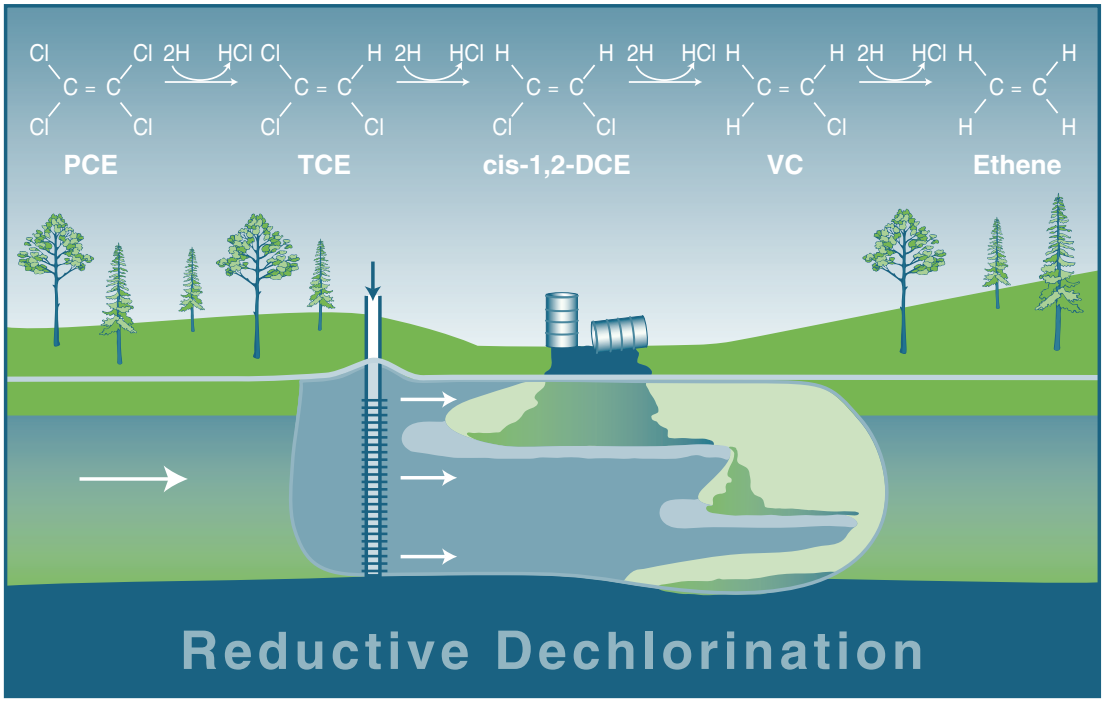
Case Study

In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies



April 2007

Prepared by
The Interstate Technology & Regulatory Council
Bioremediation of DNAPLs Team

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EXECUTIVE SUMMARY

The Interstate Technology & Regulatory Council's Bioremediation of DNAPLs (BioDNAPLs) Team was formed in 2004 with the aim of developing the technical and regulatory requirements needed to support the use of bioremediation as a treatment option for subsurface dense, nonaqueous-phase liquids (DNAPLs) contamination, particularly that associated with chlorinated ethenes. Chlorinated solvents were once widely used throughout a number of industries, leading to numerous environmental contamination problems. Both the U.S. Department of Defense and the U.S. Department of Energy face DNAPL contamination problems at many of their facilities similar to those of industry. DNAPLs, primarily those containing chlorinated solvents, pose one of the most widespread and prominent types of contamination associated with Superfund sites. Current DNAPL remediation technologies require the use of energy, fluids, or oxidants to mobilize DNAPL for subsequent recovery or to destroy it. A potential advantage of bioremediation is that microorganisms—which can proliferate and attack the contaminant at or near the DNAPL interface without mobilization—may provide a far more efficient, effective, and economical remediation.

As part of its strategic approach, the BioDNAPLs Team determined that an independent evaluation of the status of bioremediation was needed, that review of a "data rich" set of case studies would be the best evaluation approach, and that a forum would be an appropriate setting for the process. The team gathered and evaluated a number of proposed case studies and selected a group of six that would demonstrate bioremediation of DNAPLs in a wide range of conditions. The selected case studies can be classified as demonstrations, pilot-scale tests, those in design, and full-scale cleanups.

For each case study, background information was compiled into a 10–15 page summary, together with data reports and other information. This information was sent to a panel of experts from industry, academia, and the regulatory community who were recognized experts in the field of groundwater remediation—but not necessarily in bioremediation—and who could thus provide an independent review. The review included evaluation of technical approaches and performance of each case study, as well as its regulatory aspects, remediation goals, and applicability to other sites. Reviewer comments were provided to the sponsors of the case studies, who then incorporated responses into the presentations made at the Long Beach, California Case Studies Forum, held in late March 2006 and including the expert reviewers and members of the BioDNAPLs Team. At the forum, reviewers were able to ask questions stimulated by the presentation, as well as questions generated during preworkshop review of the case study data. Further, there was an extended, in-depth discussion, led by the panel of experts but including all forum participants, that explored the totality of the information presented. The goal was not to compare the case studies, but rather to distill a general understanding from the collective information.

The primary question posed to the expert panel was "Do we have credible evidence that bioremediation of chlorinated ethene source zones is a viable remediation option?" The conclusion of the panel was a unanimous "Yes." Panel members indicated that the weight of

evidence was “impressive” and that the potential for this technology was “exciting,” particularly the potential for effective use in difficult environments such as fractured media.

Within this context some caveats were recognized. The technology is still early in its development, with its niche not yet fully defined. There are concerns about the potential for mobilizing DNAPL during electron donor injections, and much of the “credible evidence” is based on measurements of aqueous-phase concentrations, which have inherent technical limitations. In addition, the overall impact that bioremediation of source zones can have on the restoration time frame is not clear. These caveats were not regarded as restrictions; rather they show the direction in which future developments and exploration must be made. The promise of bioremediation remains great, and its full realization is now closer.

This report has two purposes. First, for the record, it presents the six case histories from the Long Beach forum and the proceedings of the forum. Second, it provides state and federal regulatory agencies charged to oversee the cleanup of sites with DNAPL contamination with a thorough set of case studies presenting the best evidence supporting in situ bioremediation as a viable cleanup strategy. A companion CD contains this document, eight presentations made at the Case Studies Forum, and supporting material. It is the hope of the ITRC BioDNAPLs Team that the document will accelerate technology transfer to and among the states, saving regulators valuable time and money during selection and approval of remedial technologies.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

APPENDICES

IN SITU BIOREMEDIATION OF CHLORINATED ETHENE DNAPL SOURCE ZONES: CASE STUDIES

1. INTRODUCTION

A Case Study Forum was held in Long Beach, California, March 28–30, 2006. The forum was sponsored by the Bioremediation of DNAPLs (BioDNAPLs) Team of the Interstate Technology & Regulatory Council (ITRC). The purpose of the forum was to present six case studies of recent or ongoing applications of in situ bioremediation (ISB) of dense, nonaqueous-phase liquids (DNAPLs). DNAPLs represent a particularly challenging type of groundwater contamination. Over the past several decades numerous groundwater treatment technologies have been employed against a wide spectrum of contaminants. ISB is an attempt to remediate groundwater contamination by taking advantage of natural biological activity in the subsurface to degrade DNAPL contaminants into less toxic or, ideally, harmless substances. Significant progress has been achieved in the deployment of ISB against DNAPLs, especially chlorinated ethenes.

This report has two purposes. First, it presents the six case histories from the Long Beach forum and the proceedings of the forum. Second, it provides state and federal regulatory agencies charged with oversight of the cleanup of sites with DNAPL contamination with a thorough set of case studies presenting the best evidence supporting ISB as a viable cleanup strategy. It is the hope of the ITRC BioDNAPLs Team that the document will accelerate technology transfer to and among the states, saving regulators valuable time and money during selection and approval of remedial technologies. The case studies should not be compared to one another; they should stand on their individual merits. In presenting these proceedings, the BioDNAPL Team wishes to provide a critical review of the available information from a broad range of cases.

1.1 Background

ITRC formed the BioDNAPLs Team in 2004 as a follow-up to previous In Situ Bioremediation Teams in cooperation with the Remediation Technologies Development Forum (established by the U.S. Environmental Protection Agency [EPA] in 1992). ISB is a broad field of study and practical application known by several names. Some of the most common names that describe ISB or its components are “bioaugmentation,” “biostimulation,” “biopolishing,” and “enhanced reductive dechlorination” (ERD). ISB is related to monitored natural attenuation (MNA), but critically different: while intrinsic ISB may be one type of process occurring during MNA, interdictive ISB is characterized by the deliberate introduction of a bacterial entity or food source into contaminated groundwater for the purpose of influencing, augmenting, or accelerating the dechlorination process through microbial activity. The BioDNAPLs Team published a general technology overview in October 2005 (ITRC 2005). The team then determined that an independent evaluation of the status of the ISB technology would be appropriate. The team gathered and evaluated a number of proposed case studies to identify a group that would demonstrate ISB of DNAPLs in a wide range of conditions. The selected case studies may be classified as demonstrations, pilot-scale tests, those in design, and full-scale cleanups.

The authors of each case study were asked to follow an agreed-upon format to facilitate evaluation of their respective strengths and weaknesses. The forum consisted of visiting

professionals, academicians, regulators, and other experts in the field invited to critique the case studies. Following the forum, the case study authors and ISB proponents were encouraged to reassess their work in light of the public commentary and professional critiques and to revise their case studies. The results are the case studies presented here.

