent molecule. Other carbon substrates (e.g., alcohols, ketones, hydrocarbons, and/or natural organic compounds) serve as **electron donors** in these reactions. Figure 3 shows a “cut-away” of a TCE plume naturally attenuating, with reductive dechlorination being the predominant process.

It should be noted that all of the biological processes described above have been discovered since 1980. Biodegradation of chlorinated solvents is a new science and the state of the science is changing constantly; at least two new processes were documented for the first time in 1996.

Q 17: What are the products of chlorinated solvent biodegradation?

A 17: The aerobic mineralization of chlorinated solvents ultimately yields carbon dioxide, water, and chloride. Aerobic co-metabolic biodegradation of chlorinated solvents generally proceeds via an unstable epoxide intermediate that spontaneously decomposes to environmentally acceptable water-soluble products, carbon dioxide, and chloride (Roberts, et. al 1989). The aerobic oxidation of chlorinated solvents can ultimately yield carbon dioxide, water, and chloride or other organic by-products such as acetate. The anaerobic biodegradation of chlorinated solvents via sequential dechlorination of the parent chlorinated compound proceeds to non-chlorinated products such as ethene, ethane and methane. For example, the anaerobic dechlorination of PCE proceeds via TCE; 1,2-DCE (the cis-isomer is the predominant isomer formed); and VC to ethene and ethane. Each successive step in the dechlorination process is theoretically slower than the proceeding step and, therefore, at some sites, biodegradation may not proceed to completion. As a result, intermediate compounds (e.g., DCE) may accumulate. For a long time, it was commonly believed that VC would accumulate. However, it is now known that VC can be biodegraded under almost all of the potential conditions found in the subsurface because it can undergo direct biodegradation under both aerobic and anaerobic conditions. Complete dechlorination products such as ethene or chloride are not deemed to be a problem. For example, the maximum contaminant level (MCL) for chloride is 1,000 mg/l. TCE biodegradation in the 100 mg/l range would result in the slow release of approximately 80 mg/l of chloride over a long period of time.

Q 18: Are all of the appropriate bacteria present at every site?

A 18: In general, all "types" of bacteria (e.g., aerobic, anaerobic) are present at all sites. However, all bacteria involved in all of the potential biodegradation pathways for chlorinated solvents are not necessarily present at every site. For example, it is believed that all of the bacteria needed for the reductive dechlorination of PCE or TCE to DCE are present at approximately 90% of all sites, and all of the bacteria needed for the reductive dechlorination of PCE or TCE to ethene are present at approximately 75% of all sites.

EVALUATING NATURAL ATTENUATION

Q 19: When should natural attenuation be evaluated?

A 19: Natural attenuation should be evaluated to some degree at every site, preferably early in the site investigation process. It is important to understand the natural attenuation processes before implementing any remedial measure. A thorough understanding of natural attenuation processes is necessary if natural attenuation is to be implemented as the remedy, a portion of the remedy, or when an alternative remedy such as enhanced bioremediation is being considered. Natural attenuation should be evaluated thoroughly when:

- Natural attenuation processes are observed or strongly expected to be occurring; and
- There are no human or ecological receptors that are likely to be impacted or potential receptors in the vicinity of the plume are, or can be protected.

In addition, natural attenuation should be considered as the remedy or portion thereof when:

- It is protective of human health and the environment;
- A continuing source that cannot cost effectively be removed or contained will require a long-term remedial effort;
- Alternative remediation technologies are not cost-effective or are technically impracticable; and
- Alternative remedial technologies pose significant added risk by transferring contaminants to other environmental media, spreading contamination or disrupting adjacent ecosystems.

Q 20: When should natural attenuation <u>not</u> be considered in the remedy?

A 20: Natural attenuation should <u>not</u> be considered as the remedy or a portion of the remedy when natural attenuation will not be protective of human health and the environment or alternative remediation technologies can more reliably and cost-effectively treat the contaminants to minimize risk. Comparative costs for different technologies are presented in Table 4.

In some instances, specific regulatory guidelines or the desires of regulatory agencies at a specific site may prevent the use of natural attenuation even though it may be sufficiently protective of human health and the environment.

Q 21: What evidence is required to evaluate and implement natural attenuation?

A 21: Natural attenuation is generally evaluated using a "lines of evidence" approach. This approach forms the basis for all current protocols and guidance documents. The suggested lines of evidence are:

1. Documented reduction of contaminant mass at the site;
2. Presence and distribution of **geochemical** and **biochemical** indicators of natural attenuation; and

3. Direct microbiological evidence.

Q 22: How are the three lines of evidence documented?

A 22: Typically, the first line of evidence (i.e., loss of contaminants) is documented by reviewing historical trends in contaminant concentration and distribution in conjunction with site geology and hydrogeology to show that a reduction in the total mass of contaminants is occurring at the site. This mass loss may be in the source area and/or along the groundwater flowpath. Because most chlorinated solvents do not biodegrade on their own like petroleum hydrocarbons, biodegradation rates are more site-specific (e.g., dependent on redox conditions, electron donor concentration). Therefore, it is more important to estimate a biodegradation rate at chlorinated solvent sites from field data (Buscheck and Alcantar 1995; Weaver et.al 1996).

The second line of evidence is documented by examining changes in the concentrations and distributions of geochemical and biochemical indicator parameters that have been shown to be related to specific natural attenuation processes.

The third line of evidence (i.e., microbiological evidence) is documented through laboratory microcosm studies and is used to: 1) confirm specific chlorinated solvent biodegradation processes that cannot be conclusively demonstrated with field data alone (e.g. anaerobic VC oxidation) and/or 2) estimate site-specific biodegradation rates that cannot be conclusively demonstrated with field data alone. The need to collect the third line of evidence is evaluated on a case-by-case basis and is generally only required when field data supporting the first two lines of evidence are insufficient to adequately support natural attenuation.

Q 23: What data are required to support the three lines of evidence?

A 23: The types of data that are required to support the three lines of evidence depend on the type of site and the nature and extent of attenuation processes that are occurring. Table 5 summarizes several common patterns of chlorinate solvents in groundwater including their distribution and relates these patterns to suggested data collection tiers to support natural attenuation. The conceptual model for a given site can be compared to these common patterns to determine what data collection tier is appropriate to evaluate and support the lines of evidence approach. The specific data that should be collected for each data collection tier are listed in Table 6. Information on the ideal use of each parameter in evaluating natural attenuation and the status of its measurement (e.g., commercially available or research) is also provided in Table 6.

The list of parameters for each tier has been developed based on the experience of the authors. Collection of all parameters may not be required for all sites. The reader may benefit from customizing the data collection tiers to suit specific site conditions.

METHODS

This section provides the reader with a step-wise framework that can be used to review data for a given chlorinated solvent site, evaluate whether the natural attenuation of chlorinated VOC is occurring, identify and collect additional data that support the three lines of evidence of natural attenuation, and integrate natural attenuation into a long-term site remediation/management strategy. It is anticipated that these activities can be conducted concurrent with other investigation and remediation planning activities. Figure 4 summarizes this information in a flowchart format.

Step 1. Review Available Site Data

The first step in evaluating natural attenuation is to review available site data. For Superfund sites, data is typically available from Remedial Investigation (RI), Risk Assessment, and Feasibility Study (FS) documents. For Resource Conservation and Recovery Act (RCRA) facilities, data will typically be available from RCRA Facility Investigation (RFI) and Corrective Measures Study (CMS) documents, and/or RCRA Alternate Concentration Limit Demonstration reports. Monitoring reports for existing remediation systems may also be available for review. It is important to identify potential receptor exposure points (e.g., drinking water wells, surface or groundwater discharge points) at this time if not yet identified.

Site characterization is necessary for sites with insufficient data. Appendix B references site investigation protocols. Evaluating natural attenuation should be incorporated into the site investigation at uncharacterized sites since the costs of collecting the additional data to evaluate natural attenuation are outweighed by the cost savings that may be realized if natural attenuation is integrated into the long-term site remediation strategy. Step 4 discusses the level of natural attenuation data that should be collected at uncharacterized sites.

Step 2. Review/Develop the Site Conceptual Model

Review the available data to determine whether a **site conceptual model** has been developed. The site conceptual model is a representation of the site-specific groundwater flow and solute transport system. This model is typically used to:

- Present and explain chemical distributions in the site groundwater in relation to groundwater flow and transport processes; and

- Facilitate the identification of risk assessment elements used in exposure analysis, including sources, release mechanisms, transport pathways, exposure points, and potential receptors.

RI documents typically present a site conceptual model that is based on available geological, hydrogeological and chemical data. These models generally do not adequately integrate chemical fate due to degradation (biological and abiotic) processes, and these processes are very site-specific for chlorinated solvents. However, as they exist, site conceptual models are useful to identify:

- Reduction of chemical mass in relation to groundwater flow and transport;
- Locations at the site (relative to sources, receptors or site boundaries) where additional data is required to document reduction of chemical mass and presence of geochemical indicators of natural attenuation processes; and
- Specific types of data that should be collected at the locations selected.

A site conceptual model is necessary if it is not presented in the available site documents. Appendix B references protocols for conceptual model development.

Step 3. Screen the Data for Evidence of Natural Attenuation and Develop Hypothesis to Explain the Attenuation Processes.

The available site data and site conceptual model should be screened both to assess whether natural attenuation is occurring and to develop a hypothesis regarding the processes that are promoting the attenuation. Screening for natural attenuation can be conducted by reviewing the information and answering the following questions:

1. Do the existing data provide evidence for reduction of chemical mass (line of evidence #1)?
    - Have concentrations of known or suspected parent chlorinated solvents decreased over time?
    - Do observed chlorinated solvent distributions differ (decrease along the flow path) from distributions predicted from expected transport in groundwater?
2. Do the existing data provide evidence for the presence of geochemical or biochemical indicators of natural attenuation (line of evidence #2)?
    - Are known degradation products (e.g., cis-1,2-DCE, VC, or ethene at a TCE site, see Table 5) present in the groundwater? Have ratios of dechlorination daughter products to parent solvents increased over time and is cis-1,2-DCE the predominant DCE isomer?

- Do available data indicate production or consumption of carbon sources or production of inorganic constituents consistent with known biodegradation reactions (e.g., increased alkalinity, chloride and/or dissolved iron concentrations in source area wells)?

Yes answers to any/all of these questions typically indicates that biodegradation processes are occurring and should be further evaluated following Steps 4 through 9. Figures 5 and 6 provide examples (accompanied by explanations) of several common patterns of chlorinated solvent biodegradation in anaerobic and sequential anaerobic/aerobic systems, respectively. Sites where screening does not indicate the occurrence of these **biological** processes may still be candidates for natural attenuation, depending on the results of exposure pathways analysis, and should be further evaluated by advancing to Step 8.

Step 4. Identify Additional Data Requirements

Identification and selection of additional data to test the natural attenuation hypothesis and support the lines of evidence approach is a site-specific process. However, the process can generally be conducted as follows:

1. Compare the conceptual model for the given site to the common patterns of chlorinated solvent presence and distribution presented in Table 5. Select the pattern that best approximates conditions at the given site and identify the suggested data collection tier. Using Table 6, identify the specific data parameters that correspond to the selected data collection tier. As an example, the conceptual model for a site having 1,2-DCE and VC in the groundwater near a TCE storage or disposal area should be similar to Pattern 3 and would warrant collection of Tier 2 data.

2. Select locations for additional data collection based on the site conceptual model. Locations should be selected to represent upgradient (background), lateral, source and several downgradient conditions, including at least one well beyond the terminus (toe) of the VOC plume. For sites having significant vertical flow components, locations should be selected to represent the vertical profile as well. The adequacy of existing well coverage to test/support the natural attenuation hypothesis should be evaluated. Additional monitoring locations may need to be installed to adequately test/support the natural attenuation hypothesis. For example, the capacity of the natural system to degrade chlorinated hydrocarbons that are directly oxidized is almost totally dependent on the amount of electron acceptors in background groundwater just as it is with petroleum hydrocarbons; therefore, the need for a true “background” well is important. However, the installation of new wells in what might be considered the “source area” at a DNAPL site is highly discouraged (see Chapter 13 of Pankow and Cherry , 1996).

3. Critically evaluate the need for microcosm studies. Microcosm studies provide direct microbiological evidence and are used to: 1) confirm specific chlorinated solvent

biodegradation processes and/or 2) estimate site-specific biodegradation rates that can not be conclusively demonstrated with field data alone. Because microcosm studies are both expensive and time consuming, they should only be performed when the information cannot be obtained from field data. Microcosm studies are designed using aquifer sediment and groundwater samples collected from the site and should provide direct evidence for natural attenuation of chlorinated solvents under simulated redox conditions that occur at the site. If these studies are required, they can also be used to characterize: i) soil adsorption potential; ii) mass balance; iii) the role of available electron donors/co-metabolites in supporting natural attenuation processes; and iv) factors that may affect/inhibit natural attenuation over time, including the ability to enhance the natural processes.

For uncharacterized sites, a minimum of Tier 1 data should be collected during site characterization to evaluate the potential for natural attenuation. An evaluation of site use history should indicate whether Tier 2 or Tier 3 data should also be collected. For example, if site records indicate that waste solvents (e.g., TCE) were used and disposed of along with sewage, petroleum hydrocarbons, or other solvents (e.g., acetone, methanol, methylene chloride), then it is likely that some degree of intrinsic biodegradation has occurred; therefore, collection of Tier 2 or 3 data during site characterization may be warranted.

Step 5. Collect Additional Data

Data should be collected following appropriate protocols to ensure the quality and integrity of the data. Appendix B is a resource guide that references accepted protocols for well installation and development, well purging and sampling, field parameter measurement, chemical and microbial analyses, and QA/QC procedures.

Step 6. Refine the Site Conceptual Model

The site conceptual model should be refined by incorporating new data and reinterpreting site conditions as indicated below. Appendix B references protocols for tasks listed below (e.g., calculation, modeling).

1. Reconstruct:

   - Potentiometric surface (water table) maps with updated data and data from any new monitoring points to assess lateral components of groundwater flow.
   - Hydrogeologic cross-sections parallel and perpendicular to the groundwater flow path with updated data and data from new monitoring points to assess vertical (upward/downward) components of groundwater flow.

- Isopleth contour maps and vertical cross sections (if warranted) of key groundwater chemistry parameters. Maps existing for the initial site conceptual model (e.g., VOC, possibly anions) should be updated to include new data. Maps should be prepared for new data parameters [e.g., degradation products, redox parameters, electron donors/co-metabolites, electron acceptors, conservative tracers (chloride)].

- Plots of concentration versus time or concentration versus distance for key groundwater chemistry parameters for wells located on the groundwater flowpath(s).

2. Estimate:

   - Mass balance for parent and daughter products, including both metabolic intermediates (e.g., DCE, VC) and final products (e.g., ethene, ethane, methane, inorganic chloride).

   - Flux of parent and daughter products and, if possible, electron donors, electron acceptors, and co-metabolites.

   - Sorption and retardation of chemicals (from literature or laboratory tests).

   - Biodegradation kinetics such as half-life or degradation rate constants. Biodegradation kinetics can be estimated by evaluating field data (changes in concentration over distance) or laboratory microcosm studies.

   - Estimate the long-term capacity of the aquifer to sustain natural attenuation (e.g., half-life/degradation rate of electron donors/acceptors/co-metabolites promoting degradation).

3. Conduct:

   - Fate and transport modeling if the site hydrogeology is complex enough to warrant the effort to better understand the flow regime. Groundwater fate and transport models are currently available to simulate groundwater flow and solute transport (see Appendix B). Models incorporating biodegradation kinetics for natural attenuation of chlorinated solvents are currently under development.

   - Compare concentration profiles generated for various time intervals in model simulations conducted with and without incorporating biodegradation kinetics.

   - Perform a sensitivity analysis for key geological, hydrogeological, and attenuation factors. Assess the need to refine the available data.

Step 7. Interpret the Data and Test/Refine Conceptual Model

Review the refined site conceptual model and determine whether the data fit this conceptual model.

If the data support the natural attenuation hypothesis developed in Step 3 (i.e., distributions of parent and daughter products are consistent with redox and distribution of electron donors/acceptors, metabolic products and site hydrogeology), then exposure pathways analysis should be conducted (Step 8).

If data do not support the hypothesis developed in Step 3 (i.e., the redox and/or distributions of electron donors/acceptors or metabolic products do not support the distribution of parent and daughter products), then the hypothesis should be refined and re-tested. In most cases, the available data is sufficient to test new or refined hypotheses. However, some additional data collection (a return to Step 4) may be required to test new/refined hypotheses at complex sites.

Step 8. Conduct an Exposure Pathway Analysis

The refined conceptual model should be examined in association with identified human and ecological risks and the following questions should be answered:

- Are the rates of natural attenuation processes sufficient to reduce risk (now and in the future) to human and ecological receptors to acceptable levels?

If yes, then the site is a strong candidate for a natural attenuation alternative and implementation of natural attenuation should be considered as discussed in Step 9. If no:

- Can other engineering controls or technologies control or further reduce this risk such that natural attenuation is sufficient?

If yes, then these options should be further evaluated/implemented. Integration of natural attenuation into the overall remediation strategy should then be considered where it may be cost-effective. If implementation of engineering controls is technically impracticable (e.g., at some DNAPL sites), then natural attenuation may be the primary mechanism of risk reduction and therefore natural attenuation should be incorporated into the long-term site management strategy.

Step 9. If Accepted, Integrate Natural Attenuation into the Long-Term Site Management Strategy

The long-term prognosis of natural attenuation should be assessed by answering the following question:

- Will factors promoting natural attenuation be sustained over the long term (e.g., is the amount of available electron donor/acceptor/co-metabolite sufficient to maintain intrinsic degradation or will additional electron donor need to be added at a later date, and when)?

If yes, then develop a strategy for long-term management that incorporates monitoring and process validation to ensure that regulatory requirements are met (e.g., no adverse impact). If no, evaluate whether it will be possible to enhance the naturally occurring processes in the future (at such time this is required) or whether other remediation technologies can be implemented currently or at a later date to support natural attenuation. A backup remedial technology should be selected at a conceptual level along with natural attenuation even when natural attenuation is selected as the sole remedy.

Findings and the proposed strategy should be presented to regulatory agencies (and the public where appropriate) and final acceptance should be pursued. Upon acceptance, a natural attenuation strategy should be implemented. This final step occurs here exactly as in the AFCEE protocol. In the future, when natural attenuation is as accepted a technology as others currently in use, this step will belong here. In the interim, it is highly recommended that any proponent of natural attenuation actively seek the involvement of regulatory agencies and other stakeholders as early as possible in the process. Involvement should ideally occur after Step 2 or 3, when the proponent has convinced themselves that natural attenuation is worth investigating, but prior to collection of additional data. Acceptance by regulatory agencies at this point will ensure that money is not wasted on additional investigation and that all required data is collected efficiently.

Table 7 contains the elements of a long-term monitoring plan and Figure 7 shows the locations of monitoring wells.

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APPENDIX A

GLOSSARY OF TERMS

GLOSSARY OF TERMS

This glossary has been adapted from National Research Council (1993).

Abiotic - Occurring without the involvement of microorganisms.

Accelerated Anaerobic Bioremediation - Addition of carbon sources (electron donors) and/or nutrients to the subsurface in order to stimulate bacteria which can destroy chlorinated solvents by using them as an electron acceptor in the process of reductive dechlorination.

Advection - Transport of molecules dissolved in water along the groundwater flow path at an average expected velocity.

Aerobic - Environmental conditions where oxygen is present.

Aerobic Respiration - Process whereby microorganisms use oxygen as an electron acceptor to generate energy.

Aliphatic Hydrocarbon - A compound built from carbon and hydrogen atoms joined in an unsaturated ring (e.g., benzene ring). Most environmentally significant petroleum hydrocarbons are aromatic hydrocarbons.

Anaerobic - Environmental conditions where oxygen is absent.

Anaerobic Respiration - Process whereby microorganisms use a chemical other than oxygen as an electron acceptor. Common "substitutes" for oxygen are nitrate, sulfate, iron, carbon dioxide, and other organic compounds (fermentation).

Aquifer - An underground geological formation that stores groundwater.

Aquitard - An underground geological formation of low permeability that does not readily transmit groundwater.

Aromatic Hydrocarbon - A compound built from carbon and hydrogen atoms joined in an unsaturated ring (e.g., benzene ring). Most environmentally significant petroleum hydrocarbons are aromatic hydrocarbons.

Bacterium - A single cell organism of microscopic size. Bacteria are ubiquitous in the environment, inhabiting water, soil, organic matter and the bodies of plants and animals.

Bedrock - Any solid rock exposed at the surface or overlain by unconsolidated material.

Biochemical - produced by, or involving chemical reactions of living organisms.

Biodegradation - biologically mediated conversion of one compound to another.

Biomass - Total mass of microorganisms present in a given amount of water or soil.

Bioremediation - Use of microorganisms to control, transform, and/or destroy contaminants.

Biotransformation - Microbiologically catalyzed transformation of a chemical to some other product.