1.2 Overview

Finding DNAPLs is challenging, typically requiring extensive investigations. Direct removal of the pure product has proven equally difficult and expensive. ISB of DNAPLs is an attempt to work with nature, as stated in a previous U.S. Department of Energy (DOE) document: "The in situ bioremediation (ISB) process is one that enhances the ability of native microorganisms to degrade subsurface contaminants through biochemical processes" (DOE 2002). Although this definition does not include bioaugmentation, the challenge is to determine and introduce the best biological amendments (or stimulate those already present) that will degrade the DNAPL and use it as an energy source.

State and federal regulators charged with the protection of our environment have a difficult job. Whether through the National Environmental Policy Act, Resource Conservation and Recovery Act, Comprehensive Environmental Resource Conservation Liability Act (CERCLA), or other state processes, regulators often find themselves required to select and/or approve a proposed cleanup technology from a list of remedial options. Some of the more common options employed for the remediation of DNAPLs are in situ chemical oxidation/reduction, surfactants (solvent-enhanced flushing), thermal treatment, extraction (dual phase, water flood, or pump and treat), and in situ air sparging. One of the newest options is ISB.

As ISB matures, it is becoming clear that regulators will have to consider many specific issues when selecting or authorizing ISB as a remedial strategy. ISB may not be suitable for some sites because site geology, morphology, groundwater flow, proximity to municipal production wells, and the nature and extent of DNAPL contamination may dictate more aggressive remedial action. Public perception and understanding may also play a major role in the decision-making process. These case studies demonstrate that ISB is a viable option under the appropriate circumstances.

Remediation of groundwater is always an expensive and time-consuming endeavor. At a time when exorbitant cleanup costs often push regulators toward some form of MNA, ISB proactively optimizes the natural component to control costs. Introduction of suitable microbial agents or the artificial stimulation of in situ agents can manipulate both the time frame and end products to produce calculable results. Instead of waiting to see what natural attenuation may produce, ISB provides regulators with a tool that can achieve measurable results within predictable time frames. Evidence thus far also shows that ISB can achieve these results economically. It remains for regulators to find the right match between site conditions and ISB technologies to take full advantage of this new and flexible technology. If these forum proceedings add clarity and enhance regulators' confidence in their decision-making processes, the endeavor will have achieved its objectives.

1.3 Synopsis of the Case Studies

Beginning over a year before the actual Case Studies Forum, a set of case studies was selected, and for each a 10–15 page project summary, together with data reports and other information, was assembled. This information was sent to a panel of experts (from industry, academia, and the regulatory community) who were recognized experts in the field of groundwater remediation, but not necessarily experts in bioremediation, and who could thus provide an independent review. The review included evaluation of technical approaches and performance of each case study, as well as its regulatory aspects, remediation goals, and applicability to other sites. Comments from the expert reviewers were provided to the sponsors of the case studies, who then incorporated responses to them, as appropriate, in the case study summaries and the presentations that were made at the Long Beach, California Case Studies Forum. At the forum, each case study sponsor gave an introductory presentation that overviewed the project. The expert panel then asked questions that were stimulated by the presentation, as well as questions that were generated during preworkshop review of the case study data. During the presentations the majority of the interaction was between the panel of experts and the case study sponsors. After all presentations had been made, there was an in-depth discussion, led by the panel of experts but including all forum participants, of the totality of the information presented. The goal was not to compare the case studies, but rather to distill a set of issues, guidance, and conclusions from the collective information.

These six case studies represent only about one-third of the available studies of ISB of DNAPLs in the United States. These particular case studies represent a mature collection within the literature that provide extensive data and robust analysis which demonstrate successful application of the technology in a diverse set of ecological environments. Each of the case studies is the property of its respective authors and therefore reflects the style and technical approach of the researchers involved.

In the **Test Area North (TAN)** site of the National Engineering and Environmental Laboratory (INEEL), contamination consisted of a trichloroethene (TCE) residual source area and a nearly two-mile-long dissolved-phase plume. The plume—located within the deep, fractured basalt of the Snake River Plain aquifer—is the result of historical disposal practices at the site. A Technical Support Facility (TSF) centrally located at TAN consists of several experimental and support facilities used in the past to conduct research in support of the U.S. Air Force aircraft nuclear propulsion project and other nuclear reactor performance studies. An injection well was operated from the 1950s to 1972 to dispose of all liquid waste streams generated at TAN, including low-level radioactive wastewater, industrial wastewater (including organic liquids), and sanitary sewage, approximately 200–300 feet below ground surface (bgs). The nature and extent of the groundwater contamination and the complex properties of the aquifer system posed significant challenges in the development of a remedial strategy. A process was initiated under CERCLA to develop and implement a remedial strategy for the contaminant plume. One of the key elements of this strategy was the successful demonstration and application of enhanced ISB (EISB) to treat the residual source area of the plume.

The **Dover National Test Site** (DNTS) case study features a pilot-scale demonstration to evaluate the effects of biological activity on enhancing dissolution of an emplaced perchloroethene (PCE) DNAPL source. The demonstration used PCE as the primary DNAPL in

a porous media groundwater system. The field demonstration was conducted at DNTS in Dover, Delaware, which has five hydraulically contained sheet pile cells. In July 2001 a group of researchers from the University of Wyoming and Oregon State University released PCE as a DNAPL into the vadose zone and the saturated zone in DNTS Test Cell #1 in research focused on noninvasive techniques to map DNAPL source zones but did not remove mass from the test cell. Subsequently, the Naval Facilities Engineering Service Center (NFESC) and a Geosyntec research team conducted a bioaugmentation using the PCE previously released. During the demonstration the test cell was flushed at constant groundwater velocity, and a number of test phases evaluated the rate of DNAPL removal and the extent of volatile organic compound (VOC) treatment. Each phase was operated for sufficient duration to establish a near steady-state rate of DNAPL removal under each of the different operating conditions (i.e., without nutrients, with nutrients, and with nutrients and bioaugmentation).

In the **Cape Canaveral Launch Complex 34** (LC34) case study, the location was a launch facility at the Kennedy Space Center, which is also the site of historic releases. Up to 40,000 kg of TCE is present in the aquifer below LC34, which suggests that centuries will be required to restore groundwater using intrinsic remediation processes. A demonstration of EISB of TCE via anaerobic reductive dechlorination was initiated in May of 2002. The demonstration was conducted in a shallow, unconfined aquifer where the target depth interval (from the water table at ~5 feet bgs to 26 feet bgs) consists of medium- to coarse-grained sand and crushed shells. The underlying sediment is believed to be less permeable. Recharge of the aquifer is through the infiltration of precipitation, and—as a consequence of the limited topographic relief–groundwater velocities at the site are low (~2 feet/year). The goal of the study was to complete a carefully controlled evaluation of the performance of EISB in a source area containing DNAPL; however, the study was completed purely as a research effort and was not an integrated component of the LC34 remediation program. The treatment system consisted of a 22 × 22 foot test plot equipped with a network of injection, extraction, and monitoring wells. Three phases of the study were completed: recirculation of unamended groundwater, recirculation of electron donor–amended groundwater, and bioaugmentation with recirculation of electron donor–amended groundwater.

The **ARCADIS PCE** case study is drawn from a demonstration project undertaken at a private-sector site in the United States. The client agreed to allow use of the project data for consideration by ITRC on the condition that it remain anonymous and that no site-identifying characteristics be disclosed in the data. The case study was accepted for presentation at ITRC because the data collection intensity was very high relative to most commercial-scale technology applications and the project has been under way long enough (nearing three years) for its effects to be evident. The case study facility is the site of a PCE DNAPL release that likely occurred more than 20 years ago; a groundwater extraction system has been in place for more than 15 years. The study unit is approximately 9 m thick and covers an area of approximately 19,000 m^2. Aquifer permeability is generally low, and groundwater migration is believed to be limited to a stratum <2 m thick in the lowermost portion of the study zone. The site provided a valuable testing ground because the generally low aquifer permeabilities limited fluid movements and the groundwater containment system provided protection against mobilization of contaminant, if that were to occur. The objectives of the demonstration were to answer the following questions:

- Can complete reductive dechlorination be established at a site containing DNAPL PCE through carbohydrate-driven biostimulation?
- Does the reductive dechlorination process draw nonaqueous-phase mass out of the formation (either sorbed mass or nonaqueous-phase liquids)?
- Are the attainable source mass reductions sufficient to cause a commensurate decrease in the long-term due care costs for the site?

The **Portland, Oregon Dry Cleaner Site** case study addressed groundwater impacts at an active dry cleaner facility located in a strip mall. The area surrounding the dry cleaner is composed mainly of residential properties, with some commercial development. An investigation in 1999 revealed that dry cleaning contact water saturated with PCE (150,000 µg/L) and pure-phase PCE were probably discharged to a floor drain that discharges to a utility trench. Leaks from the floor drain and the utility trench appear to have resulted in impacted soils and groundwater. The Oregon Department of Environmental Quality (ODEQ) had determined that maintaining current activities at the site required that an unobtrusive, semipassive remediation technology be used. Accelerated bioremediation using Hydrogen Release Compound (HRC®) within the plume and source area was selected as the remedial approach as it requires modest site access and minimal operation activity. A pilot test was conducted to determine whether this option is an appropriate remedy for the reduction of high concentrations of PCE and some of its daughter products in site groundwater.

In the **Tarheel Army Missile Plant** (TAMP) case study in Burlington, North Carolina, Emulsified Oil Substrate (EOS®) is being used to remediate a TCE source area. TAMP is a government-owned, formerly contractor-operated 33-acre facility with a 50-year history of use for production of defense-related and private-sector electronics. Releases from manufacturing operations and underground storage tanks (USTs) have impacted soils and groundwater at TAMP with petroleum hydrocarbons and chlorinated volatile organic compounds (CVOCs). Soil and groundwater contamination were first detected at TAMP in 1993 after the removal of several USTs on the facility. Soil and groundwater samples collected after closure showed the presence of BTEX (benzene, toluene, ethylbenzene, and xylenes) and CVOCs. The CVOCs were believed to be from a chlorinated solvent cleaning machine and an associated disposal sump. Subsequent investigations led to the conclusion that there were plumes of both CVOCs and petroleum hydrocarbons in groundwater at the facility. Ten years of active remediation, including pump-and-treat, in situ soil vacuum extraction (SVE), and air sparging (AS), have been effective in reducing the BTEX. However, these efforts have had little effect on the dissolved-phase TCE groundwater plume. In preparation for transfer of ownership of the property, the Army elected to evaluate bioremediation alternatives for the TCE in groundwater. Solutions-IES, Inc. conducted a pilot-scale study to test the ability of EOS to reduce the CVOCs in groundwater. The pilot test was designed to treat a 100 × 100 foot zone believed to be the primary source area for the TCE plume.

1.4 Structure of this Document

Since the purpose of the forum was to use actual case studies of current or ongoing applications of ISB to clearly demonstrate the existence of well-established and credible evidence for use of ISB as a viable environmental remediation technology option, the majority of this document is devoted to presenting the evidence as collected by the BioDNAPLs Team.

Chapters 2–7 present the case studies in the order in which they were presented at the Case Studies Forum in Long Beach, California, March 28–30, 2006. Each chapter summarizes the case study with technical details of the bioremediation and presents a set of questions from reviewers based on examination of the initial draft of the case study summary:

- Chapter 2. Test Area North Site at Idaho National Engineering and Environmental Laboratory
- Chapter 3. Pilot-Scale Evaluation Using Bioaugmentation to Enhance PCE Dissolution at Dover Air Force Base (AFB) National Test Site
- Chapter 4. Launch Complex 34 at Cape Canaveral
- Chapter 5. Demonstration of Enhanced Bioremediation in a TCE Source Area
- Chapter 6. Source Area Remediation at a Portland, Oregon, Dry Cleaner Site
- Chapter 7. Enhanced Anaerobic Bioremediation of a TCE Source Area at the Tarheel Army Missile Plant Using EOS

Chapter 8 presents a summary of the entire body of knowledge developed by the ITRC BioDNAPL Team from the case study summaries; the reviewers' comments on the summaries, the presentations given by the case study sponsors at the Case Studies Forum; and the collective discussions of presenters, sponsors, reviewers, and other BioDNAPL Team members at the Case Studies Forum.

Chapter 9 presents information on the simulation and optimization of subsurface environmental impacts. It is set forth in the form of a paper based directly on a presentation given at the Case Studies Forum by Mr. Larry Deschaine. The purpose of the presentation, and of this chapter, is to provide the reader with an overview of modeling and simulation of bioremediation systems; a reasonably detailed discussion of the models, physics, and numerical methods; and examples of codes that can be downloaded from developer sites.

1.5 Companion CD

The CD that accompanies this document (see pocket inside back cover) contains files providing supporting and background information:

- This document in PDF
- Eight presentations made at the Case Studies Forum—opening presentation, the case study presentations, and the presentation for Chapter 9
- Two appendices referenced in Chapter 5 and background information referenced in Chapter 9

1.6 References

DOE (U.S. Department of Energy). 2002. *DNAPL Bioremediation—RTDF*. DOE/EM-0625. Office of Environmental Management, Office of Science and Technology, Subsurface Contaminants Focus Area.

ITRC (Interstate Technology & Regulatory Council). 2005. *Overview of In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones.* BioDNAPL-1. Washington, D.C.: Interstate Technology & Regulatory Council, Bioremediation of DNAPLs Team. www.itrcweb.org.

2. TEST AREA NORTH SITE AT IDAHO NATIONAL LABORATORY CASE STUDY SUMMARY

The presentation associated with this case study, given by Ryan Wymore, Tamzen Macbeth, and Kent Sorenson at the forum on March 28, 2006, is included on the CD accompanying this document. The reviewers for this case study were Jeff Marqusee, Lenny Siegel, Mike Kavanaugh, and Tom Sale.

2.1 Scale and Purpose

INEEL is an 890-square-mile facility operated by the U.S. Department of Energy (DOE) in eastern Idaho. The TAN complex is located approximately 50 miles northwest of Idaho Falls, Idaho, on the northern portion of INEEL. An injection well was operated from the 1950s to 1972 to dispose of all liquid waste streams generated at TAN. These included low-level radioactive wastewater, industrial wastewater (including organic liquids), and sanitary sewage, which were injected approximately 200–300 feet bgs. The result of this waste injection was the evolution of a nearly 2-mile-long TCE plume (Figure 2-1). Estimates of total TCE injected range from 350 to 35,000 gallons.

For purposes of discussing the various components of remediation, the plume was divided into three sections: the hot spot, which encompasses the residual TCE source area; the medial zone; and the distal zone. The original record of decision (ROD) (DOE-ID 1995) for the TAN groundwater contamination selected pump and treat as the default remedy for all three plume zones. However, it allowed for evaluation of five innovative technologies for their potential to enhance or replace pump and treat:

- metal-enhanced reductive dechlorination
- monolithic confinement
- in situ chemical oxidation
- enhanced in situ bioremediation
- monitored natural attenuation

The first three technologies were evaluated to differing degrees and eliminated for various reasons as described in the *Field Demonstration Report, Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2000). A nine-month full-scale field evaluation of ISB was performed at TAN beginning in January 1999 (INEEL 2000). The overall objective of the enhanced ISB field evaluation was to determine whether the intrinsic biodegradation of TCE in the plume's residual source area could be enhanced through addition of an electron donor. The results showed that complete biodegradation of TCE to ethene in the residual source area was achieved as a result of electron donor injections.

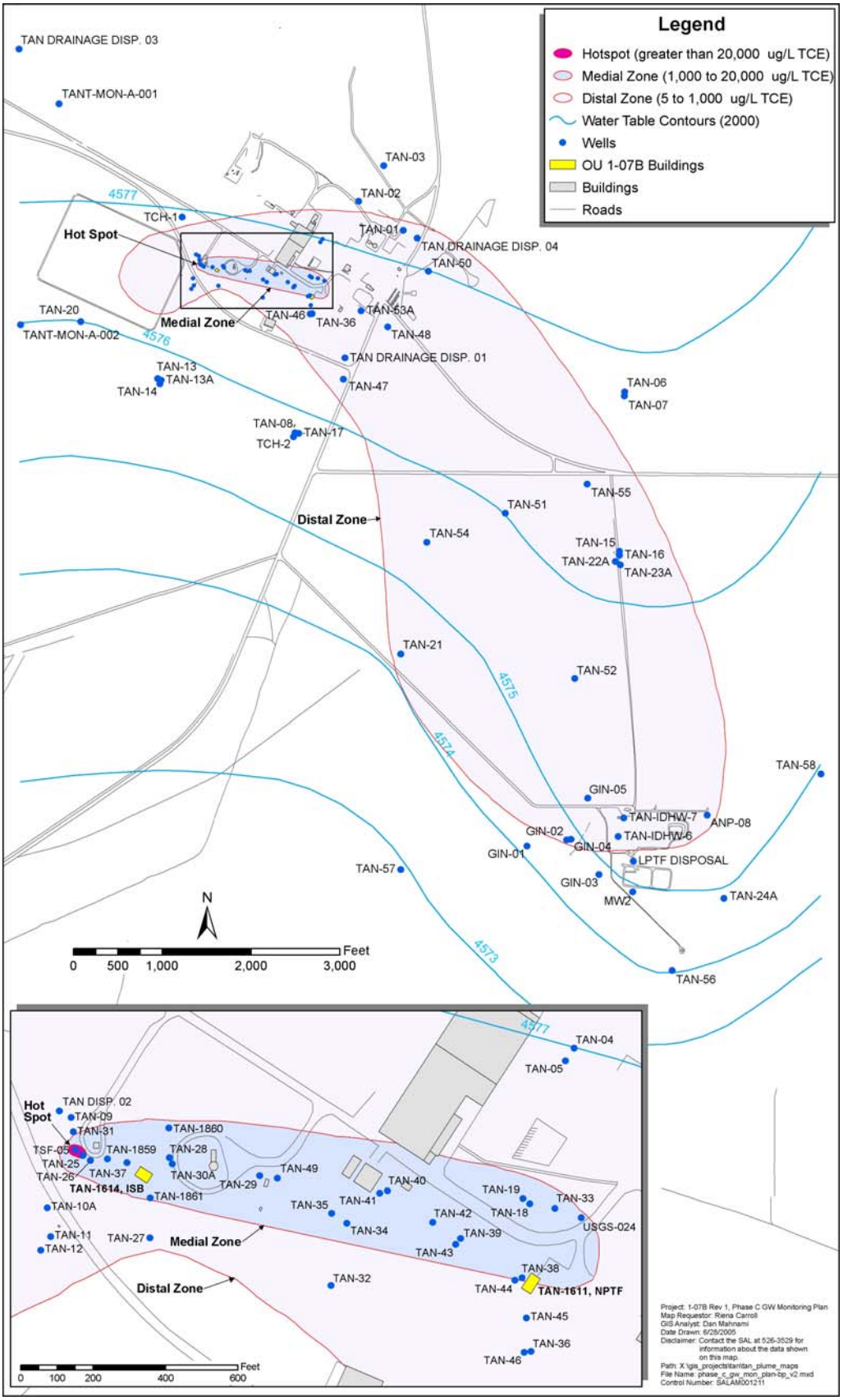

Figure 2-1. Test Area North TCE plume map.