Chlorinated Solvent - A hydrocarbon in which chlorine atoms substitute for one or more hydrogen atoms in the compounds structure. Chlorinated solvents commonly are used for grease removal in manufacturing, dry cleaning, and other operations.

Co-metabolic Bioventing - A form of bioventing where a compound (primary substrate) is added that can support microbial growth or stimulate the appropriate enzymes to degrade the compound of concern.

Co-metabolism - A reaction in which microbes transform a contaminant even though the contaminant cannot serve as an energy source for the organisms. To degrade the contaminant, the microbes require the presence of other compounds (primary substrates) that can support their growth.

Degradation - Destruction of a compound through biological or abiotic reactions.

Dechlorination - The removal of chlorine atoms from a compound.

Desorption - Opposite of sorption; the release of chemicals attached to solid surfaces.

Diffusion - Dispersive process that results from the movement of molecules along a concentration gradient. Molecules move from areas of high concentration to low concentration.

Dilution - The combined processes of advection and dispersion resulting in a reduced concentration of the molecules (solute) in the groundwater (solvent).

Dispersion - The spreading of molecules along and away from the expected groundwater flow path during advection as a result of mixing of the molecules (solute) and groundwater (solvent) in individual pores and channels.

Electron - A negatively-charged subatomic particle that may be transferred between chemical species in chemical reactions. Every chemical molecule contains electrons and protons (positively charged particles).

Electron Acceptor - Compound that gains electrons (and therefore is reduced) in oxidation - reduction reactions that are essential for the growth of microorganisms. Common electron acceptors are oxygen, nitrate, sulfate, iron and carbon dioxide. Highly chlorinated solvents (e.g., TCE) can act as electron acceptors.

Electron Donor - Compound that loses electrons (and therefore is oxidized) in oxidation - reduction reactions that are essential for the growth of microorganisms. In bioremediation organic compounds serve as electron donors. Less chlorinated solvents (e.g., VC) can act as electron donors.

Geochemical - produced by, or involving non-biochemical reactions of the subsurface.

Growth Substrate - an organic compound upon which a bacteria can grow, usually as a sole carbon and energy source.

Hydraulic Conductivity - A measure of the rate at which water moves through a unit area of the subsurface under a unit hydraulic gradient.

Hydraulic Gradient - change in head (i.e., water pressure) per unit distance in a given direction, typically in the principal flow direction.

Inorganic Compound - A chemical that is not based on covalent carbon bonds. Important examples are metals, nutrients such as nitrogen and phosphorus, minerals, and carbon dioxide.

Intrinsic Bioremediation - A type of in situ bioremediation that uses the innate capabilities of naturally-occurring microbes to degrade contaminants without taking any engineering steps to enhance the process.

Intrinsic Remediation - in situ remediation that uses naturally-occurring processes to degrade or remove contaminants without using engineering steps to enhance the process.

Metabolic Intermediate - A chemical produced by one step in a multistep biotransformation.

Metabolism - The chemical reactions in living cells that convert food sources to energy and new cell mass.

Methanogen - A microorganism that exists in anaerobic environments and produces methane as the end product of its metabolism. Methanogens use carbon dioxide or simple carbon compounds such as methanol as an electron acceptor.

Microcosm - A laboratory vessel set up to resemble as closely as possible the conditions of a natural environment.

Microorganism - An organism of microscopic or submicroscopic size. Bacteria are microorganisms.

Mineralization - The complete degradation of an organic chemical to carbon dioxide, water, and in some cases inorganic ions.

Natural Attenuation - naturally occurring processes in soil and groundwater environments that act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in those media.

Nonaqueous Phase Liquids (NAPL) - Organic liquid that maintains as a separate layer when mixed with water.

Oxidization - Loss of electrons from a compound, such as an organic contaminant. The oxidation can supply energy that microorganisms use for growth. Often (but not always), oxidation results in the addition of an oxygen atom and/or the loss of a hydrogen atom.

Oxygenase - An enzyme that introduces oxygen into an organic molecule.

Petroleum Hydrocarbon - A chemical derived from crude oil by various refining processes. Examples include components of gasoline, fuel oils, and jet fuels.

Plume - A zone or distribution of contaminants, usually originating from a source area, and extending in the direction of gravity, preferential pathways, and/or groundwater flow.

Primary Substrates - The electron donor and electron acceptor that are essential to ensure the growth of microorganisms. These compounds can be viewed as analogous to the food and oxygen that are required for human growth.

Reduction - Transfer of electrons to a compound such as oxygen. It occurs when another compound is oxidized.

Reductive Dechlorination - The removal of chlorine atoms from an organic compound and their replacement with hydrogen atoms (same as reductive dehalogenation).

Reductive Dehalogenation - A variation on biodegradation in which microbially-catalyzed reactions cause the replacement of a halogen atom (e.g., chlorine) on an organic compound with a hydrogen atom. The reactions result in the net addition of two electrons to the organic compound.

Saturated Zone - Subsurface environments where pore spaces are filled with water.

Site Conceptual Model - A hypothesis about contaminant distribution at a release site as to how the release occurred, the current state of the source area, the possible geochemical site type, the current plume characteristics, and potential future plume characteristics.

Sorption - Attachment of a substance on the surface of a solid by physical or chemical attraction.

Stabilization - Process whereby chemical molecules become chemically bound by a stabilizing agent (e.g., clay, humic materials), reducing the mobility of the molecule in the groundwater.

Substrate - A compound that microorganisms can use in the chemical reactions catalyzed by their enzymes.

Sulfate reducer - A microorganism that exists in anaerobic environments and reacts with sulfate ions to form hydrogen sulfide.

Unsaturated Zone - Soil above the water table, where pores are partially or largely filled with air.

Vadose Zone - See "Unsaturated zone."

Volatilization - Transfer of a chemical from the liquid to the gas phase (as in evaporation).

Volatile Organic Compound(s) (VOC) – Organic chemical having a boiling point between 6%C and 160%C, meaning that these chemicals will produce considerable vapors.

APPENDIX B

RESOURCE GUIDE TO METHODS, PROTOCOLS, AND FURTHER READING

RESOURCE GUIDE TO METHODS, PROTOCOLS, AND FURTHER READING

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APPENDIX C

CASE STUDIES

Table 2 (in appendix D) provides over 20 case studies (most with published references). RTDF members are currently preparing manuscripts that present the results of natural attenuation study of chlorinated solvents conducted at the Dover AFB. These manuscripts will be published in a peer-reviewed journal in the near future.

APPENDIX D

TABLES AND FIGURES

TABLE 1: ADVANTAGES AND DISADVANTAGES OF USING NATURAL ATTENUATION

Advantages	Disadvantages
In-situ destruction - no wastes generated and no cross-media transfer	Time frames may be as long as remediation by groundwater extraction and treatment
Natural attenuation is already operating at most sites	Long-term monitoring
The most toxic and mobile contaminants usually biodegrade most quickly and reliably	Aquifer heterogeneity complicates site characterization (not unique to natural attenuation)
Non-intrusive	Intermediates of biodegradation may be more toxic than the original contaminants
Cost-effective	Occasionally more expensive than other remedies, especially pump and treat (due to monitoring requirements)
Easily combined with other remedies	
No down time due to equipment failures	

TABLE 2: SELECTED NATURAL ATTENUATION CASE STUDIES WITH REFERENCES

Site #	Location Facility Type Date	Geology	Predominant Redox	Parent/Daughter Chemicals	Electron Donors	Microbial Processes	Studies to date	Papers/Reports
1	Toronto, Ontario Chemical Transfer Facility 1989-Present	Low K Silt Till Shallow, <30 ft bgs	Anaerobic	PCE -> ethene	Methanol, Acetate	Methanogenesis Acetogenesis Sulfate-reduction	NA Investigation Laboratory Study 8 In Situ Microcosms NA Remedy	Major et al., 1991 Major and Cox, 1992 Major and Cox, 1993 Major and Cox, 1994
2	Sacramento, CA Industrial Facility 1994-Present	Unconsolidated Alluvium Silty Sand, Gravel Deep, 70 ft bgs	Generally Aerobic Anaerobic Source	TCE -> ethene VC -> CO2 TCA -> ethane CF, DCM	Septage	Methanogenesis Aerobic oxidation Cometabolic oxidation?	NA Investigation (Groundwater) Laboratory Study NA Investigation (Unsaturated zone) Site-Wide Intrinsic Review (> 50 sites)	Cox et al., 1995 Edwards and Cox, 1997 BEAK Report, 1996b BEAK Report, 1996a
3	Auburn, NY Industrial Facility 1992-Present	Overburden Fractured Bedrock	Anaerobic	TCE -> ethene	acetone, methanol	Methanogenesis Acetogenesis Sulfate-reduction Iron-reduction	Intrinsic Biodegradation Investigation Conceptual Design	Major et al., 1994 Major et al., 1995
4	Portland, OR Chemical Transfer Facility 1995-Present	Sand and Fill Shallow, < 30 ft bgs Clay Confining Layer	Anaerobic	PCE/TCE -> ethene DCM, Toluene, xylene	DCM (acetate), alcohols, TEX	Methanogenesis Acetogenesis Iron-reduction Sulfate-reduction	NA Investigation (Groundwater) Lab study of NA and enhanced (proposed)	Lehmicke et al., 1996
5	Kitchener, Ontario Industrial Facility 1995-present	Silty Sand Shallow, < 30 ft bgs Clay Confining Layer	Aerobic Anaerobic Source	TCE -> ethene	Acetone, DCM, TX	Methanogenesis Acetogenesis Sulfate-reduction Iron-reduction	NA Investigation (Groundwater) Lab study of NA and enhanced Pilot Test (ongoing)	Edwards and Cox, 1997 Edwards and Cox, 1997
6	Farmington, NH Landfill	Landfill, Rubber Silty Sand to 65 ft bgs	Aerobic Anaerobic Source	TCE, DCE, VC trace ethene	TX, DCM, ketones	Acetogenesis Methanogenesis	NA Investigation (Groundwater)	Cox et al., 1996 Cox et al., 1997

TABLE 2: SELECTED NATURAL ATTENUATION CASE STUDIES WITH REFERENCES

Site #	Location Facility Type Date	Geology	Predominant Redox	Parent/Daughter Chemicals	Electron Donors	Microbial Processes	Studies to date	Papers/Reports
	1995-Present	Bedrock		DCM, TEX, ketones		Cometabolic oxidation	Laboratory Study	Edwards and Cox, 1997
7	St. Joseph, MI	Fine and medium sand	Background aerobic	TCE->VC, ethene	Unidentified TOC	Methanogenesis	NA Investigation (Groundwater)	McCarty et al., 1991
	Industrial Facility	to 65 - 95 ft bgs	Anaerobic plume			Sulfate-reduction		McCarty and Wilson, 1992
	1991-present							Kitanidis et. al., 1993
								Wilson et. al., 1994
								Weaver et. al., 1996
							Laboratory Tests of enhanced (cometabolic)	McCarty et al., 1991
								Dolan and McCarty, 1994
8	Plattsburgh, NY	Fine and medium sand	Background aerobic?	TCE->VC, ethene	BTEX, jet fuel	Methanogenesis	NA Investigation (Groundwater)	Wiedemeyer et. al., 1996b
	Air Force Base	0 - 90 ft bgs	Anaerobic plume			Sulfate-reduction		
	1995-present					Iron-reduction		
9	New Jersey	Fine to course sand,	Background aerobic?	TCE->VC, ethene	Unidentified TOC	Methanogenesis	NA Investigation (Groundwater)	Imbrigiotta et. al., 1996
	Picatinny Arsenal	discontinuous silt/clay	Anaerobic plume			Sulfate-reduction		
	199?-199?	to 50 - 70 ft bgs				Iron-reduction		
10	Dover, DE	Fine to course sand,	Background aerobic	TCE->VC, ethene	BTEX, jet fuel	Methanogenesis	NA Investigation (Groundwater)	Ellis et. al., 1996
	Dover Air Force Base	some silt	Anaerobic source		Unidentified TOC	Cometabolic oxidation?		Klecka et. al., 1997
	1995-present	to 30 - 60 ft bgs				Aerobic oxidation	Lab study of Enhanced Anaerobic	Harkness et. al., 1997
							Lab study of Cometabolic Bioventing	Moser et. al., 1997
							Cometabolic Bioventing pilot test	Sayles et. al., 1997
							Enhanced Anaerobic pilot test	Buchanan et. al., 1997

TABLE 2: SELECTED NATURAL ATTENUATION CASE STUDIES WITH REFERENCES

Site #	Location Facility Type Date	Geology	Predominant Redox	Parent/Daughter Chemicals	Electron Donors	Microbial Processes	Studies to date	Papers/Reports
11	Alaska Eielson Air Force Base 1992-present	course sand and gravel to 180 - 300 ft bgs	Background aerobic Anaerobic plume	TCE->VC, ethene	BTEX, jet fuel	Methanogenesis Sulfate-reduction Iron-reduction	NA Investigation (Groundwater)	Dupont et. al., 1996
12	Oscoda, MI Wurtsmith Air Force Base 1994-present	Medium to fine sand, course sand and gravel to 60 - 90 ft bgs	Background aerobic Anaerobic plume	PCE/TCE-> DCE, trace VC	BTEX, jet fuel	Methanogenesis Sulfate-reduction Iron-reduction	NA Investigation (Groundwater)	Barcelona et. al., 1996
13	Richmond, CA Chemical Plant 1996-present	estuarial deposits of clays, silts and sands to 130 ft bgs	Background aerobic Anaerobic source	PCE/TCE-> VC and ethene	Unidentified TOC	Some unidentified Sulfate-reduction	NA Investigation (Groundwater)	Buscheck et. al., 1997
14	Niagara Falls, NY Landfill ~1994	overburden fractured bedrock	Background aerobic Anaerobic plume	PCE/TCE-> VC TCA, DCA, CA CT, CF, DCM, CM ethene and ethane	Landfill leachate other chemicals	Methanogenesis Sulfate-reduction	NA Investigation (Groundwater)	Lee et al., 1995
15	Niagara Falls, NY Chemical Plant ~1994	overburden fractured bedrock	Background aerobic Anaerobic plume	PCE/TCE-> VC TCA, DCA, DCM	DCM, others?	Methanogenesis Sulfate-reduction	NA Investigation (Groundwater)	Buchanan et al., 1995
16	Hawkesbury, Ontario	Till, reworked sand and	Background aerobic?	PCE/TCE -> VC	DCM, methanol	Methanogenesis	NA Investigation (Groundwater)	Fiorenza et al., 1994

TABLE 2: SELECTED NATURAL ATTENUATION CASE STUDIES WITH REFERENCES

Site #	Location Facility Type Date	Geology	Predominant Redox	Parent/Daughter Chemicals	Electron Donors	Microbial Processes	Studies to date	Papers/Reports
	Carpet Manufacturing ~1992	silts over unweathered sandy silt and fractured bedrock	Anaerobic source?	TCA-> DCA and CA ethene and ethane DCM	naphtha	Sulfate-reduction Iron-reduction Acetogenesis		
17	Gulf Coast Chemical Plant ~1995	Peat, clay and silt layers	Aerobic and Anaerobic	1,2-DCA 2-chloroethanol ethanol, ethene, ethane	1,2-DCA Unidentified TOC	Methanogenesis? Sulfate-reduction Iron-reduction	NA Investigation (Groundwater) Laboratory study	Lee et. al., 1996
18	Netherlands VC Production Plant ~1995	4 m of sand fill over natural material	Aerobic and Anaerobic	1,2-DCA VC, ethene, ethane	1,2-DCA Unidentified TOC	Methanogenesis? Sulfate-reduction	NA Investigation (Groundwater)	Bosma et. al., 1997
19	Louisiana VC Production Plant ~1995	very fine sand to 20 ft clay aquitard	Background aerobic? Anaerobic plume	VC release ethene	VC Unidentified TOC	Methanogenesis Sulfate-reduction Iron-reduction Aerobic oxidation	NA Investigation (Groundwater)	Leethem and Larson, 1997
20	Cecil County, MD Landfill 1995-1996	sand and fill over fractured saprolitic bedrock	Background aerobic? Anaerobic plume	VC release	VC	Aerobic oxidation Anaerobic oxidation?	NA Investigation (Groundwater)	Personal communication from John Wilson, 1997
21	Pinellas, FL	Marine Deposits	Anaerobic	TCE -> VC	BTEX, Ketones	Unidentified	Pilot Test of enhanced	Acree et al., 1997

TABLE 2: SELECTED NATURAL ATTENUATION CASE STUDIES WITH REFERENCES

Site #	Location Facility Type Date	Geology	Predominant Redox	Parent/Daughter Chemicals	Electron Donors	Microbial Processes	Studies to date	Papers/Reports
	DOE Facility 1995-present	Fine sand, some silt, clay < 30 ft bgs		(suspect ethene) DCM -> CM	DCM			
22	Canoga Park, CA Industrial Facility 1996-present	shallow overburden over fractured bedrock	Generally aerobic Anaerobic Source	TCE->VC, TCA->DCA CT, CF, DCM, 1,2-DCA	benzene, DCM	Methanogenesis Nitrate-reduction Aerobic degradation	NA Investigation (Groundwater)	BEAK Report, 1997b (To be published)
23	Sacramento, CA Industrial Facility 1996-Present	Unconsolidated Alluvium Silty Sand, Gravel Deep, 70 ft bgs	Generally aerobic Anaerobic Source	TCE->VC and ethene CF, DCM, 1,2-DCA -> ethene 1,2-DCA -> CO2	alcohols, acids, ketones, BTEX	Methanogenesis Nitrate-reduction Sulfate-reduction Aerobic degradation	NA Investigation (Groundwater)	BEAK Report, 1997c (To be published)
24	Ogden, Utah Hill Air Force BAse 1995-Present	Interbedded clay, silt, sand, gravel 15 - 110 ft bgs	Generally aerobic	PCE/TCE->DCE	none	Unidentified (Abiotic processes and possibly natural phytoremediation)	NA Investigation (Groundwater and vadose)	Graves et al., 1997

TABLE 3: DEGRADATION OF COMMON CHLORINATED SOLVENTS UNDER AEROBIC AND ANAEROBIC CONDITIONS

			Compound							
Degradation Process			**PCE**	**TCE**	**DCE**	**VC**	**1,1,1-TCA**	**CT**	**CF**	**DCM**
Aerobic Biodegradation										
	As Primary Substrate		**N**	**N**	**Y***	**Y**	**N**	**N**	**N**	**Y**
Cometabolic Degradation	Supported by:	Methane or Alkanes	**N**	**Y**	**Y**	**Y**	**Y***	**N**	**Y**	**Y**
		Aromatic compounds (e.g., toluene)	**N**	**Y**	**Y**	**Y**	**N**	**N**	**N**	**N**
		Ammonia	**N**	**Y**	**Y***	**Y***	**Y**	**N**	**Y**	**Y**
Anaerobic Biodegradation										
	As Primary Substrate		**N**	**N**	**N**	**Y**	**N**	**N**	**N**	**Y**
Cometabolic Degradation	Under Conditions of:	Denitrification	**Y***	**Y***	**Y***	**Y***	**N**	**Y**	**Y***	**Y**
		Iron Reduction	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
		Sulfate Reduction	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
		Methanogenesis	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**	**Y**
Chemical Degradation (Abiotic Transformation)			**N**	**N**	**N**	**N**	**Y**	**Y***	**N**	**N**

Notes:

PCE: Tetrachloroethene (also known as perchloroethene)

TCE: Trichloroethene

DCE: Dichloroethene (statements are true for all isomers)

VC: Vinyl Chloride (also known as chloroethene)

1,1,1-TCA: 1,1,1-Trichloroethane

CT: Carbon Tetrachloride (also known as tetrachloromethane)

CF: Chloroform (also known as trichloromethane)

DCM: Dichloromethane (also known as methylene chloride)

Y: Occurs; consensus opinion in the literature

Y*: May occur; limited evidence or conflicting information

N: Does not occur; consensus opinion in the literature

Table 4: Cost Comparison of Natural Attenuation to other Remedial Technologies

Present Cost estimates for natural attenuation of a typical chlorinated solvent plume and of a typical pump and treat system as an alternative remedy.