An MNA field evaluation was conducted in conjunction with the ISB field evaluation, and the results showed that TCE attenuation was occurring. Based on the ISB and MNA field evaluation results, the regulatory agencies (i.e., the State of Idaho, EPA Region X, and DOE) accepted enhanced ISB as the selected remedy for the residual source area of the plume and MNA as the selected remedy for the distal portion of the plume (DOE-ID 2000). A ROD amendment signed in September 2001 (DOE-ID 2001) documents regulatory approval of enhanced ISB as the final remedy for the plume hot spot and MNA as the final remedy for the distal portion of the plume.

2.2 Site Conceptual Model

To fully develop the site conceptual model (SCM) for TAN, it is important to understand the history of the site. Contamination was first discovered in 1989 through sampling of groundwater wells. A sludge removal action was performed in 1990, during which 55 feet of sludge was removed from the 12-inch-diameter casing of well TSF-05. An interim pump-and-treat system was installed and operated from about November 1996 to November 1998, at which time it was placed in standby mode for the ISB field evaluation.

The SCM for TAN was developed through an iterative process of identifying data gaps, conducting activities to fill those data gaps, reporting on the results of those activities, and identifying new data gaps. This process has resulted in a series of four reports, the last of which was Wymore, Bukowski, and Sorenson (2000). Examples of characterization activities that have been conducted in the source area since the sludge removal activity was completed and before the ISB field test was implemented are as follows:

- Several wells have been installed within or adjacent to the source area.
- Pumping tests, slug tests, and tracer tests have been conducted to determine aquifer properties, from which residual source distribution has been inferred.
- Standard geophysical, gamma spectroscopy, and acoustic televiewer logging were performed in several source area wells.
- Cross-well seismic tomography was conducted.
- Extensive groundwater sampling has been conducted throughout the source area, both in support of ISB operations (see Section 2.3) and prior to initiation of ISB activities.

These activities greatly improved the understanding of aquifer hydraulic conductivity, porosity, and preferential flow paths; dissolved contaminant composition and distribution; and residual contaminant source distribution. A thorough discussion of the complete SCM was presented in Sorenson (2000).

Contaminants present in the Snake River Plain Aquifer at the TAN site include primarily TCE, PCE, and tritium. Both *cis*- and *trans*-dichloroethene (DCE) are present in the plume at low concentrations that drop below detection limits before TCE. Prior to bioremediation activities, redox conditions were mildly reducing near the injection well but were aerobic throughout most of the plume. Other contaminants of importance that appear to be associated with the sludge and are limited to the immediate vicinity of TSF-05 are cobalt (^{60}Co) and cesium (^{137}Cs). The depth to water at TAN is approximately 200 feet. The aquifer and most of the unsaturated zone are composed primarily of layered basalt flows, intercalated with sedimentary interbeds deposited during periods of volcanic quiescence. Groundwater flow in the aquifer is controlled by the

highly transmissive zones that occur during contact between individual basalt flows and, to a lesser extent, the fractured zones within flow interiors. Groundwater velocity at the site is approximately 0.4 foot/day, and porosity of the uncontaminated aquifer is 1%. Transmissivity ranges 12,000–20,000 square feet/day, with the source area being an order of magnitude less than this. The scale of the basalt geology dictates that preferential flow can be very important at spatial scales less than approximately 330 feet, after which a transition to continuum behavior occurs and the aquifer can be thought of essentially as a macroporous medium.

The most significant interbed is termed the "QR interbed," an apparently continuous stratigraphic unit located approximately 400 feet bgs near TSF-05 and dipping gradually to about 476 feet bgs just beyond the plume extent. All available data indicate this unit provides an effective bottom boundary for the contaminated aquifer. The distribution of TCE at TAN exemplifies the fringe-and-core hypothesis for the anatomy of chlorinated solvent plumes by Cherry (1997). A very large, low-concentration fringe surrounds and emanates from a much smaller, high-concentration core (Figure 2-1). Within the core is a very small residual source area that continues to contaminate fresh groundwater flowing through from upgradient. A transition occurs from the scale of the residual source, where preferential flow is significant, to the scale of the fringe, where sufficient vertical communication has been present along the flow path to create a relatively well-mixed, predictable groundwater plume

The residual source of contamination in the aquifer near TSF-05 is the sludge that was injected into the well more than 15–20 years ago. The pore water of the sludge probably contains large amounts of TCE, with PCE and tritium also present in significant amounts. Given the organic content of the sludge, sorbed PCE and TCE are also likely to be present. Some of the sludge has been shown to have TCE concentrations as high as 3% (by weight). The sludge, therefore, represents a long-term source of contamination to the aquifer. It has also significantly affected the properties of the aquifer in the area. The effective porosity near TSF-05 has been estimated to be about 0.05%, which indicates that the sludge occupies much of the pore space in the source area, and the transmissivity is about an order of magnitude lower than that of nearby wells. Both gamma logs measuring radionuclides associated with the sludge and tracer tests measuring effective porosity yield an estimated radius for the sludge distribution of about 100 feet, with most of the sludge being present in the upper 100 feet of aquifer. The sludge is also very important because of the organic material available in the residual source area that creates a very different geomicrobiological environment than is present in the fringe and even in most of the core.

2.3 Remediation Goals

The ultimate goal of OU 1-07B remedial activities is to achieve the remedial action objectives (RAOs), specified in the ROD Amendment (DOE-ID 2001) as follows:

- Restore the contaminated aquifer groundwater by 2095 (100 years from the signature of the ROD [DOE-ID 1995]) by reducing all contaminants of concern (COCs) to below maximum contaminant levels (MCLs) and a 1×10^{-4} total cumulative carcinogenic risk-based level for future residential groundwater use and, for noncarcinogens, until the cumulative hazard index is less than 1.

- For aboveground treatment processes in which treated effluent will be reinjected into the aquifer, reduce the concentrations of VOCs to below MCLs and a 1×10^{-5} total risk-based level.

- Implement institutional controls to protect current and future users from health risks associated with (1) ingestion or inhalation of, or dermal contact with, contaminants in concentrations greater than the MCLs; (2) contaminants with greater than a 1×10^{-4} cumulative carcinogenic risk-based concentration; or (3) a cumulative hazard index of greater than 1, whichever is more restrictive. The institutional controls shall be maintained until concentrations of all COCs are below MCLs and until the cumulative carcinogenic risk-based level is less than 1×10^{-4} and, for noncarcinogens, until the cumulative hazard index is less than 1. Institutional controls shall include access restrictions and warning signs.

The implementation of ISB in the hot spot to achieve these RAOs has been divided into individual phases with specific objectives for each phase. The *In Situ Bioremediation Remedial Action Work Plan for Test Area North Final Groundwater Remediation, Operable Unit 1-07B* (DOE-ID 2002a) and supporting documents, specifically the *In Situ Bioremediation Remedial Action Groundwater Monitoring Plan for Test Area North, Operable Unit 1-07B* (INEEL 2003) and the *ISB Operations and Maintenance Plan for Test Area North, Operable Unit 1-07B* (DOE-ID 2002b), are the governing documents. The phases are described below:

- Interim Operations Phase (11/2002–10/2003): This ISB remedy officially began in November 2002 with the Interim Operations Phase. This phase included activities designed to support a better understanding of alternate electron donors, development of injection strategies to support the Initial Operations Phase, ISB model refinement, continued ISB sodium lactate addition, and construction of the ISB facility. The results and details of activities conducted during the Interim Operations Phase are reported in the *Annual Performance Report for In Situ Bioremediation Operations November 2002 to October 2003, Test Area North Operable Unit 1-07B* (Armstrong et al. 2004).

- Initial Operations Phase (10/2003–current): The completion of the ISB facility marked the start of the Initial Operations Phase. The goal of this phase is to reduce VOC concentrations in downgradient wells TAN-28 and TAN-30A to below MCLs (Figure 2-2). The Initial Operations Phase will be complete when it is determined that downgradient flux from the hot spot has been reduced such that VOC concentrations remain less than MCLs at TAN-28 and TAN 30A for a period of one year. Activities conducted during this phase include injections into newly installed injection well TAN-1859 and initiation of a pilot test to evaluate the effectiveness of whey powder in March 2004.

- Optimization Operations Phase (future)—This phase will focus on reducing the flux of VOCs from the hot spot in the crossgradient direction, as measured at TAN-1860 and TAN-1861 (Figure 2-2), while maintaining VOC flux reduction in the downgradient direction. During this phase, data will continue to be gathered and analyzed relating to achievement of long-term performance objectives.

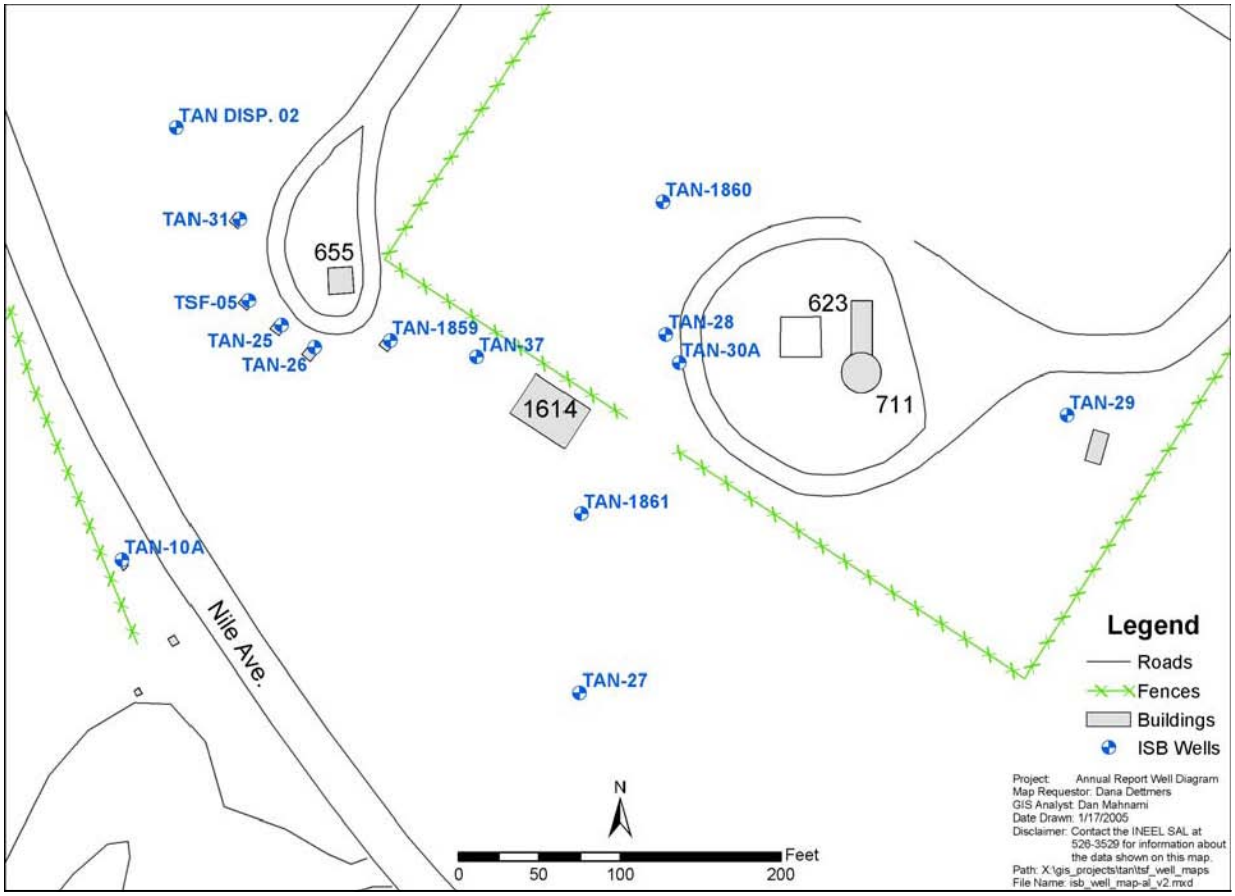

Figure 2-2. Test Area North ISB monitoring wells.

- Long-Term Operations Phase (future)—This phase will focus on achievement of hot spot source degradation, while maintaining the reduction of VOC flux from the hot spot in the crossgradient and downgradient directions.

2.4 Bioremediation Performance Monitoring

Extensive performance monitoring has been conducted for the TAN ISB project. Figure 2-2 shows the TAN monitoring well network, which includes 17 sampling locations from 14 monitoring wells. Well TSF-05 has been used as the electron donor injection well since the beginning of the project, and well TAN-1859 is designed as an additional injection well that may be used in the future. Well TSF-05 is sampled at two discrete depths, designated as TSF-05A and TSF-05B. Well TAN-37 is sampled at three discrete depths, designated as TAN-37A, TAN-37B, and TAN-37C. All wells are equipped with dedicated submersible pumps that are sampled in accordance with low-flow principles.

Sampling was performed biweekly during the field evaluation and has been performed monthly since then. The TAN ISB monitoring program maximizes cost-effectiveness by using a combination of fixed laboratory and field analyses. The program includes parameters to monitor electron donor and nutrient distribution, redox-sensitive parameters, VOC contaminants and degradation products, biological activity indicators, and water quality parameters.

During lactate injections, the analytes monitored to track electron donor and nutrient distribution are chemical oxygen demand (COD), lactate, volatile fatty acids (VFAs, i.e., acetate, propionate, and butyrate), ammonia, and phosphate. During whey powder injections, lactose rather than lactate is analyzed, and other potential fermentation products have been added.

The redox-sensitive parameters include dissolved oxygen (DO), ferrous iron, sulfate, and methane. The VOC contaminants and degradation products that are monitored include PCE, TCE, *cis*-1,2-dichloroethene (*cis*-DCE), *trans*-1,2-dichloroethene (*trans*-DCE), vinyl chloride (VC), ethene, and ethane. Alkalinity is analyzed as an indicator of biological activity (bicarbonate production). The water quality parameters measured are temperature, pH, specific conductance, and oxidation-reduction potential (ORP). Details on the ISB performance monitoring analytical methods are provided in Table 2-1. In addition to the ISB performance monitoring parameters, radiological parameters gross alpha, strontium-90, and gamma spectroscopy are measured once annually from a subset of wells to ensure that ISB activities do not result in unacceptable mobilization of radionuclides. Tritium has been analyzed monthly.

Table 2-1. Test Area North ISB performance monitoring parameters

Parameter	Analytical method and laboratory
Chlorinated ethenes (INEEL internal laboratory)	Solid-phase microextraction–gas chromatography/ flame ionization detector (SPME-GC/FID)
Chlorinated ethenes (off-site laboratory, split samples)	EPA SW-846 8260B
Ethene/ethane/methane	SPME-GC/FID
Lactate/lactose	Ion chromatography
Volatile fatty acids	SPME-GC/FID
Sulfate	Hach Field Test Kit Method 8051
Ferrous iron	Hach Field Test Kit Method 8146
Alkalinity	Hach Field Test Kit Method 8203
Chemical oxygen demand	Hach Field Test Kit Method 10067
Tritium	Liquid scintillation counting
Ammonia (as nitrogen)	Hach Field Test Kit Method 10023
Phosphate	Hach Field Test Kit Method 8048
Temperature/pH/conductivity/dissolved oxygen/redox potential	Hydrolab™ and Troll 9000XP water quality instruments

One unique feature of the TAN monitoring program is the analysis of all VOC and ethene/ethane/methane samples using an internal INEEL laboratory. The VOC analyses are performed as a headspace analysis using SPME to sample the headspace and GC equipped with FID to analyze the samples. Ethene/ethane/methane, VFA, and lactose analyses are also performed using GC/FID. Lactate samples are analyzed using ion chromatography.

Given that a significant component of the TAN monitoring program is field and on-site laboratory measurements, extensive confirmation of these on-site results was performed during the field evaluation by sending split samples for VOCs, ethene/ethane/methane, and anions to off-site laboratories for analysis using EPA methods. Once these early operations demonstrated

good agreement between on- and off-site results, the frequency of split samples was decreased to sending only VOCs off site twice per year. For the past three years, a performance evaluation (PE) program has been implemented in which the INEEL internal laboratory receives prepared VOC samples from an independent vendor. These PE samples are analyzed along with TAN field samples, and the results are compared to the vendor's certified values for each analyte. Over this three-year time period, performance of the INEEL laboratory using the SPME method has been very good, as evidenced by the fact that most PE sampling results have been within acceptable ranges. The PE sampling results have proven to be more useful than the off-site split sampling results because they allow for a direct assessment of the laboratory's accuracy rather than a somewhat arbitrary comparison to another laboratory.

In addition to the routine ISB performance monitoring (Table 2-1), several types of innovative monitoring have been conducted periodically during the TAN ISB project. During the field evaluation, compound-specific stable carbon isotopes were analyzed to determine effects of the ISB process on carbon contained in VOC molecules. This monitoring clearly differentiated between the effects of groundwater transport, dissolution of DNAPL at the source, and enhanced bioremediation. Isotope data from all wells within the zone of lactate influence exhibited large kinetic isotope fractionation effects during the reduction of *cis*-DCE to VC and VC to ethene. Despite these large effects, the carbon isotope ratio of ethene in all these wells reached the carbon isotope ratios of the initial dissolved TCE, confirming the complete conversion of dissolved TCE to ethene. Details on this sampling are provided in Song et al. (2002).

Various molecular techniques have also been performed on TAN samples during the TAN ISB project. In 1999–2000, phospholipid fatty acid analysis (PLFA) samples were collected and analyzed to show at a community level the effects of an electron donor injection cycle (injection followed by depletion of donor). Quantitative polymerase chain reaction (PCR) for *Dehalococcoides* species was performed on samples collected throughout the ISB treatment area, including wells not impacted by electron donor injections. These results showed *Dehalococcoides* present in high numbers (~10^6 gene copies/L) in samples from donor-impacted wells and in low numbers (~10 gene copies/L) in wells that had not received donor (Rahm et al. in press).

Also, terminal restriction fragment length polymorphism (T-RFLP) community profiling has been performed using samples collected from several well locations and from the same well location over time to evaluate the relative differences in diversity. These data have suggested that the microbial communities at different well locations within and outside the residual source area at TAN are significantly different (Rahm et al. in press). In addition, microbial population dynamics during an injection cycle (defined as an electron donor injection and the period of time before the next electron donor injection) vary in response to the availability of primary substrates (i.e., lactate or lactose) and secondary fermentation products (unpublished data). The goal of this work has been understanding the competitive and symbiotic relationships between the different populations within the community and specifically how they relate to dechlorination performance.