Assume:
- 20 monitoring wells
- RI completed
- Long term monitoring PC = 11.44 x recurring charges
- 3% inflation rate and 12% discount rate

===

Present Cost of a natural attenuation remedy

Up front costs - one time costs

- Monitoring, incl intrinsic parameters		$20,000
- Groundwater modeling		$50,000
- Intrinsic proposal report		$15,000
- Negotiation support		$10,000
- Report in response to Government		$10,000
- Install three new sentinel wells @ $10,000		$30,000
		=======
	Total	$135,000

Yearly costs for lifetime of natural attenuation (based on 30-years net present value)

- 2 sampling events per year - 20 wells - analyze for VOC's and intrinsic parameters 2 mob's at $10M + $566/sample*40 samples (8015[$125];8240[$257];9060[$25];6010[$80]; 353.2[$15];375.4[$20];325.3[$10];310.1[$17]; 415.1[$17])		$42,600
- Two summary reports per year, one long one short		$15,000
- Well maintenance		$10,000
		=======
	Total	$67,600

Present Cost Estimate

- One time costs		$135,000
- Recurring charges		$773,300
		========
	Total	$908,300

==

Present cost of a simple pump and treat system

Up front costs

- Monitoring for design parameters	$ 20,000
- GW Modeling	$ 50,000
- Design and install equipment ($10M/gpm)[50gpm]	$500,000
- Design Report	$ 10,000
- Negotiation Support	$ 10,000
Total	$590,000

Yearly on-going P&T O&M Costs
Inclusive of sampling events

- ($5/1000 gallons)[25MM gallons/year]	$125,000
- Reporting	$ 10,000
Total	$135,000

Pump and treat Present Cost estimate

One time costs	$590,000
PC of O&M costs	$1,544,000
Total	$2,134,000

Cost difference between remedies

PC of pump and treat remedy	$2,134,000
PC of natural attenuation remedy	$ 908,300
Difference =	$1,225,700

TABLE 5: COMMON PATTERNS OF CHLORINATED SOLVENT PRESENCE AND DISTRIBUTION IN GROUNDWATER AND SUGGESTED DATA COLLECTION TIERS TO SUPPORT NATURAL ATTENUATION

Pattern	VOC Presence	VOC Distribution	Attenuation Mechanism(s)	Typical Case	Data Collection Tier
1	Parent VOC only (e.g., PCE, TCE, TCA, CT), no detectable degradation products (see Table 3).	Observed distribution equals expected distribution (based on groundwater transport calculations, modeling).	Physical processes only (dispersion, dilution, sorption, stabilization, volatilization).	Parent chlorinated solvents were released into an aquifer having low natural organic content and no/low released organic (other than parent VOC).	I
2	Parent VOC only (e.g., PCE, TCE, TCA, CT), no detectable degradation products (see Table 3).	Observed distribution does not correspond with expected distribution (based on groundwater transport calculations, modeling).	Physical processes, possibly biological or chemical degradation processes that do not produce detectable VOC intermediates (e.g., direct mineralization, aerobic cometabolism, abiotic transformation).	1) Physical processes dominant. 2) Parent chlorinated solvents that can be directly mineralized (e.g., DCM, see Table 3) were released. 3) Parent chlorinated solvents were released in association with a known cometabolite (e.g., toluene).	II
3	Parent VOC and degradation products (see Table 3). Ratio of parent VOC to degradation products is high (e.g., >10:1).	Observed distribution does not correspond with expected distribution (based on groundwater transport calculations, modeling).	Physical, biological, and chemical processes.	Chlorinated solvents were released into an aquifer having high natural organic content or released in association with low levels of cometabolites.	II
4	Parent VOC and degradation products (see Table 3). Ratio of parent VOC to degradation products is low (e.g., <10:1).	Observed distribution does not correspond with expected distribution (based on groundwater transport calculations, modeling).	Physical, biological, and chemical processes.	Chlorinated solvents were released as part of a mixed waste containing sewage, simple solvents such as methanol, and/or petroleum hydrocarbons.	III

Notes:

VOC - volatile organic compound

PCE (tetrachloroethene), TCE (trichloroethene), TCA (trichloroethane), CT (carbon tetrachloride), DCM (dichloromethane)

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	*****
Geological							
Area Geology	Topography/Soil Type/Surface Water/Climate	Provides inferences about natural groundwater flow systems, identifies recharge/discharge areas, infiltration rates, evaluation of types of geological deposits in the area which may act as aquifers or aquitards.	Consult published geological/soil/topographic maps, air photo interpretation, field geological mapping.	✓	✓	✓	
Hydrogeological							
Subsurface Geology	Lithology/ Stratigraphy/ Structure	Identify water bearing units, thickness, confined/unconfined aquifers, effect on groundwater flow and direction (anisotropy).	Use published hydrogeologic surveys/maps.	✓	✓	✓	
			Review soil boring/well installation logs.	✓	✓	✓	
			Conduct surface or sub-surface geophysics.			✓	
Velocity	Hydraulic Conductivity (K)/Permeability (k)	Measure of the saturated hydraulic conductivity of the geological matrix. K times the gradient gives the specific discharge (v). If site is very layered or complex, measure the vertical/horizontal K.	Estimate range based on geology.	✓	✓	✓	
			Conduct: Pump, slug or tracer tests.		✓	✓	
			Estimate with grain size analysis.			✓	
			Permeability test.			✓	
			Downhole flowmeter/dilution test				*
	Gradient (h)	Measure of potential of the fluid to move (hydraulic gradient)	Water table and piezometric surface measurements.	✓	✓	✓	
	Porosity (n)	Measure of the soil pore space. Dividing the specific discharge by porosity gives the average linear groundwater velocity.	Estimate range based on geology.			✓	
			Measure bulk and particle mass density.				

Notes: * indicates parameter is optional depending on site complexity

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	**∗**
Direction	Flow Field	Estimate direction of groundwater flow.	Water and piezometric contour maps.	✓	✓	✓	
			Downhole flowmeter.				∗
Dispersion/Sorption	Foc	Fraction of organic carbon: used to estimate the retardation of chemical migration relative to the average linear groundwater velocity.	Estimate or measure foc in soil samples, estimate from published values, or compare migration of reactive and non-reactive (tracer) chemicals in the groundwater.	✓	✓	✓	
	Dispersion	Longitudinal and horizontal dispersion (mixing) spreads out the chemical along the groundwater flow path.	Estimate based on distribution of chemicals or use tracer tests.	✓	✓	✓	
Chemistry							
Organic Chemistry	VOC	Identify parent solvents and degradation products; assess their distribution. Certain specific isomers/degradation products provide direct evidence of biodegradation (e.g., cis-1,2-DCE), while others are formed due to abiotic degradation processes (e.g., formation of 1,1-DCE from 1,1,1-TCA). In addition, aromatic hydrocarbons (BTEX) and ketones can support biodegradation of cVOC.	US EPA Method 8240.	✓	✓	✓	
	Semi VOC	Selected semi-VOC (e.g., phenol, cresols, alcohols) may support biodegradation of cVOC.	US EPA Method 8270, 8015M.			✓	
	Volatile Fatty Acids	Organic chemicals like acetic acid can provide insight into the types of microbial activity that is occurring and can also serve as electron donors.	Standard analytical methods or published modified methods using ion chromotography.			✓	

Notes: ∗ indicates parameter is optional depending on site complexity

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	*****
	Methane, Ethene, Ethane, Propane, Propene	Provide evidence of complete dechlorination of chlorinated methanes, ethenes, and ethanes. Methane also indicates activity of methanogenic bacteria. Isotope analysis of methane can also be used to determine its origin.	Modified analytical methods, GC-FID.		✓	✓	
	TOC/BOD/COD /TPH	Potential availability of general growth substrates.	US EPA Methods 415.1,405.1.		✓	✓	
	Alkalinity	Increased levels indicative of carbon dioxide production (mineralization of organic compounds).	US EPA Method 310.1.				
Inorganic/Physical	Ammonia	Nutrient. Evidence of dissimilatory nitrate reduction, and serve as a aerobic co-metabolite.	US EPA Method 350.2.		✓	✓	
	Chloride	Provides evidence of dechlorination, possible use in mass balancing, may serve as conservative tracer. Road salts may interfere with chloride data interpretation.	US EPA Method 300.0.	✓	✓	✓	
	Calcium/ Potassium	Used with other inorganic parameters to assess the charge-balance error and accuracy of the chemical analysis.	US EPA Method 6010.			✓	
	Conductivity	Used to help assess the representativeness of water samples, and assess well development after installation (sand pack development).	Electrode measurement in the field. Standard electrode.	✓	✓	✓	
	Dissolved Oxygen (DO)	Indicator of aerobic environments, electron acceptor.	Use flow through apparatus to collect representative DO measurements by electrode.	✓	✓	✓	

Notes: * indicates parameter is optional depending on site complexity

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	*****
	Hydrogen	Concentrations in anaerobic environments can be correlated with types of anaerobic activities (i.e., methanogenesis, sulfate and iron reduction) and therefore this parameter is an excellent indicator of the redox environment. Hydrogen may be the limiting factor for complete dechlorination of cVOC.	Field measurement. Flow through cell equipped with bubble chamber. As groundwater flows past chamber, hydrogen gas will partition into headspace. Headspace sampled with gas-tight syringe and analyzed in the field using GC. Equipment for analysis is not yet widely available. Relationship to dechlorination activity is still unclear and subject to further R&D.				*
	Iron	Nutrient. Ferrous (soluble reduced form) indicates activity of iron reducing bacteria. Ferric (oxidized) is used as an electron acceptor.	US EPA Method 6010A.		✓	✓	
	Manganese	Nutrient. Indicator of iron and manganese reducing conditions.	US EPA Method 6010.			✓	
	Nitrate	Used as an electron acceptor by denitrifying bacteria, or is converted to ammonia for assimilation.	US EPA Method 300.0.		✓	✓	
	Nitrite	Produced from nitrate under anaerobic conditions.	US EPA Method 300.0.		✓	✓	
Inorganic/Physical	pH	Measurement of suitability of environment to support wide range of microbial species. Activity tends to be reduced outside of pH range of 5 to 9, and anaerobic microorganisms are typically more sensitive to pH extremes. pH is also used to help assess the representativeness of the water sample taken during purging of wells.	pH measurements can change rapidly in carbonate systems, and during degassing of groundwater. Therefore, pH measurements must be measured immediately after sample collection or continuously through a flow through cell.	✓	✓	✓	

Notes: * indicates parameter is optional depending on site complexity

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	**∗**
	Phosphorous	Limiting nutrient.	US EPA Method 300.0			✓	∗
	Redox Potential	Measure of oxidation-reduction potential of the environment. Ranges from +500 mV for aerobic environments to –500 mV for anaerobic environments.	Use flow through apparatus in the field to collect representative redox measurements by electrode. Standard. Redox measurements can be affected be geochemical speciation of organic/inorganic chemical species. The measured redox (using probes) can be confirmed by examining chemical speciation of redox couples.	✓	✓	✓	
	Sodium	Evaluate whether chloride may be associated with road salt.	US EPA Method 6010.			✓	
	Sulfate	Used as electron acceptor. Changes in its concentration may provide evidence of activities of sulfate reducing bacteria.	US EPA Method 300.0.		✓	✓	
	Sulfide	May provide evidence of sulfate reduction. May not be detected even if sulfate-reducing bacteria are active because it can react with various oxygenated chemical species and metals.	US EPA Method 376.1.		✓	✓	
	Temperature	Used to help assess the representativeness of water samples, and to correct temperature sensitive parameters/measuring devices. Microorganisms are active over a wide temperature range.	Field Measurement. Standard thermometer.	✓	✓	✓	
Inorganic/Physical	Toxic Metals	The presence of metals (e.g., lead, copper, arsenic) can reduce microbial activity. Microorganisms are generally resistant.	US EPA Method 6010.				∗

Notes: ∗ indicates parameter is optional depending on site complexity

Table 6: Data Collection Tiers for Evaluation and Implementation of Natural Attenuation

Parameter	**Data Type**	**Ideal Use, Value, Status and Comments**	**Method**	**Data Collection Tier**			
				I	**II**	**III**	**∗**
Microbiology							
Biomass	Microorganisms Per Unit Soil or Groundwater	Microbial population density between impacted and non-impacted/treated areas can be compared to assess whether microbial populations are responsible for observed degradation. The value of biomass measurements is still being explored for cVOC biodegradation.	There are three general techniques available: culturing (plate counts, BioLog, MPN enumerations); direct counts (microscopy); and indirect measurement of cellular components (ATP, phospholipid fatty acids).				∗
	Biodegradation Rate and Extent	Demonstrate the indigenous microorganisms are capable of performing the predicted transformations. Determine nutrient requirements and limitations. Measure degradation rates and extent.	Varied. Shake flasks, batch, column, bioreactors designs.				∗
	Species/Genera/ Functional Group	The presence of certain microbial species of functional groups (e.g., methanogenic bacteria) that have been correlated with cVOC biodegradation can be assessed. Research is being conducted to identify patterns of microbial composition that are predictive of successful cVOC biodegradation.	There are three general techniques available: culturing and direct counts; indirect measurement of cellular components; and molecular techniques (16s RNA, DNA probes, RFLP).				∗

Notes: ∗ indicates parameter is optional depending on site complexity

TABLE 7: ELEMENTS OF THE LONG-TERM NATURAL ATTENUATION MONITORING PLAN

Monitoring Well	Location*	Purpose	Parameters Sampled	Frequency
Upgradient	Upgradient of the source, preferably along the groundwater flowpath	Purpose is to be most representative location for background conditions	VOC, all organic, inorganic and field parameters that are sampled in downgradient wells	Every event as dictated by the regulatory agency involved Frequency may decline over time***
Source	Closest well to source area along groundwater flowpath	Purpose is to be representative of source term; installation of new well is usually not warranted.	VOC, all organic, inorganic and field parameters that are relevant to site pattern** Measure NAPL if present	as above
Downgradient 1	Downgradient of source area, ~1/3 of the way along the groundwater flowpath	Primary purpose is to monitor VOC and other parameters as they migrate from source area	VOC, all organic, inorganic and field parameters that are relevant to site pattern	as above
Downgradient 2	Downgradient of source area, ~2/3 of the way along the groundwater flowpath	Primary purpose is to monitor change (decline) in VOC and other parameters along flowpath	VOC, all organic, inorganic and field parameters that are relevant to site pattern	as above
Downgradient 3	Downgradient of source area, slightly beyond the end of the plume	Primary purpose is to document downgradient limit of VOC and change in redox and other parameters along the flowpath	VOC, all organic, inorganic and field parameters that are relevant to site pattern	as above
Transgradient 1	Transgradient of the plume, ~ halfway along the groundwater flowpath	Primary purpose is to document lateral movement (stability) of the VOC plume	VOC, all organic, inorganic and field parameters that are relevant to site pattern	as above
Transgradient 2	Transgradient of the other side of the plume, ~ halfway along the groundwater flowpath	Primary purpose is to document lateral movement (stability) of the VOC plume	VOC, all organic, inorganic and field parameters that are relevant to site pattern	as above
Compliance (1-3)	Two or three wells perpendicular to the groundwater flowpath and slightly upgradient of the compliance boundary	Primary purpose is regulatory: documenting that the plume is stable and has not crossed the compliance boundary	VOC alone should be sufficient, any organic or inorganic parameters still present at high concentrations at Downgradient 3 suggested	as above

* **All wells must be screened in the hydrogeological unit that contains the plume**

** **Field parameters would include DO and Redox; inorganic parameters would include chloride and relevant electron acceptor indicators like sulfate or iron;** organic parameters would include methane, VFAs and any specific or general electron donor indicators (hydrocarbons, ketones, alcohols, TOC etc)

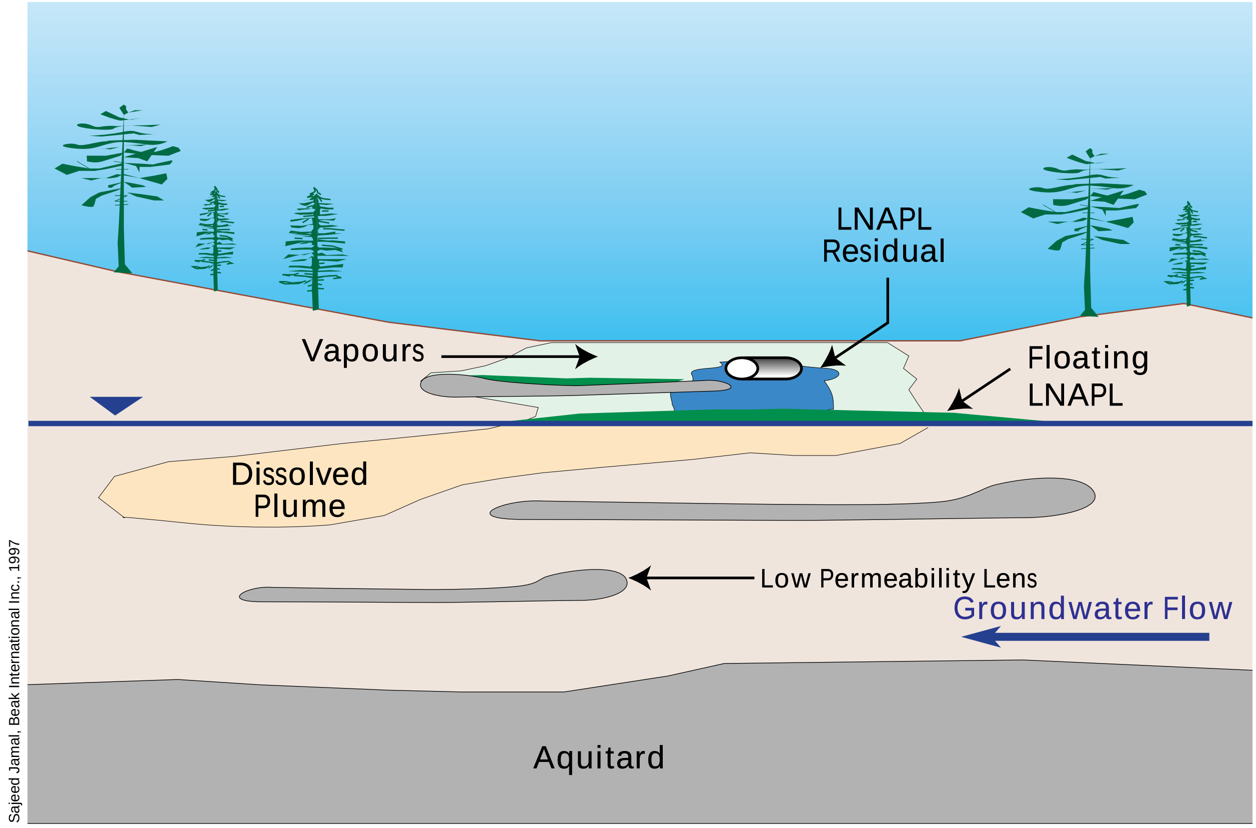
*** **Frequency may be lower for sites with low hydraulic conductivity. Frequency may also decline for some organic or inorganic parameters over time** Frequency for field parameters and VOC will likely remain constant.