Results from recent molecular work are published in Macbeth et al. (2004). Overall results show high diversity in the TAN microbial community, as well as significant changes in community

structure in response to electron donor injections. One important conclusion from this work is that, under aquifer conditions, methane appears to be generated primarily via the acetoclastic pathway, using acetate generated from lactate fermentation, rather than via the hydrogenotrophic pathway.

2.5 Results

Periodic injection of high-concentration sodium lactate solution approximately from the water table (210 feet) to 300 feet bgs into TSF-05 was conducted during an enhanced ISB field pilot study at TAN in 1999. Groundwater samples were collected to assess redox conditions, bioactivity, and reductive dechlorination. Data collected within the residual source area during the field pilot study demonstrated that sodium lactate injections stimulated complete biological conversion of all aqueous-phase TCE to ethene within one year (Song et al. 2002). The stable carbon isotope data collected by Song et al. (2002) also showed that the isotope ratio of the TCE changed over time, suggesting that the nature of the source term was impacted. Since then, data collected over the course of ISB operations show significant production of ethene (Figures 2-3 and 2-4), indicating complete dechlorination of aqueous-phase TCE.

During the field evaluation, increases in total molar concentrations of VOCs at well locations impacted by the electron donor injections suggested that enhanced mass transfer of TCE from the residual source was occurring as a direct result of the injections. For instance, total chloroethenes in TAN-26, a deep well sampled at 389 feet bgs and approximately 50 feet downgradient from the injection well TSF-05, increased over an order of magnitude in molar concentration during injection of 30% and 60% sodium lactate (Figure 2-4). At least three potential mechanisms could have contributed to this observation:

- physical displacement of the TCE from the residual source
- desorption of TCE from the residual source
- the electron donor solution itself interacting with the residual source to enhance the dissolution and/or increase effective solubility

The first mechanism was ruled out because, while TCE concentrations increased dramatically in TAN-26, the aqueous inorganic components of the sludge, most notably tritium, did not. At the time this work was performed, the potential importance of the second and third mechanisms was not suspected. It was proposed that the mass transfer of TCE within the residual source to the aqueous phase was somehow being preferentially enhanced by the injected sodium lactate. Subsequent interfacial tension (IFT) measurements between TCE DNAPL and different concentrations of sodium lactate suggested that the sodium lactate might be acting as a mild surfactant or cosolvent by lowering IFT between the residual TCE and the surrounding groundwater (Sorenson 2002). In addition, this newly mobilized TCE was efficiently biodegraded.

The use of high-concentration electron donor solutions to enhance mass transfer of contaminants into the aqueous phase to facilitate rapid reductive dechlorination and residual source depletion is referred to as Bioavailability Enhancement Technology (B.E.T.™, U.S. Patent 6,783,678). At TAN, the use of B.E.T. was critical for demonstration that enhanced ISB was a viable option for remediation of the chlorinated solvent residual source area because accelerated mass transfer of

contaminants from the residual phase to the aqueous phase makes the contaminants available for biological degradation and significantly shortens the overall remedial time frame.

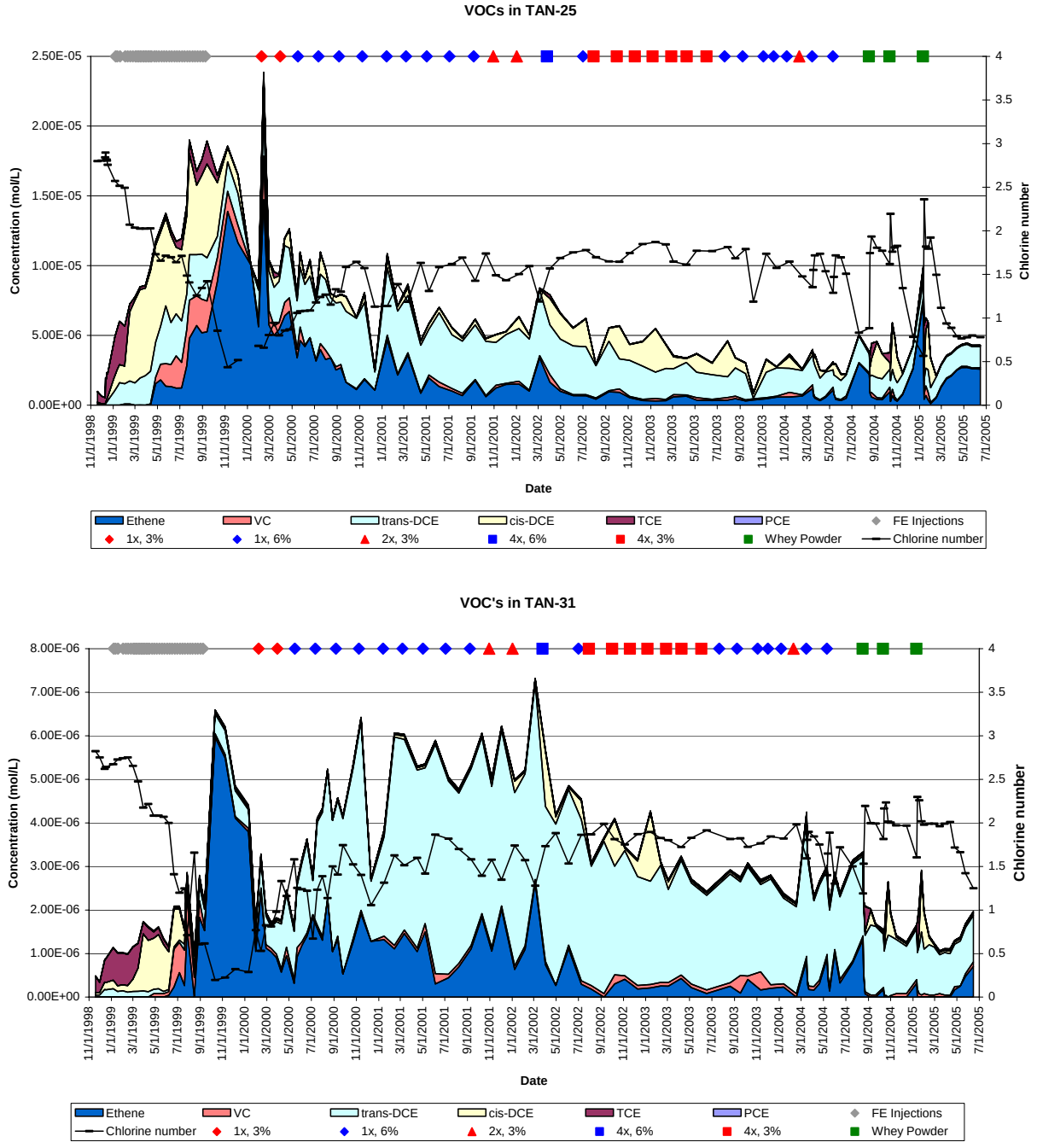

Figure 2-3. VOCs in two TAN monitoring wells from 1/99 through 7/05, showing complete dechlorination-donor injections as symbols along secondary x-axis.

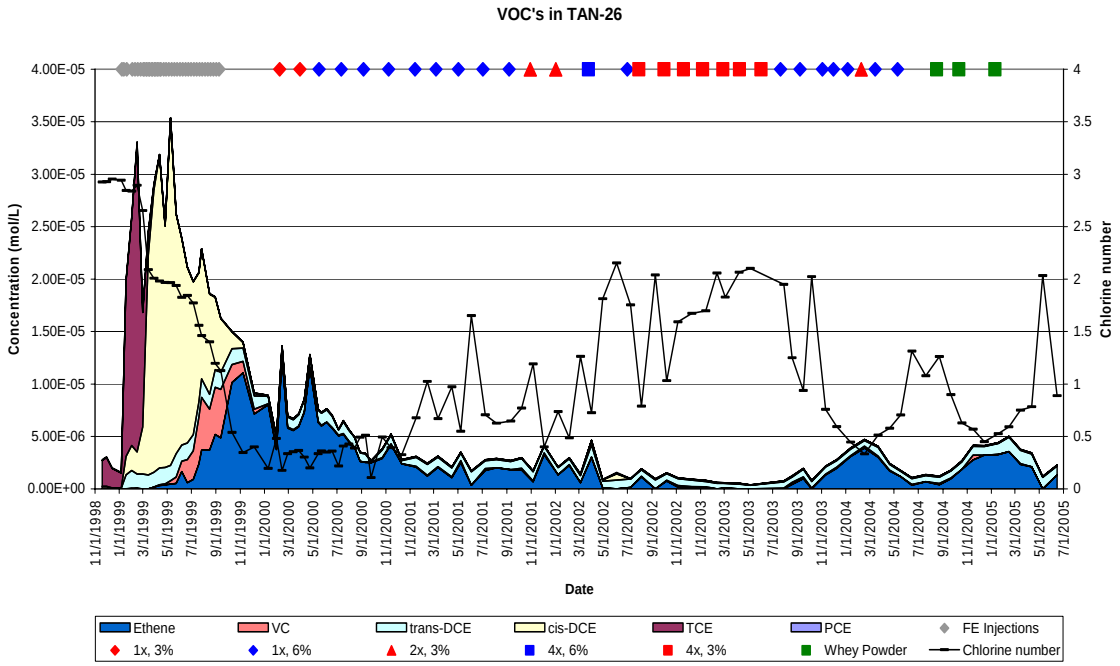

Figure 2-4. VOCs in Well TAN-26, showing donor injections as symbols along secondary x-axis.