TABLE B1: RESOURCE GUIDE TO METHODS, PROTOCOLS, AND FURTHER READING

Topic	Relevant References
Soil Boring and Sampling	
Equipment Decontamination	3, 27
Drilling	3, 16, 19, 39, 42
Cone Penetrometer Testing	35, 36
Sample Collection	2, 3, 7, 8
Soil Headspace Screening for VOC	34
Analytical Methods	7, 8, 46, 47, 48, 51, 52, 53
Data Quality Assurance/Quality Control	46, 47, 48, 49, 50, 51, 52, 53
Borehole Abandonment	3, 56
Well Installation	
General Topics	22, 28, 29, 36, 42, 43, 44
Equipment and Material Decontamination	3, 27, 28, 30
Well Casing	6, 19, 29, 32
Well Construction Materials	3, 4, 19, 29, 33, 44, 45
Well Screen Placement	12, 19, 43, 44
Filter Pack Material and Placement	19, 43, 44
Annular Sealant	19, 29
Protective Casings	29
Well Development	3, 19, 25
Well Abandonment	3, 19
Groundwater Sampling	
Equipment Decontamination	3, 27
Total Depth and Water Level Measurement	15, 19
Well Purging	4
Field Measurement	11
NAPL Detection	31
Sample Collection	1, 2, 5, 7, 8, 11, 23, 43, 44, 56, 57
Cone Penetrometer Testing	40, 41, 58, 59
HydroPunch Testing	40, 41, 58
Sample Shipment and Chain of Custody	45, 49, 54
Analytical Methods	7, 8, 10, 24, 46, 47, 49, 50, 51, 52, 53
Data Quality Assurance/Quality Control	5, 18, 46, 47, 48, 49, 50, 51, 52, 53, 54
Aquifer Characterization	
Water Level Measurements	15
Aquifer Testing	17, 26, 38, 55
Conceptual Model Development	17, 20, 56, 57
Fate and Transport Modeling	9, 21, 31, 37

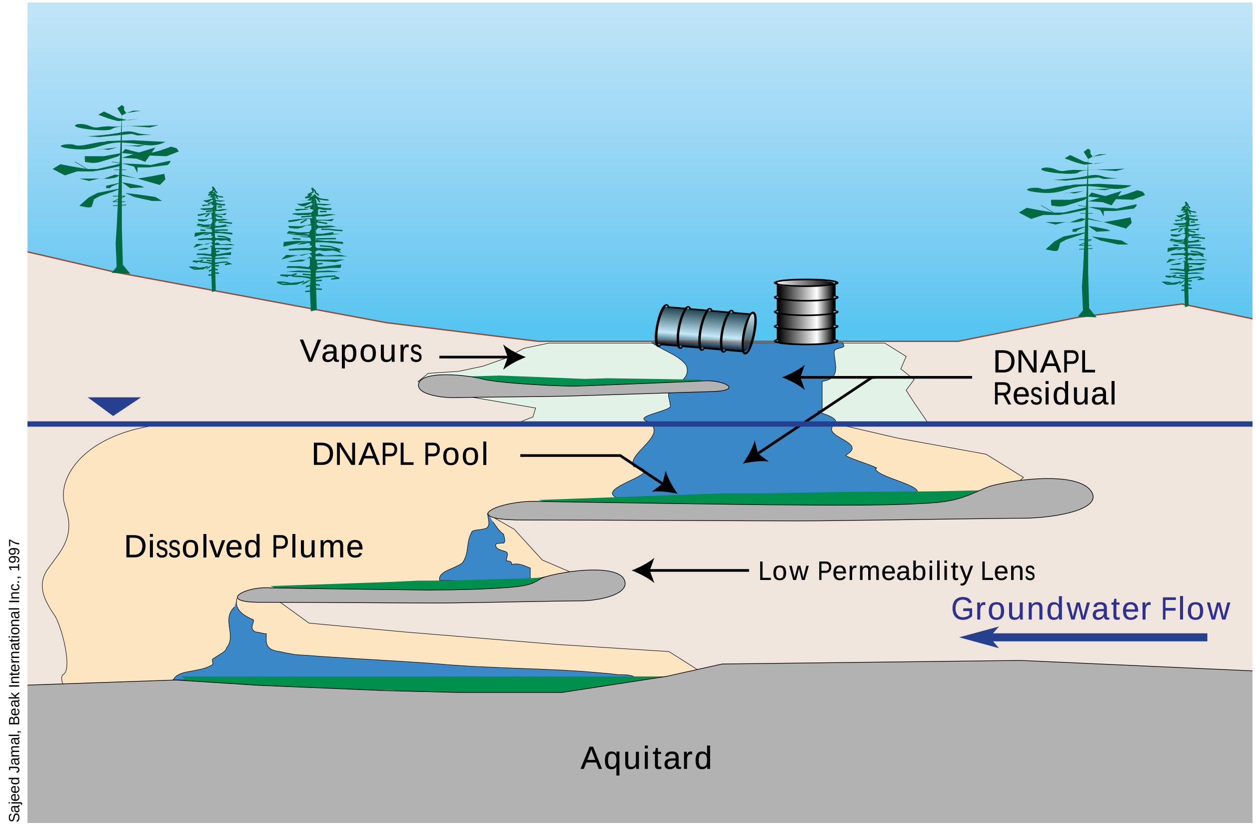
Figure 1: Distribution of Non-Aqueous Phase Liquids (NAPLs) in the Subsurface

Light Non-Aqueous Phase Liquids (LNAPLs)



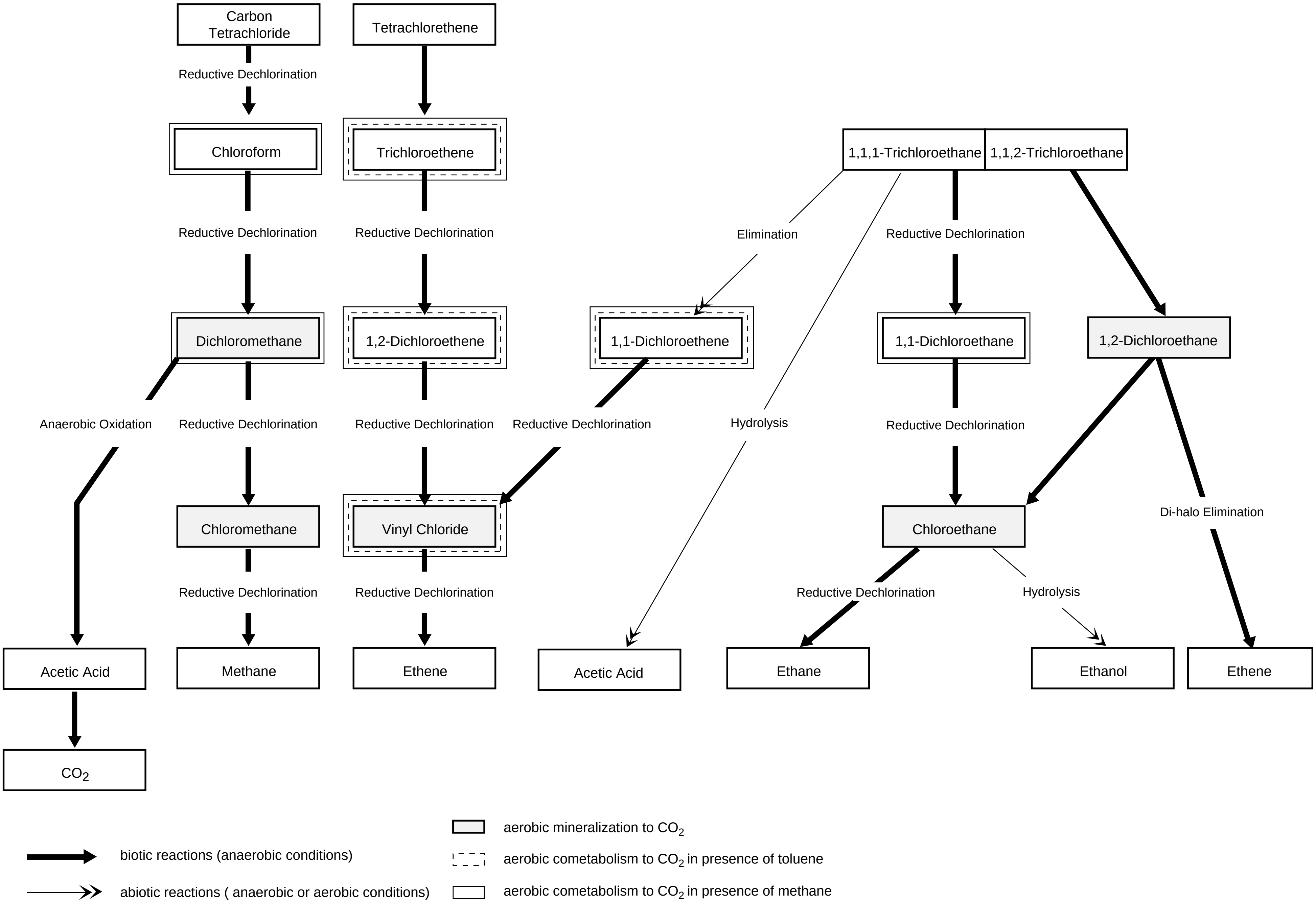
Sajeed Jamal, Beak International Inc., 1997

Dense Non-Aqueous Phase Liquids (DNAPLs)



Sajeed Jamal, Beak International Inc., 1997

Figure 2: Common Degradation Pathways



Sajeed Jamal, Beak International Inc., 1997

Figure 3: Anaerobic Reductive Dechlorination of a Trichloroethene Plume

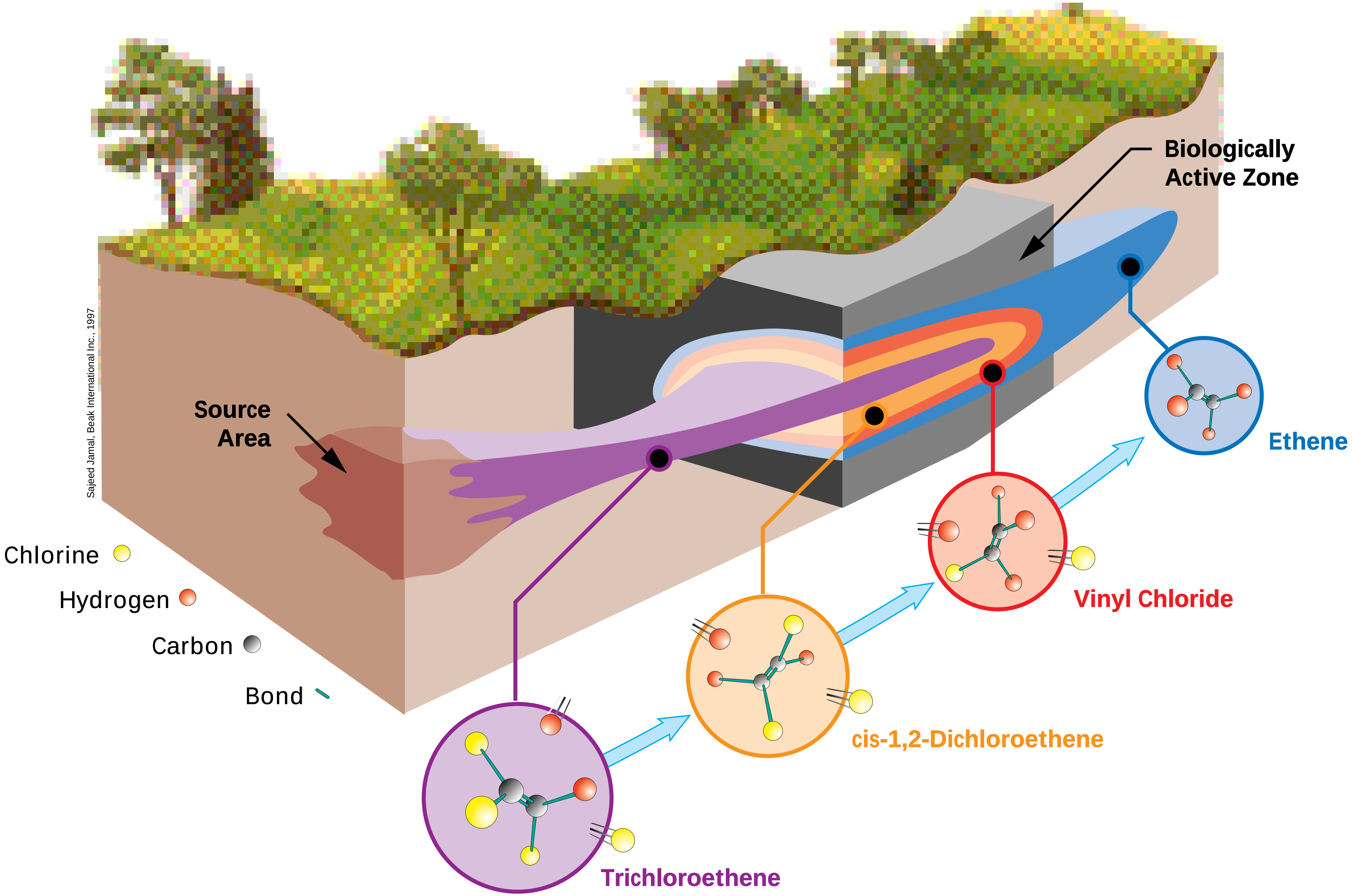
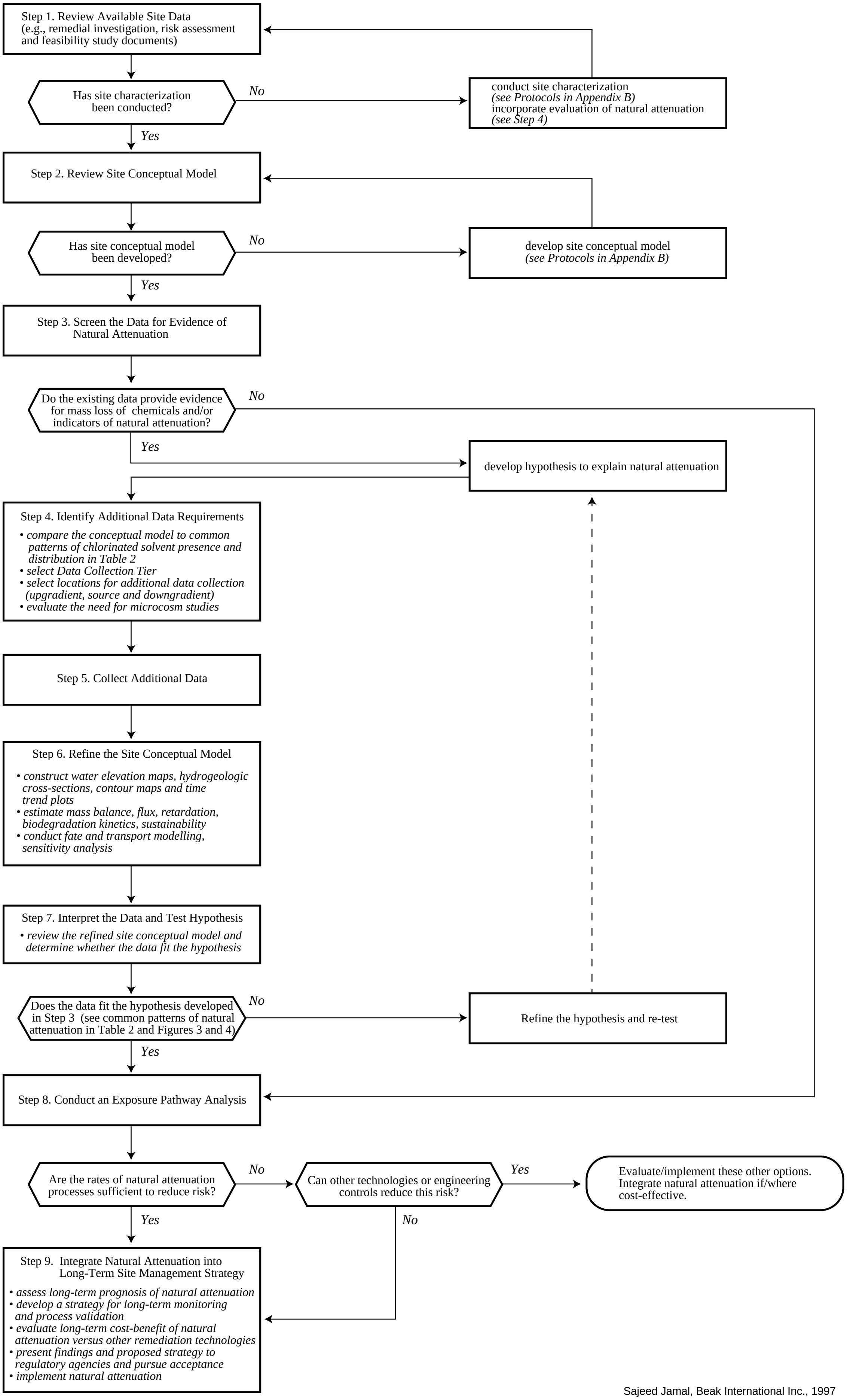
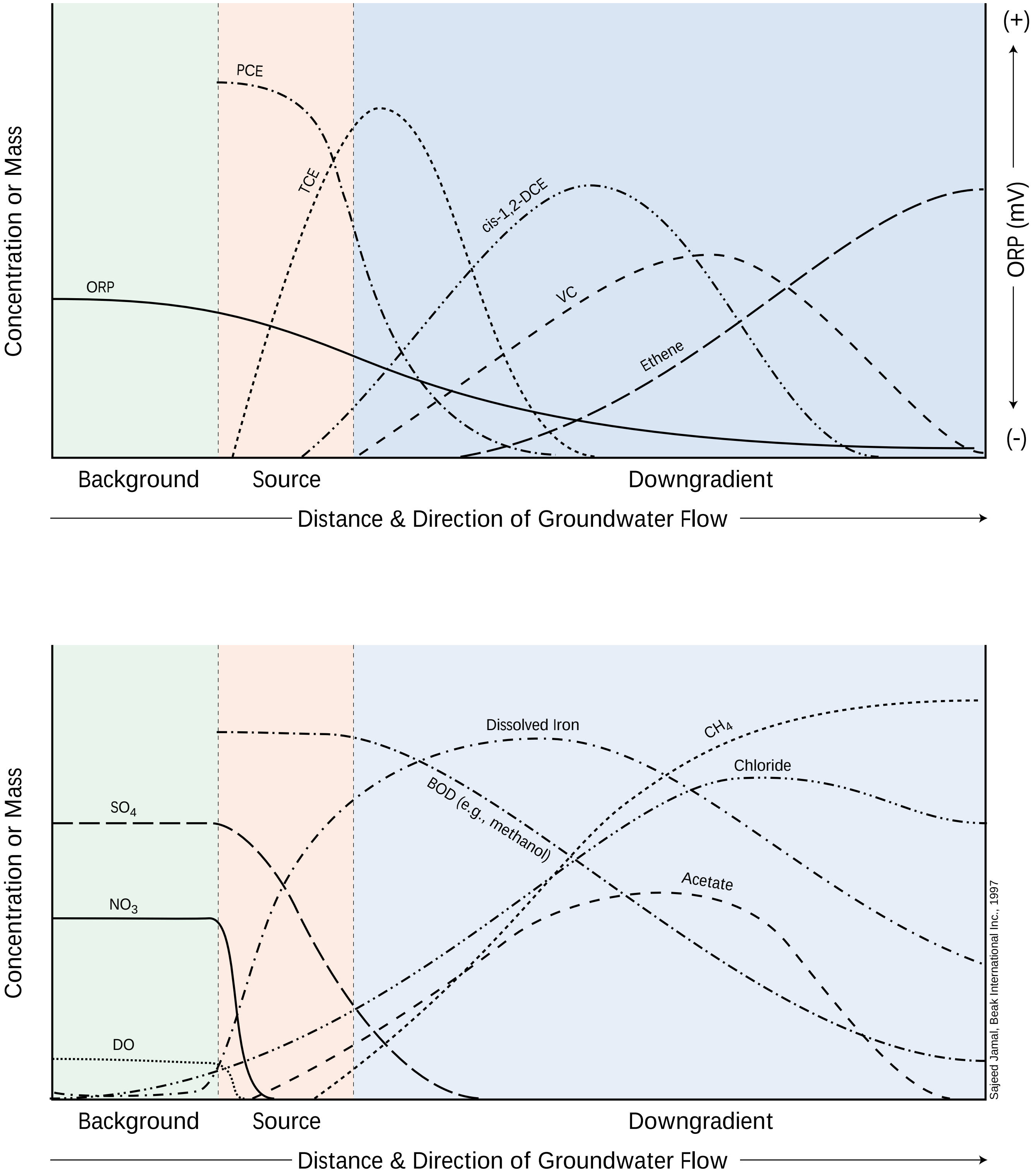


Figure 4: Flowchart to Evaluate and Implement Natural Attenuation



Sajeed Jamal, Beak International Inc., 1997

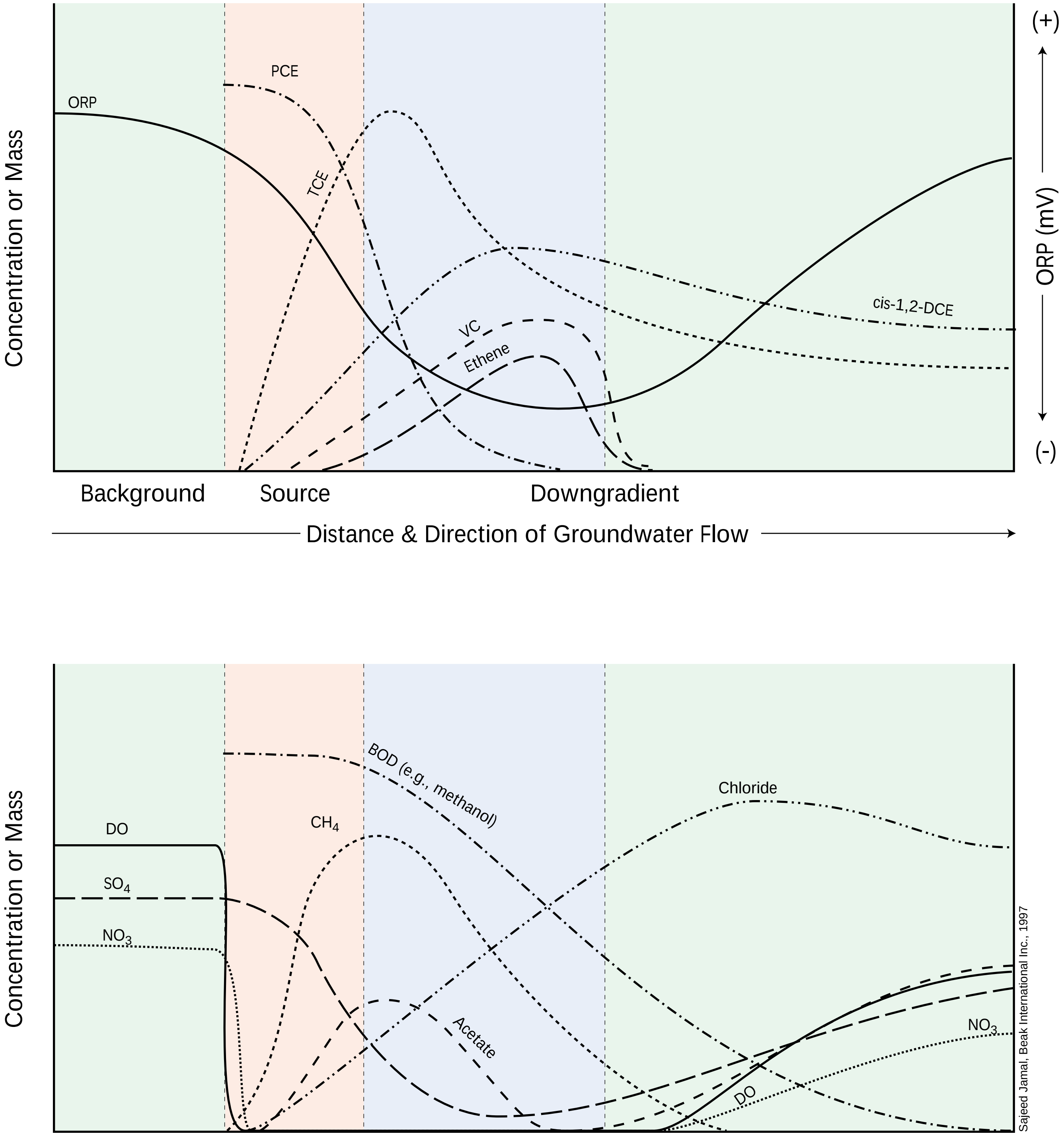
Figure 5: Common Patterns of Chlorinated Solvent Biodegradation in an Anaerobic System



Sajeed Jamal, Beak International Inc., 1997

Interpretation: BOD (e.g., methanol) is supporting the growth of anaerobic bacteria as shown by the production of methane and acetate, and depletion of sulphate. Sulphate-reducing and possibly iron-reducing bacteria appear responsible for the initial dechlorination of PCE through to DCE. As the sulphate concentrations decreases, the activity of methanogenic bacteria increases. Under methanogenic/acetogenic conditions 1,2-DCE and VC are dechlorinated to ethene.

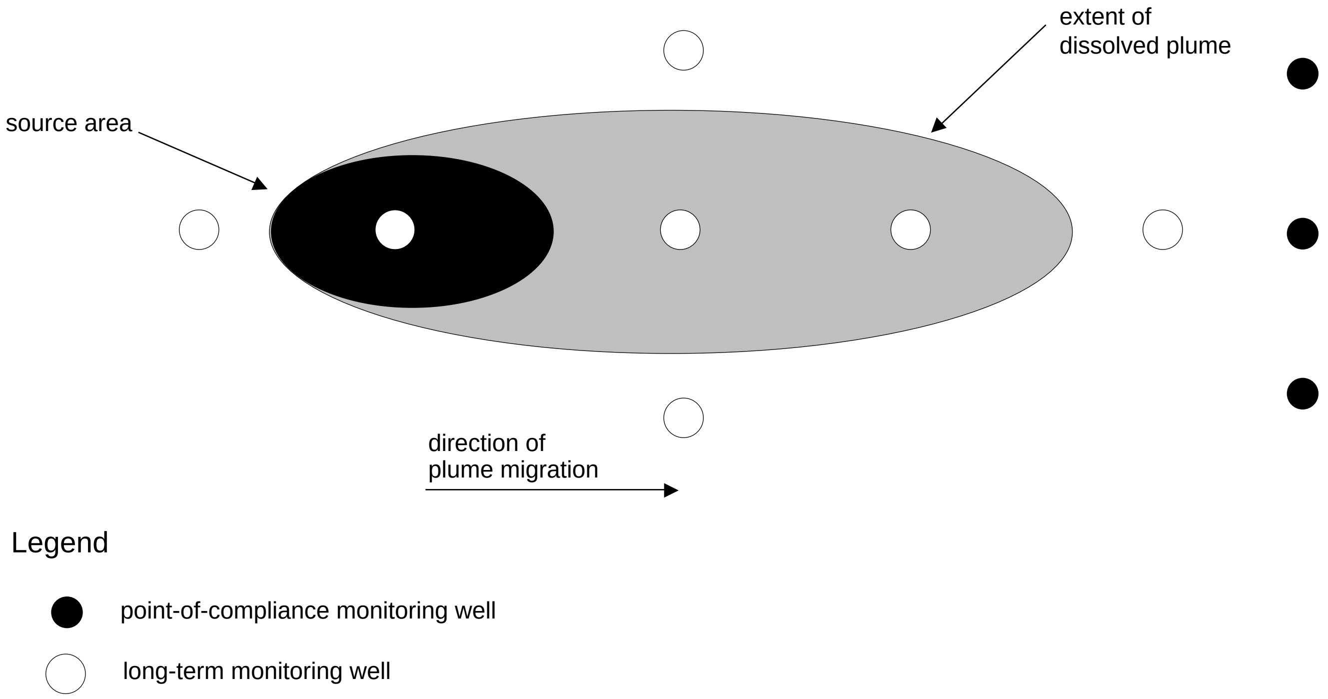
Figure 6: Common Patterns of Chlorinated Solvent Biodegradation in a Sequential Aerobic/Anaerobic System



Sajeed Jamal, Beak International Inc., 1997

Interpretation: An anaerobic zone has developed in an aerobic groundwater system due to the metabolism of the BOD (e.g., methanol) in the source area. In the anaerobic zone PCE is dechlorinated to TCE, DCE, VC and finally ethene. Methanogenic, sulphate-reducing, iron-reducing, and acetogenic bacteria are active, and their interactions are responsible for the dechlorination. However, the dechlorination rate is in insufficient to cause all of the TCE and DCE to be dechlorinated in the anaerobic zone. These chemicals along with methane, ethane and vinyl chloride migrate into the transition and aerobic zones. In the transition zone the TCE and DCE is partially cometabolized by methanotrophs growing on the methane. Ethene and VC are mineralized to CO_2 by aerobic bacteria in the aerobic zone.

Figure 7:Theoretical Well Locations for Monitoring Natural Attenuation



Note: The number and placement of monitoring wells will be site-specific and will vary depending on site complexity. Layout depicted is conceptual.

APPENDIX E

ITRC INFORMATION AND WORK TEAM CONTACTS

INTERSTATE TECHNOLOGY & REGULATORY COOPERATION WORK GROUP

Promoting innovative environmental technologies

April 1999

ITRC is a state-led national coalition dedicated to helping regulatory agencies, technology developers and vendors, and technology users achieve better environmental protection through the use of innovative technologies. By working together and sharing knowledge among themselves and with federal, industrial, and stakeholder partners, ITRC states are creating products and offering services to build the collective confidence of state regulators about using new technologies. ITRC also helps the environmental technology market by bolstering multistate deployments of better technologies.

BENEFITS

The benefits ITRC offers state regulators, technology developers and vendors, technology users, and stakeholders include

- helping regulators build their knowledge base about new technologies,
- raising the comfort level of state regulators about using new technologies,
- helping regulators save time and money when evaluating technologies for cleanup,
- helping technology vendors avoid the time and expense of conducting duplicative and costly demonstrations,
- guiding technology developers in the collection of performance data to satisfy the requirements of multiple states,
- providing the environmental technology industry a predictable regulatory path for commercializing new technologies,
- improving environmental protection, and
- lowering the overall cost of remediation.

PRODUCTS

To date, ITRC has developed approximately 30 guidance documents intended to help regulatory staff and technology vendors in the deployment of innovative technologies. In general, ITRC guidance documents provide a regulatory perspective on the informational needs (background and/or regulatory requirements) of state environmental agencies to approve the use of a specified technology. These documents offer a consistent approach for reviewing and approving specified technologies. A list of ITRC's documents and most of the documents themselves are available on the ITRC Web site. ITRC guidance documents fall into three categories:

Technical/Regulatory Guidelines

Previously called protocols, these documents reflect a consensus of state technical/regulatory concerns that should be considered when approving the use of a specified technology or in demonstrating a technology. Documents of this nature are formally circulated to state environmental agencies to seek their concurrence to use the proposed guidance.

Technology Overviews

These documents may come in the form of status reports on emerging technologies, descriptions of how state regulatory practices treat certain types of technologies, or state regulatory perspectives and input into guidance documents developed by complementary organizations.

Case Studies

These documents may come in the form of benchmarking state practices in demonstrating and approving the use of environmental technologies, as well as documenting state approaches to implementing various programs and policies that support the use of new technologies. These case studies often identify barriers to the deployment of innovative technologies and sometimes offer preliminary findings.

> ***"The whole process—from design through installation—took less than four months. That level of accelerated review is based upon a common pool of knowledge provided in the ITRC documents."***
>
> Steve Tappert, Consultant, Vectre Corporation

SERVICES

In addition to producing and disseminating guidance documents, ITRC also offers benefits through other services.

Training

During 1998, ITRC brought its first course, Natural Attenuation of Chlorinated Solvents in Ground Water, to more than 750 regulators from 43 states. The success of the course led ITRC to begin planning a series of workshops on permeable reactive barriers for delivery during 1999 and 2000. The workshops are being developed in cooperation with the industrial members of the Remediation Technologies Development Forum and the Technology Innovation Office of the U.S. Environmental Protection Agency.

Information sharing

ITRC participants grow professionally as they share experiences in evaluating innovative technologies. ITRC involvement offers an opportunity to tap into networks of technical resources and support when making decisions about approving the use of an innovative technology.

Innovative technology advocates

Each of the 25 states actively participating in ITRC has assigned a staff member from its environmental agency to serve as the ITRC point of contact (POC). State POCs are knowledgeable and help convey information about ITRC to people within their states who can benefit from ITRC's products and services. POCs also help gain state concurrence on ITRC's technical/regulatory guidelines. POCs are part of ITRC's State Engagement Team, which is led by Mary Yelken of Nebraska, (402) 471-3388. A list of state POCs is on ITRC's Web site.

> ***"It is clear that the ITRC training has been very helpful to our staff in evaluating these sites."***
>
> Gary Baughman,
> Colorado Department of Public Health
> & Environment

TECHNICAL TEAMS

ITRC technical work teams focus on developing guidance documents and providing opportunities for formal training and informal information sharing. State regulators lead the teams, which include representatives from federal agencies, industry, and stakeholder groups. In 1999, ITRC has nine active teams. An additional five teams closed out their activities in previous years. Many of the final documents are available on the ITRC Web site, or contact the team leads listed below for information about a team or its products.

LEADERSHIP TEAM

A 10-member Leadership Team provides advice and guidance for running ITRC. Members of the Leadership Team represent the various groups important to ITRC: state agencies, industry, and stakeholders. Representatives from federal agencies and state associations serve as ex officio members. The ITRC co-chairs are

- **Brian Sogorka, New Jersey**–(609) 633-1344
- **Roger Kennett, New Mexico**–(505) 845-5933

HISTORY

Originating in 1995 from a previous initiative by the Western Governors' Association, ITRC has expanded to include the environmental agencies of 25 states, three federal partners, and public and industry stakeholders. In January 1999, ITRC affiliated with the Environmental Research Institute of the States. ERIS is a 501(c) 3 nonprofit educational subsidiary of the Environmental Council of the States (ECOS), an organization of state environmental agencies. ITRC continues to receive regional support from the Southern States Energy Board (SSEB) and the Western Governors' Association (WGA) and financial support from the U.S. Department of Energy, U.S. Department of Defense, and the U.S. Environmental Protection Agency.

ADDITIONAL RESOURCES

To learn more about ITRC

- Check out the Web site at http://www.sso.org/ecos/itrc.
- Contact Rick Tomlinson, ITRC project manager, at (202) 624-3660.

New and Ongoing Technical Teams for 1999

Team Name	Team Lead	Phone Number	e-mail address
Denitrification	Bart Faris, New Mexico	(505) 841-9466	Bart_Faris@nmenv.state.nm.us
In Situ Chemical Oxidation and Dense Nonaqueous Phase Liquids	Tom Stafford, Louisiana Baird Swanson, New Mexico	(225) 765-0487 (505) 841-9458	t_stafford@deq.state.la.us baird_swanson@nmenv. state.nm.us
Permeable Barrier Walls	Matt Turner, New Jersey	(609) 984-1742	mturner@dep.state.nj.us
Phytoremediation	Bob Mueller, New Jersey Dib Goswami, Washington	(609) 984-3910 (509) 736-3015	bmueller@dep.state.nj.us dibakar_goswami@rl.gov
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APPENDIX F

ACRONYMS

ACRONYMS

AFC	Air Force Center for Environmental Excellence
CT	Carbon Tetrachloride
1,2 DCA	1,2-dichloroethane
DCE	Dichloroethene
DNAPL	Dense Nonaqueous Phase Liquid
EPA	Environmental Protection Agency
LNAPL	Light Nonaqueous Phase Liquid
MCL	Maximum Contaminant Level
NAPL	Nonaqueous Phase Liquid
OSWER	Office of Solid Waste and Emergency Response
PCE	Perchloroethene, Tetrachloroethene
TCE	Trichloroethene
VC	Vinyl Chloride
VOC	Volatile Organic Compound

APPENDIX G

RESPONSE TO PEER REVIEW COMMENTS

Response to Additional State Comments (4/98)

Comments from individual states are listed as received with the response following.

Department of Environmental Protection - New Jersey

Dear Mr. Hadley:

We have reviewed the August 1997 Draft Version 3.0 document entitled “Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices.” Our comments are as follows:

GENERAL COMMENTS

(1) The ITRC document (as well as, the recent ITRC Natural Remediation training which New Jersey Department of Environmental Protection staff attended in Pennsylvania) implies that natural attenuation of chlorinated solvents can be considered when sources, such as DNAPL, remain or are not contained. This policy directly conflicts with New Jersey's promulgated "Technical Requirements for Site Remediation" at N.J.A.C. 7:26E, which specifically requires sources to be removed or contained. Containment is mentioned in the ITRC document, but does not always come off as a prerequisite to having the dissolved portion of the plume considered as a candidate for natural attenuation. In order for New Jersey to accept the document, we believe the document should be modified to acknowledge various states’ regulations.

RESPONSE 1

In earlier comments, specifically from the US EPA, the document was criticized for sounding like a “policy document”. This is not the intent. Both the ITRC document and the training course are scientific, technical approaches to looking at natural attenuation of chlorinated solvents. Because of the variation in policies between states and the EPA, it would be impossible to address all regulatory “policy concerns” and please everybody. Therefore, we have avoided policy as much as possible.

From a technical standpoint, natural attenuation may be appropriate even if DNAPL remains and no other containment is used. As a project manager, I am working on just such a site. DNAPL levels of PCE, TCE, 1,1,1-TCA and Dichloromethane (methylene chloride), LNAPL levels of toluene and xylene and high levels of dissolved alcohols are all present in the source area. The direct biodegradation of methylene chloride, toluene, xylene and alcohols has resulted in their own attenuation within a few hundred feet as well as their serving as electron donors in the destruction of the PCE, TCE and 1,1,1-TCA through reductive dechlorination within the same distance. Any attempt to remove NAPL from the site would likely result in the more rapid removal of the more soluble contaminants that are serving as electron donors and would undermine the naturally-occurring processes. In fact, at a “sister” site to the one described here, a groundwater extraction and treatment system was installed several years ago and has resulted in a decline in destruction of the chlorinated solvents at the site. In the instance described here, NAPL removal is not only unwarranted, it would be counterproductive.

We believe it is New Jersey's responsibility to point out to its own staff, responsible parties and consultants as it did here, that there may be a conflict with state policy.

(2) The document must state that the fate and transport of non-priority pollutant by-products and breakdown products must also be determined, as necessary. For instance, non-priority pollutants can affect the potability of an aquifer.

RESPONSE 2

We agree that an understanding of the fate and transport of byproducts produced is important. In most instances, non-priority by-products or breakdown products would be produced in much smaller quantities than the original contaminant. Additionally, these byproducts are usually more biodegradable than the original contaminant and are usually metabolized to CO_2.

SPECIFIC COMMENTS:

(1) Q14

It should be clarified that proven technologies exist for CONTAINMENT of sources, and that many states require containment of sources. Also, by rule (as in New Jersey) or policy do not allow for natural attenuation of source areas. For clarification, New Jersey defines source areas as areas that are known, by direct observation, or suspected (by a combination of history and concentrations found in groundwater) of having free or residual product. In addition, the National Academy of Sciences document referenced in the ITRC document makes a clear distinction that technologies such as pump and treat are more than adequate for containment purposes.

Suggested language addition for Q14 in capitals as follows:

Proven, safe, and cost-effective technologies to remediate DNAPL sources in most groundwater environments are currently not available, ALTHOUGH PROVEN CONTAINMENT TECHNOLOGIES ARE READILY AVAILABLE AND ARE REQUIRED BY SOME STATES FOR DNAPL SOURCES. Conventional groundwater remediation technologies in place at chlorinated solvent sites (e.g. groundwater extraction and treatment) remove solvents that have dissolved in the groundwater. These technologies employ long-term active processes that are often costly and quickly reach a point of diminishing returns IF THE AREA BEING ACTIVELY REMEDIATED INCLUDES BOTH THE SOURCE AREA AND DISSOLVED PHASE AREA. As indicated above, small amounts of DNAPL mass can re-contaminate groundwater, generally making remediation of DNAPL sources areas to current regulatory criteria technically impracticable. Technical impracticability (TI) waivers are an appropriate regulatory mechanism IN MANY CIRCUMSTANCES and have been recognized by the EPA as appropriate tool for DNAPL sources. SOME STATES, SUCH AS NEW JERSEY, SPECIFICALLY REQUIRE CONTAINMENT OF DNAPL SOURCE AREAS AS A MINIMUM REQUIREMENT PRIOR TO CONSIDERATION OF A NATURAL ATTENUATION REMEDY FOR THE DISSOLVED PHASE PORTION OF THE PLUME.

RESPONSE 3

In some instances, natural attenuation can contain a source area as well as dissolved plumes. The specific site case study provided in Response 1 is an example. In addition, the first sentence of the second paragraph of Answer 14 in the RTDF document states that the main objective at a DNAPL site should be containment. The next sentence states that natural attenuation (where effective is implied) can be ideally integrated into such a strategy. The third paragraph tells the reader where to go for more detailed information on remediation of DNAPL. This document is not a document on other methods of remediation and therefore, contains no details on containment methods. As stated in Response 1, we are avoiding discussing specific regulatory policies and therefore will not use any language that mentions a specific state by name.

(2) Q20

Delete: “in some instances, specific regulatory guidelines or the desires of regulatory agencies at a specific site may prevent the use of natural attenuation even thought it may be sufficiently protective of human health and the environment."

Add "Some states, such as New Jersey, may not allow natural attenuation of source areas and require containment or removal of source areas in all cases. This is primarily based on the concept of groundwater as a resource, and the legislative intent of some states to restore and enhance the quality of it’s groundwater to the extent possible."

RESPONSE 4

We have used the criteria of “sufficiently protective of human health and the environment” throughout the document because in concept that is a criteria accepted by all regulatory agencies we know of. The idea of “groundwater as a resource” is not so universally considered. Although we understand the concept and believe groundwater is an important resource we do not believe that groundwater is a “receptor”. In addition, a technical evaluation of the effects of other remediation technologies on “groundwater as a resource” is usually never considered. Traditional groundwater extraction and treatment systems designed to “clean up a plume” to drinking water standards will likely extract somewhere between 5 and 20 plume volumes of groundwater during their lifetime, of which 4 to 19 plume volumes must come from clean, unimpacted groundwater surrounding the plume.

As stated in Responses 1 and 3, we are avoiding discussing specific regulatory policies and therefore will not use any language that mentions a specific state by name. The statement is being left unchanged.

(3) Page 18-24 Methods

The end of the methods section does a good job of pointing out that the regulatory agencies should be brought into the process as early as possible, typically after Step 2 or 3. In order to ensure awareness, it may be valuable to incorporate and expand upon these statements in Step 2 or 3.

RESPONSE 5

We agree.

(4) Table l

It should be added that one disadvantage of natural attenuation is that time frames may be LONGER than remediation by groundwater extraction and treatment.

It should also be added that in some situations, additional aquifer material may be contaminated as the plume moves during the time frame of natural attenuation.

RESPONSE 6

As stated above, time frames may be longer, however, they also may be shorter than other remedies so there is no point in emphasizing the negative only. Table 1 points out that natural attenuation may take as long as traditional groundwater extraction and treatment systems, which can be a very long time.

Natural attenuation is usually more acceptable when a plume is "stable" (not expanding). However, it could still be acceptable with a moving or slightly expanding plume. There is a certain inherent "stable size" for individual plumes. If expansion to this stable size is not large (<< twice its current size for example), and does not impact any receptors, it may be logical to let it do so. As pointed out in Response 4 above, a traditional groundwater extraction and treatment system may extract many additional plume volumes of clean, unimpacted groundwater during its lifetime and yet this is never considered as an impact.

(5) Table 6

Under the Date Collection Tier part of the table, why do some columns have a check while some have the number three?

RESPONSE 7

Apparently this is an error that occurred while converting the table to various formats. We have changed the "3"s to check marks.

We appreciate the opportunity to review this ITRC document. Please call Section Chief Karen Fell or me at (609) 292-8427 if there are any questions.