Since the field evaluation, enhanced ISB operations over the last six years have resulted in the continued degradation of contaminants within the residual source area impacted by electron donor injections, as evidenced by ethene accumulation. The kinetics of the degradation reactions are such that liberated contaminants are generally observed as elevated concentrations of ethene, as opposed to TCE, *cis*-DCE, and VC concentrations, following injection events. Therefore, residual source degradation at TAN appears to be limited not by the kinetics of the degradation reactions but by the dissolution of TCE from the residual phase into the aqueous phase. Thus, optimization activities at TAN have been focused on enhancing mass transfer of VOCs to the aqueous phase to maximize degradation of the residual source, as well as reducing operation and monitoring costs and accomplishing site remediation goals. These activities have included laboratory and field tests to evaluate alternate electron donors that might be more effective than sodium lactate for ISB within a residual source area.

Laboratory studies were performed to assess several important properties of electron donors used for ISB, including effectiveness in stimulating degradation reactions, longevity or utilization rate of the electron donor, the ability to distribute electron donor over a large area through a single injection location, and ability to enhance the mass transfer of TCE DNAPL (Macbeth et al. 2006). The laboratory studies included IFT analyses of different concentrations of the electron donor solutions, microcosm studies using a TCE-dechlorinating culture enriched from TAN groundwater, molecular characterization of the microbial communities stimulated by the various electron donors, and column studies to evaluate the abiotic enhanced dissolution effect of high and low concentrations of the electron donors on TCE DNAPL. The results of the abiotic column studies confirmed that the dissolution of TCE DNAPL was enhanced during amendment with high concentrations of some electron donors. Of these, a whey powder solution enhanced TCE

DNAPL dissolution by a factor of 6 over that observed during potable water amendment, while sodium lactate had a much smaller impact (Macbeth et al. 2006).

Based on the collective results of the laboratory studies, a field-scale pilot test was conducted to examine the extent of enhanced mass transfer and subsequent dechlorination of TCE from the residual source area at TAN in response to injections of whey powder as compared to sodium lactate.

The pilot test was implemented in two phases, the first of which involved high-resolution monitoring following two injections of sodium lactate conducted in March and May of 2004. Following these injections, spikes in TCE and *cis*-DCE concentrations from a baseline near 0 µg/L up to 300–400 µg/L at the injection well, and up to 25–75 µg/L 25 feet downgradient were observed. In addition, there were dramatic increases in ethene concentrations within 48 hours, indicating rapid dechlorination of the newly bioavailable TCE.

Phase 2 of the pilot test involved three cycles of whey powder injections conducted in August and October 2004 and January 2005. These injections resulted in spikes in TCE and *cis*-DCE concentrations from near 0 µg/L up to 400–600 µg/L within the injection well (Figure 2-5), and up to 250–400 µg/L 25 feet downgradient (Figure 2-6). In addition, the total chloroethene and ethene molar areas were evaluated during these injection cycles to compare the total mass of contaminants liberated and subsequently degraded to ethene. The total molar areas were approximately three times greater during a whey injection cycle compared to sodium lactate (Figures 2-7 and 2-8). The rate at which the molar area increased (indicator for mass removal rate) was calculated to be 50%–250% higher during a whey powder injection cycle than for sodium lactate. These data indicate that whey powder enhanced mass transfer and degradation of TCE to a greater degree than sodium lactate. The use of whey powder for long-term ISB operations is expected to increase the rate of contaminant source depletion, ultimately resulting in a reduction of the remediation time frame at TAN.

2.6 Summary

The source area bioremediation at TAN remains one of the largest-scale projects in a source area of its kind in the world, certainly in deep, fractured rock. An area approximately 60 m (200 ft) in diameter is being treated, initially across an aquifer thickness of 60 m (200 ft). As contaminants have been removed in the deepest part of the contaminated aquifer, which presumably was limited to aqueous- (and possibly some sorbed-) phase contamination, the focus is now on the upper 30 m (100 ft) of the aquifer. Both field and laboratory data have demonstrated that bioremediation through injection of high concentration electron donor solutions has enhanced depletion of the residual source by enhancing mass transfer into the aqueous phase. The biodegradation kinetics have largely remained faster than the mass transfer kinetics, leading to an optimization strategy largely devoted to accelerating mass transfer rates even further. This requires continued injections of high concentration electron donors throughout the area impacted by residual source material. As the volume of this area is large and the transmissivity of the aquifer is very high, injection volumes are larger than at many other chlorinated solvent sites.

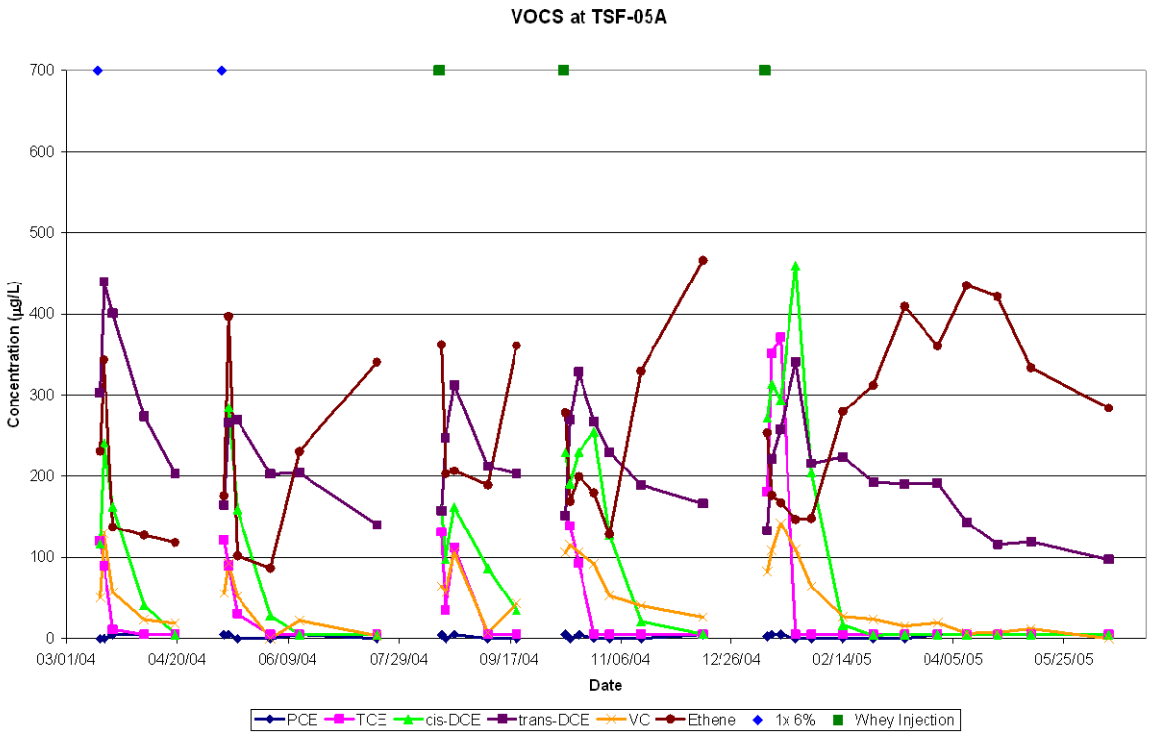

Figure 2-5. VOC response at TSF-05 to sodium lactate (diamonds) and whey powder (squares) injections.

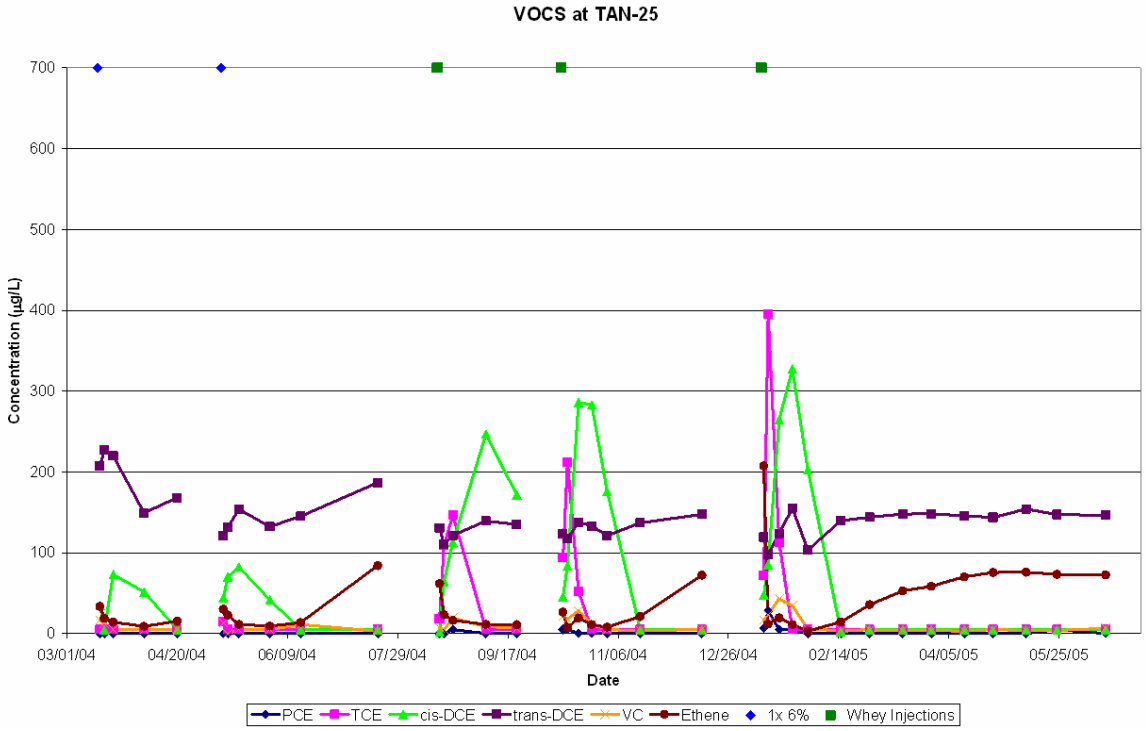

Figure 2-6. VOC response at TAN-25 to sodium lactate (diamonds) and whey powder (squares) injections.