Sincerely,
David Sweeney, Bureau Chief
Bureau of Groundwater pollution Abatement

State Water Resource Control Board
Mailing Address:
P.O. Box 944212
Sacramento, CA
94244-2120

James George Giannopoulos, Chief
Regulatory Programs Branch
DIVISION OF CLEAN WATER PROGRAMS

DATE: MARCH 3, 1998

SUBJECT: REVIEW OF REPORT ON "NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER"

I am responding to your request for review of the document, "Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices," with the following comments:

The subject document would be useful for regulatory oversight of chlorinated solvent cleanup. The Regional Water Quality Control Boards (RWQCBs) implement regulations regarding chlorinated solvent cleanup on a site-specific basis. We understand that you have sent this package to each of the RWQCBs, who would be able to comment directly on its appropriateness for use at particular sites.

Please, also note that the State Water Resources Control Board and RWQCBs do not have the regulatory authority to endorse specific technologies, methodologies, or processes. While our agency cannot approve or endorse the document, we believe it will be a useful reference tool in evaluating the natural attenuation potential at appropriate solvent sites.

If you have any further questions, please call Heidi Temkco at 227-4376.

cc:Harry M. Schueller, Chief
Division of Clean Water Programs

RESPONSE 8

<u>The usage you have described in the last paragraph above was the intent of the document.</u>

Central Coast Regional Water Quality Control Board
81 Higuera Street
Suite 200
San Luis Obispo, CA
93401-5427
PHONE: (805) 549-3147
FAX: (805) 543-0397)

Dear Mr. Hadley:

REVIEW OF DOCUMENT TITLED, "NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER: PRINCIPLES AND PRACTICES"

As you requested, Dr. Wei Liu of my staff reviewed the subject document and developed comments in the attached internal memo dated February 18, 1998. If you have any further questions, you may refer them to Dr. Wei Liu at (805) 542-4648 or Mr. Jay Cano, Chief of the Underground Tank Unit, at (805) 549-3699.

Sincerely,

Roger W. Briggs
Executive Officer

(COMMENTS)
TO: Jay Cano FROM: Wei Liu

DATE: February 18, 1998 SIGNATURE: (signed by Wei Liu)

SUBJECT: Natural Attenuation of Chlorinated Solvents Document

Per your request, I have reviewed the "Natural Attenuation Of Chlorinated Solvents In Groundwater: Principles and Practices." Due to the time limit, I cannot comment on it in detail, but can only provide some general impressions/comments as follows.

Overall, this document provides good information on principles of natural attenuation of chlorinated solvent and the procedures for evaluation of the process. However, it appears to lead readers to believe natural attenuation is the best, if is not the only, solution for cleanup chlorinated solvent contamination in groundwater. Although the intent of the document is to demonstrate the natural attenuation works (at some sites), some important facts still need to be mentioned or adequately stressed. Those are: natural attenuation does not occur at every site; where it occurs, its effectiveness varies considerably; it usually takes substantially long time to complete; and it cannot control the contamination plume from expending or migrating down gradient.

RESPONSE 9

In regards to "....lead readers to believe natural attenuation is the best, if not the only, solution for cleanup chlorinated solvent contamination in groundwater."

<u>This is a document on natural attenuation and therefore emphasizes the attributes of that process. An English dictionary might lead one to believe English is the only language.</u>

In regards to "....natural attenuation does not occur at every site; where it occurs, its effectiveness varies considerably;"

<u>The answer to Question 3 in the RTDF document addresses how often natural attenuation might be expected to be completely effective (20% of the time) and how often natural attenuation might be expected to be partially effective (another 50% of the time). This suggests that it does not occur at every site and the effectiveness is variable.</u>

In regards to "....it usually takes substantially long time to complete;"

<u>As stated above, in Response 6, time frames may be longer, however, they also may be shorter than other remedies.</u>

In regards to "....it cannot control the contamination plume from expending or migrating down gradient."

<u>This statement is incorrect. Biodegradation is emphasized as a key component of natural attenuation, and, as a destructive process, it can often control migration of chlorinated solvent plumes just as it does with petroleum.</u>

In addition, the document puts too much emphasizes on the difficulty or almost impossibility to locate, contain and/or remove the DNAPL sources. Particularly, it appears to use these difficulties or "challenges" as justification or basis to imply or suggest natural attenuation is the only solution, at least for now, and "should" be considered at most sites because no other "proven, safe, and cost-effective technologies" currently available. This is misleading because same as other remedial alternatives natural attenuation has its own limitations, face the same challenges, and does not work (alone) at most sites (80%). To date, it still cannot be classified as proven, safe (due to more hazardous by-product) and, not necessarily, cost-effective technology.

RESPONSE 10

In response to "....suggest natural attenuation is the only solution, at least for now, and "should" be considered at most sites because no other "proven, safe, and cost-effective technologies" currently available.."

<u>As stated in Response 9, this is a document on natural attenuation and therefore emphasizes the attributes of that process. It is stated in the answer to Question 19 in the RTDF document that natural attenuation should be "evaluated" at every site and gives an additional technical reason for understanding natural attenuation processes but it does not state it should be the only remedy. The answer to Question 20 in the RTDF document</u>

states when natural attenuation should not be considered as a remedy: “when natural attenuation will not be protective of human health and the environment or alternative technologies can more reliably and cost-effectively treat the contaminants to minimize risk.” Although this is a broad statement, it clearly implies that natural attenuation is inappropriate at certain sites and that other remedies may be more appropriate.

In response to “To date, it still cannot be classified as proven, safe (due to more hazardous by-product) and, not necessarily, cost-effective technology;”

Nowhere is it stated that natural attenuation is a “proven” technology. It has been stated that other technologies are not (proven) for DNAPL sites. The subject of “more hazardous by-products” is addressed in the answer to Question 17 in the RTDF document. It is believed that natural attenuation is usually more cost-effective than other technologies as pointed out in Tables 1 and 4 in the RTDF document.

Although the document mentioned the natural attenuation is not a “do nothing” approach, the arguments to support this are very weak and unconvincing. Especially when the document strongly emphasizes that source removal/containment is very difficult, if not impossible, and that the natural attenuation should be considered as a sole-remedy at a considerable percentage of all sites, the natural attenuation as presented in the document is basically a “do nothing” remedy. Except long-term monitoring, all other actions listed in the document (bullets 1 to 3, Q&A 2) are required for evaluating the selected remedy during selection of remedial alternatives for every site.

RESPONSE 11

In response to “....the document strongly emphasizes that source removal/containment is very difficult, if not impossible, and that the natural attenuation should be considered as a sole-remedy at a considerable percentage of all sites.”

As stated in our answers to Questions in the RTDF document, source removal is very difficult at DNAPL sites (Answer 12) and therefore source containment is recommended (Answer 14). Response 9 above and the answer to Question 3 in the RTDF document addresses how often natural attenuation might be expected to be the “sole-remedy” at sites (20% of the time). This is a figure suggested by John Wilson of the EPA and is not empirical.

In response to “....natural attenuation as presented in the document is basically a “do nothing” remedy. Except long-term monitoring, all other actions listed in the document (bullets 1 to 3, Q&A 2) are required for evaluating the selected remedy during selection of remedial alternatives for every sites.”

Question and answer 2 in the RTDF document address why natural attenuation is not a “do nothing” remedy. Portions of bullets 1 and 2 may be required at all sites. The document has pointed out that the equivalent effort is required to document natural attenuation, and often this effort is specific to natural attenuation. For example, characterization of processes relevant to natural attenuation has usually not been done historically in site investigations (bullet 1). "Ensuring that these (natural attenuation) processes can reduce the mass, toxicity.....to acceptable levels" is not done for other remedies (bullet 2). "Evaluating the factors that will affect the long-term performance of natural attenuation" is never done for other remedies (bullet 3).

Additionally, the recent EPA OSWER Directive on Monitored Natural Attenuation has stated that natural attenuation is not a "do nothing" approach.

Based on the above, the following are some suggestions:

_ Stress that natural attenuation is not occurring everywhere, or at least it is not technically effective everywhere.

_ Stress that natural attenuation is a slow process and usually takes longer, sometimes much longer, than other active remedial alternatives, such as pump and treat, to cleanup the site.

RESPONSE 12

In response to the first bullet:

Since natural attenuation includes the physical processes of dispersion and dilution, it is by definition, occurring everywhere. Question and Answer 3 in the RTDF document address how often natural attenuation is effective. No changes will be made.

In response to the second bullet:

As stated in response 6 above, time frames may be longer, however, they also may be shorter than other remedies so there is no point in emphasizing the negative only. Table 1 points out that natural attenuation may take as long as traditional groundwater extraction and treatment systems which (implied) can be a very long time. No one has a long list of chlorinated solvent sites cleaned up by pump and treat.

Department of Environmental Protection, Commonwealth of Mass. Executive Office of Environmental Affairs
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To: Linda Benevides@Commissioner
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Cc: Claire Barker@Commissioner,David Salvadore@DEV@DEP
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Bcc:
Subject: Natural Attenuation of Chlorinated Solvents
Attachment:
Date: 2/19/98 8:17 AM

Linda, I reviewed the draft Natural Attenuation of Chlorinated Solvents in Groundwater - Principals and Practices that you sent us. We're involved with natural attenuation remedies at several oil contaminated sites at Devens and have a chlorinated solvent site (PCE @ 41,000 ppb in groundwater) which is currently going through the RI/FS. I anticipate that the Army's draft proposed plan will focus on a natural attenuation remedy. So as you can imagine, I was quite interested in the document and am glad the DEP is exploring the decision-making processes for implementation of natural attenuation.

I have only two comments to make: (1) I do not consider natural attenuation to be a "do nothing" approach. The natural attenuation RODs that we have concurred with have incorporated both modeling efforts and extensive long term groundwater monitoring plans. The RODs detail cleanup goals, and should natural attenuation fail to meet the goals we are prepared to implement additional contingency remedies. (2) I've had the opportunity to previously review one of the references "Overview of Technical Protocol for Natural Attenuation of Chlorinated Aliphatic Hydrocarbons in Groundwater Under Development for the U.S. Air Force center for Environmental Excellence" by Wiedemeier et al, noted in the review document. The Weidemeier study utilizes a screening process combined with a point system to evaluate the potential effectiveness of a proposed natural attenuation remedy. Weidemeir also estimates that for discharges of chlorinated aliphatic hydrocarbons, natural attenuation alone will be protective of human health and the environment in an estimated 20% of cases as opposed to an 80% success rate in the case of fuel hydrocarbons. If this is true, I guess we need to closely screen & evaluate sites before concurring with natural attenuation remedies for chlorinated HC Sites.

No Response required.

(Separate/second response submitted as part of Dept. of Enviro. Protection - Commonwealth of Mass. Executive Office of Enviro. Affairs)

MEMORANDUM

TO: Linda Benevides, IT Coordinator, DEP Boston
From: Radesha Thuraisingham, DEP, CERO
DATE: February 10, 1998
SUBJECT: Natural Attenuation of Chlorinated Solvents in Groundwater: Principal and Practice.

1.Page 6 Q 1: MA DEP regulations, does not consider transfer to another media, such as volatilization, and adsorption or migration to surface water such as dilution as a viable remedial alternative. Therefore volatilization, adsorption and dilution, although are naturally-occurring process, are excluded from the definition of Natural Attenuation.

RESPONSE 13

The document states a technical approach on natural attenuation, which includes the physical processes of dispersion and dilution. If a specific regulatory agency does not include these processes in their definition of natural attenuation, it is their responsibility to point that out to the appropriate parties within their jurisdiction. We would like to point out that in the recent EPA OSWER Directive on Monitored Natural Attenuation, these physical processes are included in the definition of natural attenuation.

2.Page 14 0 17: Vinyl Chloride (VC) will readily biodegrade…only in the presence of oxygen. In general, the condition in the environment is anaerobic and thus VC is dechlorinated. This process has a very long half-life and therefore VC is persistent in the environment.

RESPONSE 14

This statement is incorrect on several counts. As stated in the latter portion of the answer to Question 17 in the RTDF document, VC can "undergo direct biodegradation (oxidation) under both aerobic and anaerobic conditions." We refer the reader to a paper by Bradley and Chapelle (1996) that is referenced on p 25 in the RTDF document (References for Text and Tables). These authors have shown VC is oxidized to CO_2 under iron-reducing conditions (which are anaerobic). In addition, the same author (Bradley) has more recently shown the same process occurs under sulfate-reducing conditions (submitted to Anaerobe, 1998), and more interestingly, DCE is oxidized to CO_2 under manganese-reducing conditions (also anaerobic). The reference is Bradley et. al., Applied and Environmental Microbiology, 64:1560-1562, April, 1998. In addition, recent studies at Stanford have shown that the rate of VC dechlorination to ethene may be more rapid than the rate of DCE dechlorination to VC. We have a culture from a field site that dechlorinates VC to ethene with a half-life of < 1 day. This is not slow!

3.Page 15 Q 20: Natural attenuation also should not be considered as the remedy when the concentration of chlorinated solvents is too high and toxic to microorganisms. It is useful if the author could list the concentration in the groundwater. (Some researches have found this concentration to be approximately 7,500 PPM in soil. Is there one for groundwater?). Natural attenuation also should not be considered as a remedy if the site conditions (such as pH, moisture content, and electron availability) do not favor biodegradation.

RESPONSE 15

It is not known what concentration in groundwater is “too high” for bacteria. However, very efficient reductive dechlorination of TCE all the way to ethene has been observed at sites where the TCE concentration is clearly indicative of DNAPL (800 mg/l) in the source area. We refer the reader to the paper by Major et. al. (1995) that is referenced in the RTDF document (References for Text and Tables). The technical approach described to evaluate natural attenuation will identify if processes are occurring or not for whatever reason, and therefore, details on specific conditions which might inhibit biodegradation were not included.

Colorado Department of Public Health and Environment
4300 Cherry Creek Dr. S.
Denver, Colorado 80246-1530
PHONE: (303) 692-3300
FAX: (303) 759-5355)

Dear Paul:

I am writing to provide you with comments from our Colorado reviewers on the draft document "Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices" dated August 1997.

As a general matter, we did not find this document to be particularly helpful, and as such would not accept the document in its present form for use in Colorado. Following are some specific comments from our reviewers.

_ This document gives a very general overview of what is involved in a natural attenuation remedy. I would like to see them add a lot more references for recent Natural Attenuation guidance material. One in particular which is not mentioned is the OSWER Directive 9200.4-17 titled "Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites" (DRAFT Interim Final, December 1, 1997). This document gives a lot of scientific background information and "how to" information on monitoring for natural attenuation. One of the comments made in the OSWER document when discussing chlorinated solvents is that “Because of the nature and the distribution of these compounds, natural attenuation may not be effective as a remedial option. If they are not adequately addressed through removal or containment measures, source materials can continue to contaminate groundwater for decades or even centuries". I think that the RTDF document should stress the importance of source removal in order to achieve success with natural attenuation. I also feel that the advantages and disadvantages in the OSWER documents are more realistic.

RESPONSE 16

In response to the OSWER Directive 9200.4-17:

We think it is somewhat unreasonable to believe we should have described the OSWER Directive “(DRAFT Interim Final, December 1, 1997)” in a document published in August, 1997.

As stated previously in Response 1, we have avoided policy as much as possible. The OSWER Directive is clearly intended as a policy document and as such, the RTDF document will continue to avoid those issues where possible. The RTDF document has as much technical information as the OSWER Directive and references to far more.

In response to: “This document gives a lot of scientific background information and "how to" information on monitoring for natural attenuation”

The RTDF document has as much technical information as the OSWER Directive and supplies references to far more. The EPA in presentations at both the RTDF course and at other conferences has specifically stated that the OSWER Directive is NOT a "how to" document.

In response to: "Because of the nature and the distribution of these compounds, natural attenuation may not be effective as a remedial option. If they are not adequately addressed through removal or containment measures, source materials can continue to contaminate groundwater for decades or even centuries". I think that the RTDF document should stress the importance of source removal in order to achieve success with natural attenuation.

The OSWER Directive and the reader are partially correct in this statement. Source materials will continue to contaminate groundwater for decades or even centuries. However, this will most likely continue to occur even if source removal is performed. the idea of source removal at a DNAPL site apparently gives a "warm and fuzzy" feeling that something useful has been done, when in fact, the impact is minimal. Questions and Answers 11 - 14 in the RTDF document address why. If the reader does not believe the RTDF authors, we refer them to Pankow and Cherry (1996).

In response to: "......the advantages and disadvantages in the OSWER documents are more realistic."

The OSWER Directive (p. 7) contains 5 bullets on the potential advantages of natural attenuation; the RTDF document (Table 1) contains 7. Four of the bullets (in situ destruction, non-intrusiveness, combining with other remedies and cost effectiveness) are essentially identical. Two of the additional advantages mentioned in the RTDF document (natural attenuation is already occurring and no equipment failures) are very realistic and important, but the EPA has failed to acknowledge them.

The OSWER Directive (p. 7) contains 8 bullets on the potential disadvantages of natural attenuation, the RTDF document (Table 1) contains 5. Four of the bullets (long time frames, complex site characterization, toxic intermediates and long-term monitoring) are essentially identical. In addition, the RTDF document points out an additional realistic disadvantage (natural attenuation is not always cost effective). Institutional controls and the potential for continued migration, two of the additional disadvantages suggested by the OSWER Directive, are possible with many remedies, not just natural attenuation. The potential for continued migration and the potential for geochemical conditions amenable to natural attenuation changing, additional disadvantages suggested by the OSWER Directive, are both covered by the adoption of a contingency remedy which the OSWER Directive requires. The potential need for extensive outreach efforts to the public, an additional disadvantage suggested by the OSWER Directive, is a function of any new unknown remedy and not just natural attenuation. Surely, the EPA does not believe that the need to explain something to the public outweighs the advantages of advancing a new technology that works.

_ I do not support the adoption of this document for any purpose as it is presently written.

_ I do not find this document presents the principles of natural attenuation of chlorinated solvents in groundwater in the most direct manner. It suggests what information needs to be collected to make decisions about natural attenuation, but it does not say why. It waffles a lot and does not present the actual physical conditions necessary for different types of natural or bio attenuation. It does not try to integrate the different physical process such as adsorption/desorption, media partitioning, and dispersion with bio-regulated degradation.

RESPONSE 17

In response to “It suggests what information needs to be collected to make decisions about natural attenuation, but it does not say why.”:

The three lines of evidence presented in the document state why the information is collected. These are the identical lines of evidence recommended by the OSWER Directive and all other documents on natural attenuation. Table 6 of the RTDF document states the “Ideal Use and Value...” of every single parameter that might be collected. The OSWER Directive has no such information.

In response to: “It waffles a lot and does not present the actual physical conditions necessary for different types of natural or bio attenuation........”

The Principles and Practices document is not intended to be a “How to” cookbook as the AFCEE document is. It is intended to present a scientific, technical approach to evaluating natural attenuation. Interpretation of data, its incorporation into a conceptual model, and understanding the implications on the site, are things learned through years of experience and the proper training. Several of the authors of the RTDF document can “evaluate natural attenuation of chlorinated solvents in their sleep” for lack of a better expression, but that may be the single most difficult concept to put in writing in a simple and concise manner.

_ The OSWER DIRECTIVE No.9200.4-17 DRAFT INTERIM FINAL MONITORED NATURAL ATTENUATION POLICY is the better document: better written and more acute technically.

As you can see, our reviewers felt that the recent OSWER directive on natural attenuation was a more useful document. I am not aware whether the In-Situ Bioremediation Task Group, had the opportunity to review the OSWER document as part of your efforts or not.

RESPONSE 18

As stated in a well written and as an acute technical manner as possible in Response 16 above, it is difficult to review a document released December, 1997, in a document published in August, 1997.

It is reasonable to assume that the reviewer, as a regulator, might find the OSWER Directive to be a more useful document since it is clearly intended as a policy document. However, both the reviewer and the authors of the OSWER Directive continue to misunderstand several key technical issues (see the second half of Response 16 above as an example). The RTDF document has as much technical information as the OSWER Directive and supplies references to far more. The EPA in presentations at both the RTDF course and at other conferences has specifically stated that the OSWER Directive is not a "how to" document.

We appreciate the opportunity to provide you with these comments. If you have any questions, please feel free to contact me at (303) 692-3338. I would also invite you to contact our reviewers directly to discuss their perspectives. Sheila Gaston may be reached at (303) 692-3332, and Edgar Ethington may be reached at (303) 692-3438.

Sincerely,

Gary W. Baughman, Manager
Compliance Program

Illinois Environmental Protection Agency
1021 North Grand Avenue East,
P.O. Box 19276,
Springfield, Illinois 62794-9276)
217/524-3300

February 9, 1998

Mr. Paul Hadley
California EPA
400 P Street, 4th floor
P.O. Box 806
Sacramento, CA 95812-0806

Re: 9060000000 -- California
ITRC Workgroup
General Correspondence

Dear Mr. Hadley:

This letter in response to your request for comments on The Natural Attenuation of Chlorinated Solvents in Groundwater: Principals and Practices Document. Please find the Agency's comments below:

1. The document should provide a little information regarding U.S. EPA's work on natural attenuation, as the U.S.EPA is an integral player in protecting the environment.

RESPONSE 19

<u>As stated in Response 16, The OSWER Directive was not released until December 1997, and the RTDF document was published in August 1997. As stated in Response 1, the intent of the document is not to address policy of individual regulatory agencies.</u>

2. The foreword needs to provide more information regarding the purpose and intent of this document. It also needs to go into a general discussion of the overall format and content of the document.

RESPONSE 20

<u>The intent of the document is provided in Question and answer 5 and the document's organization is discussed in Question and answer 7 in the RTDF document. The intent of the document and more importantly, what it is not intended to do, is briefly summarized in the forward.</u>

3. There are many technical terms in this document. The document takes this into account by containing a glossary that provides a definition of many of these technical terms. Also, it appears as though the format of the document also takes this into account by placing in bold type

those technical terms that are defined in the glossary. However, the document does not come right out and say all this. It would be very helpful if the foreword or other introductory text to the document clearly identified that there is a glossary at the end of the document which defines many of the terms in the document and that the terms which can be found in the glossary are in bold print throughout the document.

RESPONSE 21

An explanation of both the glossary and the bold print is provided in Question and answer 8 in the RTDF document. From the reviewers questions it appears they may be looking at an older version of the document.

4. The format of Sections 1 and 2 (question and answer) does not seem to be appropriate. The information in these sections forms the basis of the entire document, as they attempt to describe the fundamentals of natural attenuation. It may be clearer if it were to be formatted in the same fashion as any other technical text, broken down and organized into several subsections, as appropriate, to allow for a logical presentation of the fundamentals of natural attenuation.

RESPONSE 22

Previous reviewers and readers overwhelmingly liked the question and answer format in the first versions and so it was retained.

5. Question 15 on Page 12 gives a very brief discussion of the various processes that contribute to natural attenuation. As understanding of these processes is paramount to the understanding of natural attenuation, much more information must be provided about each of these processes. At a minimum, detailed references need to be provided as to where additional information can be found on these various processes. However, the document would be much better if it contained a two to three page discussion on each of these processes.

RESPONSE 23

Many previous reviewers and readers requested that we present more detailed information on specific processes. It was not the intent of the document to provide details but it is agreed that it would be useful to provide specific references within the text. More detailed references on every topic in the text are provided in the reference section and in Appendix B. It might also be more useful to arrange the references by topic (e.g. DNAPL, anaerobic biodegradation) and that will be considered in the next version.

6. Biodegradation is a very important aspect of natural attenuation and is discussed in Question 16 on Pages 13 and 14. The text on this issue mixes a lot of technical terms that are not clearly defined with other non-technical terms. It is recommended that the text in the answer to Question 16 be modified to the following:

Chlorinated solvents biodegrade by several processes, including:

_ **Direct bio-oxidation** whereby the chlorinated compound is directly used as a **growth substrate** (food source-the **electron donor**) and broken down to inorganic molecules such as carbon dioxide, water and chloride;

_ **Reductive dehalogenation** (in which the chlorinated compound is used as the **electron receptor** in the biodegradation process);

_ **Co-metabolism** whereby the chlorinated compound is converted to another chemical by microorganisms as a secondary food source during use of other carbon compounds as a primary food source.

In contrast to the biodegradation of **petroleum hydrocarbons** evidence suggests that only a few chlorinated solvents can be used as growth substrates. Specific chlorinated solvents that can be directly bio-oxidized are vinyl chloride (VC); dichloroethene (DCE); dichloromethane (DCM); chloromethane (CM); 1,2-dichloroethane (1,2-DCA); and chloroethane (CE) (see Table 3 and Figure 3). In **aerobic** environments (in the presence of oxygen which serves as the **electron acceptor**), chlorinated solvents are co-metabolized (i.e., used as a secondary fork source) by nonspecific microbial **oxygenase enzymes** produced by...REST OF TEST SAME AS IN DOCUMENT

Finally, it should be noted that the text after the line items on the three biochemical processes discusses co-metabolism before reductive dehalogenation. This would seem inappropriate; the order in which these processes are first discussed should be the same as they are discussed in more detail.

RESPONSE 24

<u>Some of the suggested changes will make the document read better and they have been made.</u>

7. Item l in Step 4 refers to a “Pattern 3” and a “Tier 3.” However, these terms are not defined. The overall concepts of patterns and tiers are also not defined. Furthermore, it is not clear that the “Tiers identified in Table 5 are then tied to the tiers in Table 6”. Additional text needs to be provided regarding the various tiers and patterns. See also Comment 12 below.

RESPONSE 25

<u>It is not clear to the authors that pattern and tier need to be defined as they are used here. The text in item 1 suggests that the tiers identified in Table 5 are tied to the tiers in Table 6.</u>

8. Item 2 in Step 6 of Section 3 uses many technical terms associated without **(sic)** the various processes which make up natural attenuation ("mass balance”, "parent and daughter products," "flux," "co-metabolites," "sorption and retardation of chemicals," "biodegradation kinetics"). However, these terms are not defined anywhere. As indicated above, in Comment 5 much more information needs to be provided about the various processes which make up natural attenuation and these various terms which appear in Step 6.

RESPONSE 26

Cometabolism and sorption are defined in the glossary but the other terms used here are not. It was believed that anyone using this section in a technical manner would have a technical background and understand the meaning of flux, retardation and mass balance. It may be appropriate to define daughter products and biodegradation kinetics.

9. The last point in Item 2 in Step 6 of Section 3 states: "Estimate the long-term capacity of the aquifer to sustain natural attenuation..." However, no information is provided on how to make this estimation. Overall, a detailed example should be provided in the document to show how to make this estimation.

RESPONSE 27

As stated in Response 17 above, the RTDF document was not intended to be a “How to” cookbook. Since natural attenuation has only been selected as the remedy for chlorinated solvent sites very recently, very little site data is available to answer this question. One would estimate the sustainability of the processes based on the availability of the necessary electron donors and acceptors to keep the observed processes going. This would be a complex estimate and would be very site specific, thus no details were provided. An appropriate Long-term monitoring plan assures the stability of the plume and will document if things change.

10. A term "AFCEE" is used near the end of Step 9 of Section 3. However, it does not appear as though this term has been defined previously.

RESPONSE 28

AFCEE is defined in the forward of the RTDF document.

11. The document is lacking information on the long-term monitoring which should be done at a facility implementing natural attenuation. This is the most important aspect in the actual implementation of natural attenuation and needs more discussion than just referring to Table 7. The components of the overall monitoring program need to be discussed in detail. Table 7 is good, but it cannot stand on its own.

RESPONSE 29

As stated in Response 17 above, the RTDF document was not intended to be a cookbook. A long-term monitoring plan would also be site specific, thus no details were provided.

12. What does a "3" mean in Table 6? Also, please define what “*” means on each page of the table not just at the end of the five page table.

RESPONSE 30

See Response 7 above. The * change has been made.

The Illinois EPA would be interested in any training that might be available at our offices in Springfield, Illinois on this subject.

RESPONSE 31

The RTDF course on Natural Attenuation of Chlorinated Solvents is coming to at least one site in the Midwest within the next year. A tentative schedule change has the course being in Chicago in March 1999. It will also be in Kansas City in September 1998 and in Nashville in November 1998.

If you have any additional questions in this matter, please contact Ted Dragovich of my staff at (217) 524-3306.

Sincerely,

Edwin C. Bakowski, P.E.
Manager, Permit Section
Bureau of Land

Department of Toxic Substance Control
400 P Street
4th floor
P.O. Box 806
Sacramento, CA 95812-0806

FROM: Ted N. Rauh
Deputy Director
Hazardous Waste Management Program

DATE: March 5, 1998

SUBJECT: REVIEW OF DOCUMENT TITLED, "NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER: PRINCIPLES AND PRACTICES"

Thank you for providing a copy of the document titled "Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices" (Draft Version 3.0, August 1997), including the comments and responses to previous versions of the document for our review. As you requested, we are providing input regarding the usefulness of this document to the Hazardous Waste Management Program (HWMP) and suggestions for changes that would be necessary for HWMP to use this document. In preparing these comments, we reviewed both the document, and the comments and responses prepared by the authors, the Industrial Members of the Bioremediation of Chlorinated Solvents Consortium of the Remediation Technologies Development Forum (RTDF).

No Response Necessary

Overall, the document seems to be a well-researched and concise summary of methods for evaluating and implementing natural attenuation with special emphasis on recent scientific developments and an exhaustive list of references. The document presents itself as a technical resource for assessing natural attenuation and as such its references and technical information, in particular the strategy for evaluating the suitability of natural attenuation, will be of use to HWMP. However, the document's usefulness to our program appears somewhat limited by the document's omission of some policy issues and by some explanations that seem overly abbreviated.

No Response Necessary

Both the document and responses to comments emphasize that the document is intended only as a technical resource, not to provide specific guidance or policy. Crucial to the decision process for determining whether natural attenuation can be used, however, is the consideration of implementation issues and policy determinations. To be useful the HWMP, the document should, at the very least, describe such mitigating considerations. Costs are but one such consideration that the document discusses at length; others, such as time frame limitations, cross media transfers and public acceptance are also valid components of the process of evaluation that are not discussed in this document. The document focuses primarily on technical feasibility with some discussion of costs, but a program such as the HWMP must also consider other aspects of implement ability.

No Response Necessary

As a result of its emphasis on technical feasibility, this document in some instances seems in conflict with U.S.EPA's policies, as described in U.S.EPA's Draft Directive on Monitored Natural Attenuation. For example, U.S.EPA's Draft Directive suggests that natural attenuation is not appropriate if it results in significant contaminant migration or unacceptable impacts to receptors. In contrast, the subject document indicates that migration is only acceptable if no receptors are affected. Furthermore, the document is also in conflict with State policies since in California, as in New Jersey, the groundwater itself is considered a receptor and contaminant migration is generally not allowed due to the State's non-degradation policy. By broadening its consideration of implementation issues, the document would be more useful to HWMP and would avoid misleading readers unfamiliar with such issues.

RESPONSE 32

We appreciate this reviewers understanding of the intent of the document and the effort they obviously put into reading both it and previous responses. We refer the reviewer to Response 16 regarding the timing of this document and the EPA's OSWER Directive, and to Responses 4 and 6 above regarding groundwater as a "receptor". We disagree with that concept for the reasons given and as stated previously, are making no policy statements within the document.

While the document is attractively concise, in some instances it would benefit from expanded discussions. For example, the description of the three lines of evidence used to document natural attenuation could be augmented, especially to include examples of the second line of evidence. In addition the description of the data collection tiers is somewhat confusing and the associated table is not self-explanatory and needs clarification. Similarly, the table describing long-term monitoring indicates well placement and data collection, but the document does not address other monitoring issues; such as, performance objectives or triggers for the contingency remedy.

RESPONSE 33

We appreciate this reviewers view that the document is "attractively concise". As stated in Response 17 above, the RTDF document was not intended to be a cookbook and thus a high level of detail was avoided on most topics. A long-term monitoring plan would also be site specific, thus no details were provided. Issues such as performance objectives and triggers for contingency remedies would also be agency specific and so did not warrant discussion as per the avoidance of agency specific policy.

In summary, the document's usefulness to HWMP would be enhanced if it were to address the implementation issues that temper technical feasibility, acknowledge differences with U.S. EPA's policies, and expand some descriptions of data collection and use. It is likely that such information would also be useful to the broader audience for which this document is intended. To this end, HWMP recommends accepting the document according to the second level of acceptance. Namely, the document is appropriate; however, the policy differences with U.S.EPA, as described above, creates conflict for the HWMP.

No Response Necessary

Thank you again for the opportunity to comment on this document. We look forward to using it and its revised versions as a resource for evaluating natural attenuation in the corrective action program. If you have questions regarding these comments, please contact Ms. Peggy Harris of my staff at 324-7663.

Lahontan Regional Water Quality Control Board - Victorville Office
15428 Civic Drive
Suite 100
Victorville, CA 92392
PHONE: (760) 241-6583
FAX: (760) 241-7308

MEMORANDUM

FROM: Harold J. Singer, Executive Officer

DATE: February 11, 1998

SUBJECT: **REVIEW OF DOCUMENT TITLED: "NATURAL ATTENUATION OF CHLORINATED SOLVENTS IN GROUNDWATER: PRINCIPLES AND PRACTICES"**

Thank you for the copy of the above-referenced report transmitted with your February 3, 1998 memorandum.

You have asked for our review and comment on the document. You also request our input on whether the document could be used in its current form by our organization.

I do not believe that I have the necessary staff resources to commit to the review of this extensive document. By copy of this memorandum to the State Water Resources Control Board, Division of Clean Water Programs, I am requesting that the Division take the lead in this policy development matter. I believe it would be appropriate to create a technical advisory group, with expertise from the state and regional boards, which would provide the necessary critical review and comment on this important document.

If you have any questions please call me at (530) 542-5412.

cc: Harry Schueller/CWP/SWRCB w/February 3, 1998 memorandum
Regional Board Executive Officers w/February 3, 1998 memorandum

(Cover Page)
Author: **<Allen.R.Tool@NWK01.usace.army.mil> at Internet**
Date: 3/12/98 3:11 AM
To: Steve Hill at CRC-FF

Steve,

I have attached some comments on the Principles and Practices document. They were prepared by Dr. Carol Dona of our staff. She is a leader in the area of natural attenuation within the Corps.

The Kansas City District of the Corps of Engineers has found the document to be very helpful in specific project related work. Army policy mandates that we evaluate natural attenuation at Army sites. We have found the Principles and Practices document to [be] very helpful in fulfilling the Department of Army mandate.

Our District is developing a formalized internal process for considering natural attenuation at our projects. The Principles and Practices document and its earlier drafts have been [a] real asset to our process action team.

This document really hits the level that is very useful in educating a broad range of professional staff within the Corps; as well as, our customers.

I hope these comments are helpful.

Allen Tool

PS: One of the attached documents is in W.P. 5.0 and the other is a Word document. They both contain the same information, however the W.P. document has a few format glitches.

(Attached Document)
Subject: Comments on Natural Attenuation of Chlorinated Solvents in Groundwater: Principles and Practices, prepared by the Industrial Members of the Bioremediation of Chlorinated Solvents Consortium of the Remediation Technologies Development Forum (RTDF) Version 3.0, August 1997.

General Comments

Comment I: The framework presented for evaluating natural attenuation is clear and easy to follow. The basic framework is potentially applicable to other contaminant types and media.

No Response Necessary

Comment II: The sampling methodology, case study, and cost information is detailed, relevant, and complete, providing a good reference for initial information and potential contacts for different types of sites. Particularly useful are the detailed cost itemization and comparison of pump-and-treat with natural attenuation, the geological and geochemical site descriptions and the references included in the case studies, and the tiered data collection table.

No Response Necessary

Comment III: The Common Degradation Pathway figure is useful in supplying information about what compounds are potential daughter products. The degradation pathway for carbon tetrachloride, 1,1,1-trichloroethane, and 1,1,2-trichloroethane are particularly useful.

No Response Necessary

Comment IV: The document tracks attenuation patterns by plotting the chlorinated solvent concentrations at a specified time against distance along the groundwater flow direction. An additional approach for showing attenuation would be to plot plume size and/or concentrations with respect to time (multiple sampling round data). Potential receptors could also be plotted with the data to visually show the unlikelihood that the plume would reach receptors.

Response 34

The plots mentioned are for idealized "Pattern" sites. It would be appropriate to plot data over time for an actual site if it is available and this has been done for actual sites.

Specific Comments

Comment 1, p.10, paragraph 1: The last statement states that most chlorinated solvents are DNAPL. I suggest that this sentence be amended to include that DNAPL occur only when the concentrations of the chlorinated solvents are above their respective solubility concentrations.

Response 35

The statement was meant to indicate that most chlorinated solvents are DNAPL with the emphasis on dense (meaning not LNAPL). It was not the intent to say that they always existed in that form in the environment.

Comment 2: It is not clear what form(s) of iron are involved in the dissolved iron concentration mass in the lower figure in Figure 5. Please describe the reaction(s) involved. If dissolved iron describes ferrous iron, please explain why the iron apparently peaks after the drop in sulfate concentrations and explain why the iron concentrations decrease following the iron peak.

Response 36

The form of dissolved iron is ferrous iron (Fe II or Fe^{+2}). Iron-reduction and sulfate-reduction can happen simultaneously, thus the dissolved iron "peak" is occurring at the same time that sulfate is going to total depletion. Dissolved iron would then decrease based on dilution and precipitation (possibly as FeS). Remember, this is an idealized "pattern", however, this is what is often observed at real sites.

State of Tennessee -
Department of Environment and Conservation -
Division of Solid Waste Management)

January 15, 1998

Mr. Jim Haynes, Director TDEC-DSF
Fourth Floor, L&C Annex
401 Church Street
Nashville, Tennessee, 37243-1538

RE: Review of document titled:
Natural Attenuation of Chlorinated Solvents in Groundwater: Draft Version 3.0
August 1997
and proposed ITRC Acceptance Statement

Dear Mr. Haynes:

We are pleased to respond to your request to review and comment on the referenced documents. A list of minor comments is attached. Please contact Hernan R. Flores Jr., P.E., at (615) 532-0856 with any questions you may have on our response and comments.

Sincerely,

Hernan R. Flores Jr., P.E.
Environmental Protection Specialist

c: Clayton Bullington

COMMENTS

1. On **Step 1. Review Available Site Data**, (page 18), superfund program Risk Assessments are associated with the acronym (RA). This might be confusing to those accustomed to seeing this acronym associated with Remedial Actions by Superfund Programs.

Response 37

<u>The acronym does not appear to have been used after that point in the text so we have removed it.</u>

2. On **Step 3. Screen the Data for Evidence of Natural Attenuation and Develop Hypothesis to Explain the Attenuation Processes**, (page 19), background information on the different Mechanisms of chlorinated Solvent Biodegradation, such as those described by Chapelle (1), should be presented. Also, information on the use of Redox Potentials and Hydrogen concentrations such as that presented in Wiedemeier *et. al.* (2) to identify the potentially present mechanisms should be presented.

Response 38

The use of hydrogen measurements to identify REDOX zones and where specific geochemical processes are believed to be actually occurring is becoming more popular. However, measuring hydrogen is expensive. The members of the RTDF currently place more weight on the other geochemical data in developing a site geochemical model. We have never seen a site where hydrogen measurements were done where it would have changed our interpretation of the other geochemical data to any large degree.

REFERENCES

1. Chapelle, Francis H. 1996. *Identifying Redox Conditions That Favor the Natural Attenuation of Chlorinate Ethenes in Contaminated Ground-Water Systems.* In: Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Groundwater. EPA/540/R-97/504. May 1997.

2. Wiedemeier et. al. 1996. *Overview of the Technical Protocol for Natural attenuation of Chlorinated Aliphatic Hydrocarbons in Groundwater Under Development for the U.S. Air Force Center for Environmental Excellence.* In: Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Groundwater. EPA/540/R-97/504. May 1997.

(Attachment - *Typed)*
Date: December 10, 1997

To: Jim Haynes

From: Chuck Head

Concerning:ITRC Natural Attenuation Guide

I reviewed this document from a conceptual point of view. Without discussing concerns about some statements made as fact which I would debate; it appears the document basically proposes long term monitoring of sites without taking any corrective action or limiting the amount of corrective action at a site and substituting long term monitoring for portions of the contaminant plume.

The concept of Natural Attenuation ("NA") is being discussed in many different arenas. Primarily, the NA approach promotes the long term monitoring of a site in lieu of remediation. My biggest concern with NA is that long term monitoring is proposed without any evaluation of the risk potential of the site. The movement of contamination through soil, groundwater and vapors and the proximity of the contamination to points of exposure should be determined before NA is allowed on a particular site. It seems to me rather than just using NA as an approach in lieu of corrective action, the site must be fully characterized, the migratory pathways for contaminants fully evaluated, points of exposure defined and modeling of the contaminant movement evaluated before NA is approved. I believe NA is just the last part of a scientifically based risk evaluation that determines a "site specific standard" based on unique site conditions.

The NA process is best used as a tool to validate through long term monitoring the site conditions and that the site-specific standard established through the risk assessment is valid.

Response 39

<u>The RTDF document made it clear that protection of human health and the environment is paramount. Question and Answer 20 explicitly states that NA should not be considered as the remedy when these criteria can not be met. Step 8 and Figure 4 clearly show that an exposure pathway analysis is required. The emphasis of this document is not on how to do risk assessments or evaluate exposure pathways because it is a technical document on NA.</u>

I would strongly caution against the use of NA without proper evaluation of risk on the front end. I have attached some rather cryptic notes to this memo if you are interested. Please call me if you have questions.

Thanks, Chuck.

(Attachment - Cryptic Notes, *<u>Hand written</u>*)

Jim - I did not see any mention of how NA is applied to off-site contamination. I suspect the [ITRC] folks don't see any difference. However, from a citizen's right perspective the NA approval is not a viable option.

Response 40

<u>NA would be applied to all contamination exactly the same, from a technical standpoint. Plumes are often already off-site when first defined resulting in the necessity of all remedial alternatives to address off-site plumes. The RTDF consists of several large industries and as such has considerable experience in dealing with offsite issues. In general, they can be dealt with.</u>

[ITRC] - Natural Attenuation / Chlorinated Solvents p.6

1. <u>Effectiveness of NA on Chlorinated Solvents</u>

    A. 20% of all sites by EPA & J. Wilson Personnel Communications, this is suspect to official publication from EPA/ no scientific study cited[.]

Response 41

<u>John Wilson is the EPA's most knowledgeable staff member on NA and is highly respected in all NA circles. We assume this is his opinion based on experience and not a scientific study.</u>

    B. This is not a remediation technology - it is simply an extended monitoring program with some evaluation of potential risk[.]

Response 42

NA is not a remedial "technology", it is a remedial option that is evaluated to the same degree as all other remedial options regarding its ability to reduce risk to an acceptable level.

2. Occurrence of Chlorinated Solvents p.9

Chlorinated solvents are almost "ubiquitous" because of their use in many household products - their routine occurrence is not a misconception[.]

Response 43

The reviewer's question is not clear. The RTDF document does not state that the "occurrence of chlorinated solvents" is a misconception.

3. Low Solubilities of DNAPL p.10

It takes centuries to dissolve into GW. First, for the entire amount of chlorinated solvents to dissolve into water if there is free product would take a long time. However, according to Mark TCA has a solubility of 1g TCA in 350ml of water @ 25 C° or 2800ppm while Trichloroethylene has a solubility of 1470ppm in water. These solubilities are very high considering the MCL's for these compounds are 5ppb.

Response 44

The solubility of chlorinated solvents is high relative to MCLs (hence the problem) but is low relative to what would be necessary to remove them through a long-term "rinsing program" (groundwater extraction and treatment). In addition, DNAPL exist as a separate phase through which very little water passes in the groundwater environment, thus further reducing their opportunity to dissolve. The MCL for TCA is 200 ppb.

Potential to exacerbate problem p.10

This is always a problem, it is not just a problem for chlorinated solvents[.]

Response 45

This is not "always" a problem. The problems described are associated specifically with DNAPL.

4. Site Investigations to determine DNAPL presence p.11

Site investigations which involve soil & gw sampling are very effective in determining DNAPL contamination.

Response 46

The main point of Answer 13 in the RTDF document (and following answers) was that the presence (qualitative sense implied) of DNAPL can usually be determined without doing extensive site investigations, and that it is futile to try to "find" any or all of the DNAPL for the purposes of attempting to remove it.

5. Stabilization p.12
   I don't know of any studies that demonstrate DNAPL are absorbed preferentially by clay.

Response 47

We refer the reviewer to section 8.3.3 of Chapter 8 of Pankow and Cherry (1996) and the 14 references within that text.

6. All types of bacteria available at all sites p.14
   Need to substantiate through lab cultures/tests - no studies included[.]

Response 48

All statements in Answer 18 are true. Statements regarding the percentage of sites where specific groups of dechlorinating bacteria are present comes from unpublished data by Dupont. In the future we will add this reference. The presence of bacteria that are important in a specific process is usually documented through geochemical evidence not through lab cultures.

7. When Should NA be evaluated at sites -
   This is no different that the current NFA hypothesis which can be explored at any site - especially if risk assessment is included[.]

Response 49

The intent of Answer 19 was to encourage the evaluation of NA. In the RTDF's experience, this has historically not been done at chlorinated solvent sites.

8. Three lines of evidence documented - p.16
   1. Long term monitoring is already an option for remediation[.]
   2. Must determine what parameters to model [oxygen] levels, [ ] chlorides, etc.

Response 50

This comment is not understood. Long-term monitoring and modeling are not mentioned on this page.

9. Comparison of Pump & Treatment costs vs. NA - Table 4
   [-]Vastly inflated dollars for the P&T system
   [-]High number of MW's for P&T or NA

Response 51

The costs for the P&T system are taken from Dupont's experience at its own sites.

As a side note, the author responding to these comments recently had an opportunity to evaluate NA vs P&T at a DoD site. The 30-year cost for a P&T system (based on other systems already installed onsite) was ~$200,000 more for a 30 gpm system than the 50 gpm system described in Table 4. Admittedly, DoD has bought $200 toilet seats, but that does not make the costs not "real".

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Overall the document is easy to understand and is well written, although a grammar check would be helpful in some places. The following comments may provide further clarification of some of the items.

Page 10, Bullet at top of the page: The word "immiscible phase" needs to be inserted in the 2nd parenthesis (i.e., they maintain a separate phase in water).

Response 52

<u>It is the responder's recollection that the term "immiscible phase" was used in an earlier version of the document, and another reviewer suggested the current wording as being more understandable.</u>

Page 17, A23: The second sentence should be modified for better clarification. For example, "Table 5 summarizes several common patterns of chlorinate solvents in groundwater including their distribution and relates these patterns to suggested data collection tiers to support natural attenuation." The Title of Table 5 should also be modified for clarification; it is also quite cumbersome.

Response 53

<u>The second sentence in A23 has been modified. The title of Table 5 was not changed.</u>

Table 4: Cost Comparison of Natural Attenuation to Other Remedial Technologies: The number of years used to estimate the lifetime calculations should be included.

Response 54

<u>The costs are based on 30-years net present value, as cost comparisons are at most sites. This information has been inserted in Table 4.</u>

Table 6: Data Collection Tiers For Evaluation and Implementation of Natural Attenuation: A few sections in this table need to be clarified so that the reader can better understand the use of the tier data approach. The footnote for the last column (*) should

be printed on every page. Also, the number 3 is found throughout the last column without any reference to its meaning. This also needs to be footnoted.

Response 55

Several reviewers have commented that this table needs clarification. Changes have been made. See response 7 in regards to the "3".

General Comments: Questions have arisen from several regulatory staff members regarding the end products including what happens to the ethanol, ethene, ethane, and methane. Specifically, do these compounds degrade/mineralize, or are they volatilized and enter the vadose zone? These concerns need to be addressed, specifically when the water table aquifer is shallow and there are buildings/homes with basements located either on site or near the compliance line. This information should be included on Figure 2.

Response 56

All of these compounds would be easily biodegraded if they entered an aerobic environment (the vadose zone or down gradient aerobic groundwater). Compounds such as ethanol would also be degraded in an anaerobic environment, and in the case of a chlorinated solvent site, would serve as an excellent electron donor. Ethene and Ethane may biodegrade in an anaerobic environment, however, the quantity usually produced at a site would be very small (20 mg/l maximum based on solubility) such that it should not be a concern. Methane is produced at many sites and is not a result of chlorinated solvents in particular (e.g. landfills, petroleum releases). Again, the quantity usually produced at a site would be very small (40 mg/l maximum based on solubility) such that it should not be a concern.

A brief discussion on stabilization of the plume should be included. Specifically, when is a plume considered to be stabilized. A discussion on rate of degradation versus the rate of groundwater flow might also be beneficial. Finally, a discussion on defining the compliance point and migration of the plume off site would also be beneficial.

Response 57

From a technical standpoint, plumes do not necessarily have to be stable for NA to be acceptable. Understanding the concept of a stable plume is not specific to chlorinated solvent sites, and therefore, has not been discussed. As stated in Response 33 above, certain aspects of a site specific monitoring plan such as performance objectives, triggers for contingency remedies, off site migration and compliance points would be agency specific and will not be discussed as per the avoidance of agency specific policy.

Mr. Paul Hadley
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Dear Mr. Hadley:

Re: Natural Attenuation of Chlorinated Solvents In Groundwater: Principles and Practices Draft Version 3.0

This is in response to your request to review the above referenced document and Draft Acceptance Statement for ITRC members. We agree that natural attenuation is a remedial technique which has merit and the information presented in the draft document provides sufficient information to evaluate the possibility that natural attenuation is occurring at a particular site. However, we believe that the document should present and elaborate on the benefits of addressing (e.g., treatment, control and containment) identifiable source areas of contamination. It would also be useful to present case studies where source remediation techniques have and have not worked. As you can see by the comments presented below New York State believes that addressing source areas will remain an important part of the remedial decision-making process in an effort to restore the natural resources to their pre-release conditions when and where appropriate and practical.

As for the level of acceptance and use of this document in the context of the ITRC a separate letter will be sent when the final version of the document is published and a response to our comments is provided.

Presented below are the States comments along with questions posed in your letter.

<u>Does the guidance offer enough technical detail to be useful to this agency?</u>

The document provides an adequate level of technical information to assist the agency in evaluating the potential for natural attenuation at cleanups under site remediation program (SRP). In addition, a detailed review of the case studies (as proposed for Appendix C) would be a useful tool as long as there is an opportunity for an independent review and evaluation of the data. The document addresses this issue, but it should be stressed that collection of specific data to evaluate the potential for natural attenuation should occur during the initial stages of investigation, since evaluation of this phenomenon requires time dependent information.

Is the Question and Answer format helpful?

Yes.

Is the information provided in the answers consistent with your understanding of the processes of natural remediation?

From a practical standpoint the information provided in the answers is consistent with our understanding of the processes of natural remediation.

Is there anything in this document which presents a potential conflict with state law, regulation or agency policy?

There is nothing in this document that directly conflicts with state law, regulation, or agency policy. As a matter of implementing the SRP our regulations state that the goal of the remedial program is to return a site and surrounding environment to pre-release conditions where practicable. Our regulations and policies govern the protection of groundwater as a natural resource. As with other states, our state has various classifications for groundwater. A significant portion of the State's groundwater is classified in a category which requires that it be protected for its' best use, which is as drinking water. In implementation of our SRP, our regulations require that these standards be met as part of a remedial program or be waived for reasons of technical and economic impracticability. In those instances, the feasibility study, including modeling and/or treatability studies must demonstrate that it would be impractical to meet a standard and restrictions on use of the groundwater would be required. It may be useful to elaborate how SCGs and ARARs would be addressed in the process of evaluating natural attenuation.

Does this guidance document and the information it contains encourage your state to utilize natural attenuation of chlorinated solvents in the subsurface as a remediation technique? If no, is it because of the manner in which the information is presented?

The document does provide the technical information necessary to assist the state in evaluating the possibility that natural attenuation is occurring at sites where chlorinated solvents are present as well as the appropriateness of evaluating source remedial options. We see this technique being used in combination with other remedial techniques such as source removal, treatment, containment and/or control when appropriate. In addition, if this remedial technique were selected the state would also require that a contingent remedy be included in any decision document as a precaution if monitoring indicated that the pre-remedial modeling was incorrect or a steady state condition was not achieved. Finally, we will also look at the possible techniques to enhance the natural processes to shorten remedial time frames in order to restore contaminated groundwater to their pre-release state.

Specific comments regarding the document are provided below and make use of the format contained in the document.

Other Comments

A 1: Does the National Contingency Plan address time frames that are acceptable for using natural attenuation? As written, the second to last paragraph of this section suggests that time frames are not considered.

Response 58

The OSWER directive suggests that time frames for natural attenuation should not be unreasonably lengthy when compared to the time frame for alternative remedies.

A 3: What technical information is available to support the estimated percentages of chlorinated solvent sites where natural attenuation could be used as all or part of the site remedy?

Response 59

See Response 11 above.

A 4: Table 1 indicates that where natural attenuation is used "Time frames may be as long as remediation by groundwater extraction and treatment." The table should be modified to state "... may be longer than remediation..."

Response 60

See Response 6 above.

A 12: The discussion of DNAPL should also address source containment. Furthermore, it should acknowledge that where the majority of the DNAPL have been removed, treated, or contained, restoration time frames would likely be shorter than if natural attenuation was the sole remedy.

Response 61

By definition, if one could remove the "majority of the DNAPL", restoration time frames would be shorter. However, we have pointed out the difficulties in both finding all the DNAPL and in removing it, and the implications: time frames of centuries might only be reduced to a century or two. In the big picture, we do not see this to be significant enough to warrant the effort in the first place.

The text seems to suggest that DNAPL source areas should not be investigated. However, where extreme caution is exercised in investigating such areas in a well-planned manner, the resulting information may be invaluable in the evaluation of remedial alternatives. Furthermore, where proper site characterization has been performed, the risks of inadvertently mobilizing DNAPL as a result of remedial activities should be minimal. Where risks of a planned remedial activity are evident, it might be possible to have a "remedial back up" (e.g. slurry wall) in place to minimize the migration of any re-mobilized DNAPL.

Response 62

We agree that once a proper site characterization has been performed, the risk of mobilizing DNAPL is reduced, however, it is those site characterization activities we are concerned about. Many people do not understand how DNAPL can be mobilized. DNAPL can penetrate deeper into an aquifer for instance, by dewatering in preparation of doing SVE. A slurry wall is an extremely expensive remedial measure in and of itself. If the risks of a remedial activity are high enough to warrant such extreme "backup" measures, we would suggest the activity not be performed or perhaps a slurry wall would serve as the whole remedy to containment.

The discussion of contaminant distribution, low solubilities and slow diffusion (page 10) needs further discussion to explain that for DNAPL (specifically chlorinated solvents) their slow diffusion and low solubilities means that DNAPL remains present in the subsurface for a long time. In addition, the very low MCL values for chlorinated solvents means that a minuscule amount of DNAPL, producing small amounts of dissolved contamination, would likely violate ambient groundwater quality standards.

Response 63

We thought we made this concept clear in the paragraph under "Complex Distribution".

A 13: What is meant by the phrase "... unless historical records can account for waste solvent volume (e.g., recycling, off-site treatment/disposal)"?

Response 64

We meant that unless historical records can account for all solvent used at the site where immiscible phase solvent was brought on site, it should be assumed DNAPL is present.

A 14: The text should address the use of containment technologies (e.g., slurry walls, capping) for isolating DNAPL areas at a site so that the remainder of the plume could be addressed through active remediation and/or natural attenuation.

Response 65

This is not a document on containment so it will not contain detailed discussion of containment technologies. We agree that containment technologies can isolate DNAPL areas at some sites and will likely mention it in the next version. However, we would like to point out that at many sites (fractured bedrock, or very deep sites), sources can not be efficiently isolated. At some sites, other compounds or even chlorinated solvents themselves (e.g. dichloromethane) are playing an important role as electron donors or generating cometabolites and should not be disconnected from the plume. Mixed waste landfills are classic examples.

A 18: The text should address the degree to which the necessary quantities of the various types of needed bacteria are present at sites.

Response 66

We believe the answer is sufficient considering the current state of knowledge on this subject. In the future it may be modified or updated.

Evaluating Natural Attenuation

A 19: The fourth bulleted statement also needs to address source containment. The document should emphasize the need for all appropriate measures to be taken to address/remove a continuing source before considering more long-term remedial/site strategies. One reviewer indicated that the tone of the language led him to believe that this document seems to treat NA as a "last resort" type of option. If the data indicates that natural attenuation is a viable technique then it should be given the same consideration as any other remedial technology.

Response 67

The text has been changed to read: "cannot cost effectively be removed or contained...". Obviously we do not consider natural attenuation to be a "last resort" option since we believe it should be evaluated at all sites, and we agree that it should be given the same consideration as any other remedial technology.

A 23: The manner in which Tables 5 and 6 are meant to be used is not clear. For example, what does "3" designate in the "Data Collection Tier Columns"?

Response 67

See Response 7 above.

Methods

Step 4. Identify Additional Data Requirements: Item 1 states "... the conceptual model.....should be similar to Pattern 3 and would warrant collection of Tier 3 data.". However, Table 5 indicates that Tier 2 data should be collected for the Pattern 3 scenario. This needs to be corrected as appropriate.

Response 68

<u>The text in Step 4 has been changed to read: “Tier 2 data”.</u>

Step 7. Interpret the data and Test/Refine Conceptual Model: Step 7 on Figure 4 refers to Table 2 and Figures 3 and 4. Should it instead refer to Table 5 and Figures 5 and 6?

Response 69

<u>This change has been made.</u>

Step 8. Conduct an Exposure Pathway Analysis: The second bulleted statement needs to be clarified. Does the phrase "... further reduce this risk such that natural attenuation is sufficient" refer to a situation where active groundwater remediation may not be necessary due to the implementation of some engineering controls/technologies?

Response 70

<u>Yes. Other engineering controls might include source control that would reduce the source term such that the plume will not reach a receptor under a natural attenuation scenario, and therefore, no active plume remediation is necessary. These control measures could be physical source containment, biological enhancement near the source etc.</u>

The third sentence of the final paragraph seems to suggest that the use of engineering controls is technically impracticable at DNAPL sites. As this need not be the case at many DNAPL sites, the text should be revised accordingly.

Response 71

<u>The text has been modified to read: “at some DNAPL sites…”.</u>

Step 9. If Accepted, Integrate Natural Attenuation into the Long-Term Site Management Strategy: What is meant by the third and fourth sentences of the final paragraph?

Natural Attenuation is a recognized technology/technique in the environmental industry, and is no more and no less valid at any site than any other technology/technique. The site-specific characteristics will determine the appropriate technology/techniques or combination thereof, to effectively address the issues of human health and environmental protection. The discussion on page 24 should be re-written so as not to cast any aspersions on the utility of NA technologies/techniques.

Response 72

We wish everyone shared your viewpoint (as we do) but unfortunately, at the time this document was written, many people do not. As the RTDF course makes its way around the country, perhaps this attitude will change. We definitely did not intend to cast aspersions on natural attenuation.

Perhaps we should be as optimistic as the AFCEE protocol that suggested talking to the regulatory community last, but we temporarily disagreed. As a new and somewhat controversial technology, natural attenuation of chlorinated solvents needs to gain the acceptance of the regulatory community and the public, and even where accepted, the regulatory community needs to have considerable input. In my first interaction with the EPA on natural attenuation at a chlorinated solvent site, I presented the results of an initial investigation of natural attenuation that showed great promise for the specific site. The technical support for the EPA PM was somewhat irate that we had done the study without informing him or asking his input.

We therefore suggested that these discussions take place very early on in the process. Evaluating natural attenuation can pose significant costs to the RP. There is no point in evaluating natural attenuation if it will never be accepted, and the appropriate data will be more likely collected if the regulatory community is involved. In the future, when it is viewed as just another technology as you have stated, it can be presented alongside other technologies after a technical evaluation has been completed.

The following are offered as changes to definitions and text.

The Glossary (pages 31-36) should be changed to reflect the following:

a. Accelerated Anaerobic Bioremediation - Improvement of effectiveness of microbial activity to degrade chemicals by adding nutrients or other microbes, while maintaining a deficiency of oxygen.

b. Aromatic Hydrocarbon - A compound built from . . . in an unsaturated ring (e.g., benzene ring). Most environmentally significant petroleum hydrocarbons are aromatic hydrocarbons.

c. Bedrock - Any solid rock exposed at the surface or overlain by unconsolidated material.

d. Bioremediation - Use of microorganisms to control, transform and/or destroy contaminants.

e. Dilution - The combined processes of advection and dispersion resulting in a reduction in concentration of the molecules (solute) in the groundwater (solvent).

f. Dispersion - The spreading of molecules . . . as a result of mixing of the molecules (solute) and groundwater (solvent) in individual pores and channels.

g. Non-Aqueous Phase Liquid(s) (NAPL) - Organic liquid that maintains a separate layer when mixed with water.

h. Petroleum Hydrocarbon - A chemical derived from crude oil by various refining processes. Examples include components of gasoline, fuel oils, and jet fuels.

i. Plume - A zone or distribution of contaminants, usually originating from a source area, and extending in the direction of gravity, preferential pathways, and/or groundwater flow.

j. Site Conceptual Model - A hypothesis about contaminant distribution at a release site as to how the release occurred, the current state of the source area, the possible geochemical site type, the current plume characteristics, and potential future plume characteristics.

k. Substrate - A compound . . . reactions catalyzed by their enzymes.

l. Sulfate Reducer - A microorganism that exists in anaerobic environments and reacts with sulfate ions to form hydrogen sulfide.

m. Volatile Organic Compound(s) (VOC) - Organic chemical having a boiling point between 6%C and 160%C, meaning that these chemicals will produce considerable vapors.

1. Table 1 should identify pros and cons of Natural Attenuation on its own merits; therefore, “long-term monitoring” needs to be defined, the “aquifer heterogeneity” comment should be removed from this table, and “occasionally more expensive”

comment should be removed, since monitoring is required for all remedies (including pump and treat).

2. Figure 4 (flow chart) should be changed for Steps 8-9, as follows:

Step 8. Conduct an Exposure Pathway Analysis

Response 73

Most of the above changes have been made. Item “a” and number “1” were not changed. Suggestion number “2” (above) is not clearly written and understood. Currently, Step 8 already reads as follows: “Step 8. Conduct an Exposure Pathway Analysis”. Thus, no changes were made to Steps 8 or 9 of Figure 4.