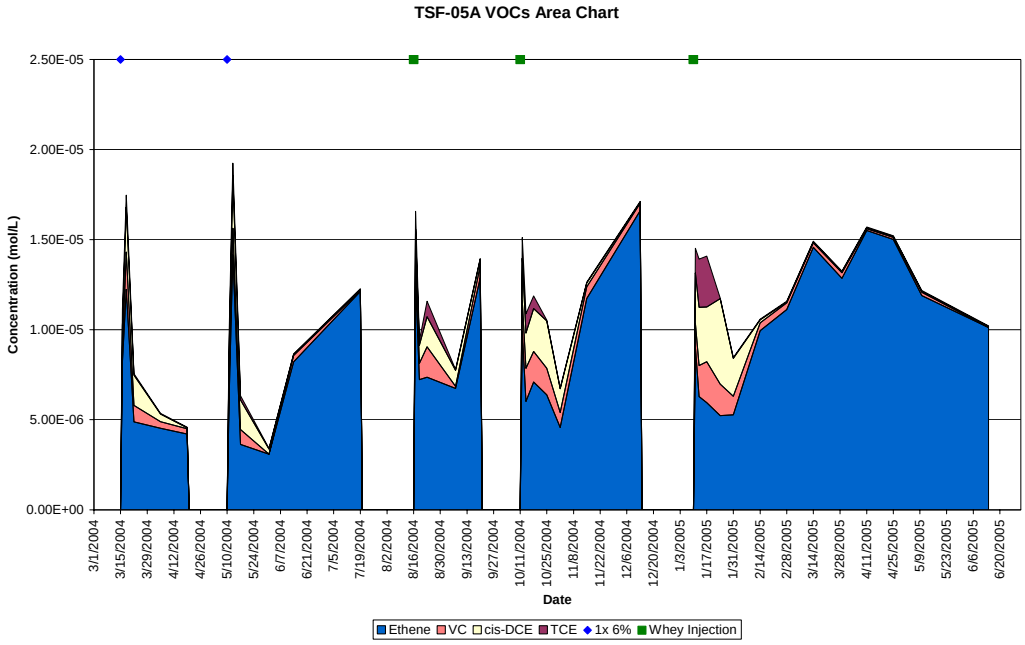

Figure 2-7. VOC response at TSF-05 shown on molar scale.

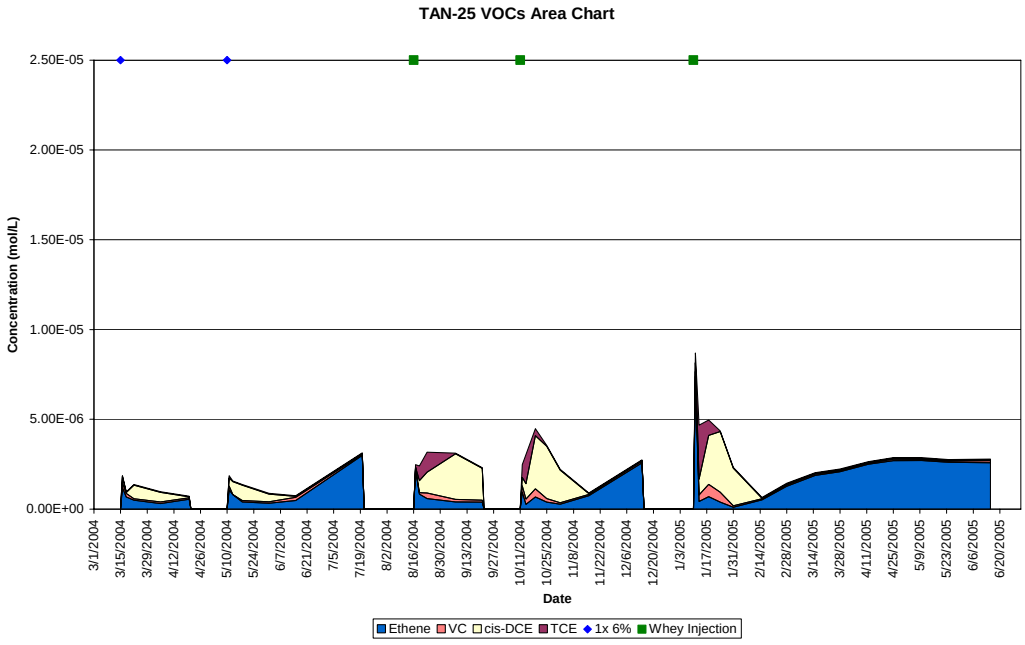

Figure 2-8. VOC response at TAN-25 shown on molar scale.

While the data indicate that the objective of accelerating source depletion continues to be met and that in some areas the residual source appears to have been completely removed, the longer-term goal of completely stopping flux from the source area has not yet been achieved. It has been determined based on both field data and numerical modeling that this objective will likely not be achieved using only one injection well, which led to the installation of a second injection well further downgradient. Once the selection of the electron donor solution for long-term operations

has been finalized, it is anticipated that the use of this second injection well will improve electron donor distribution at the downgradient fringes of the residual source that are currently not directly impacted and will therefore achieve the objective of stopping contaminant flux. Although it is clear that the remediation time frame has been significantly reduced using bioremediation relative to the default remedy for the site of pump and treat, the ultimate duration of bioremediation that will be required to achieve RAOs is still not known.

The demonstration that bioremediation can be applied successfully not only in a chlorinated solvent source area where sludge was composed of as much as 3% TCE by weight, but also in a deep fractured rock setting, illustrates that the applicability of the technology is difficult to generalize based on broad classifications of hydrogeologic conditions alone. While these are important indicators, site-specific information is critical to evaluate any technology fully for a particular site. It is important to note that the results obtained at the site would not have been possible without the development and continual updating of a technically sound SCM. Although it can be difficult in many instances to make the argument to a site owner that expending limited resources on collecting the information necessary for this process, the life-cycle costs of the project will generally be decreased.

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2.8 Reviewer Comments

2.8.1 Jeff Marqusee Comments

Comments are under each evaluation statement below; overall assessment is provided at the end.

Project Scale and Purpose

A fascinating site but probably unlike most sites of concern. The DNAPL is located in a well-defined area and is due to past injection of contaminated sludge. It is not typical of most DNAPL sites found in industry or the U.S. Department of Defense (DOD). But it does offer an excellent case study nevertheless.

Site Conceptual Model

A very well-studied site that is sufficiently understood to answer the questions posed.

Remediation Goals

The goals were clearly defined and directly involved the source zone. They are measurable and realistic.

Bioremediation Performance Monitoring

The performance monitoring was well designed. The molecular analysis and fortuitous presence of tracer compounds allows for a very detailed assessment.

Effect on the Source Area

Again, I think the assumption here is too narrow, but the study clearly does provide direct evidence of enhanced mass transfer.

Cost Information

Cost information was not provided.

Summary

This was a well-structured detailed assessment of a large-scale source zone remediation. It clearly showed that bioremediation is effective in the source and is responsible for increase mass transfer. What would be of interest is to understand how the unique conditions of this source impact the ability to extrapolate these results to other sites.

2.8.2 Lenny Siegel Comments

Much of the information under review is beyond my technical expertise, so I'll focus on those areas where I believe I can be most helpful. In general, the results of the three case studies I reviewed, Test Area North, Portland Dry Cleaner, and the Arcadis PCE Site, are impressive. The prospect of accelerating the remediation of VOCs is particularly important to the communities with which I work, not just because of the long-term savings and increased potential for reuse, but because the traditionally slow pace of remediation often means continuing exposures through the vapor intrusion pathway.

Maybe I missed it, but at what depth was waste injected through TSF-05? I can't tell whether the original release was above, below, or at the same level as the contaminated groundwater.

[*Response from Case Study Sponsor:* Text was added regarding the depth of the waste injection wells.]

In locations where the degradation products of the original COC are comparably toxic, it's important to establish a remediation goal that combines the exposures. For example, the decrease of TCE exposures below the MCL does not adequately measure the success of a remediation technology if the levels of VC are elevated above its MCL. It is possible that both concentrations would be, at some point, below the MCL but the cumulative exposure would nevertheless be unacceptable. In this case, the technology would still achieve the goals, but the goals should be more appropriately stated.

[*Response from Case Study Sponsor:* The regulatory goals require that all contaminants, not just TCE, be reduced to below MCLs.]

The inferred significance of the residual source, as well as its enhanced transfer to the aqueous phase, are important findings. Is there a way to accurately predict this phenomenon before treatment?

[*Response from Case Study Sponsor:* This site was one of the first sites at which this phenomenon was observed, so it was not predictable in this particular case. However, these effects have now been observed at enough sites that this type of response can be expected, although the magnitude and scale are not easy to predict.]

I would have found helpful a spatial representation of the injection sites and monitoring wells. It is well recognized that the injection of certain substances can accelerate the degradation of VOCs, and this study shows that one substance (whey powder) achieves more powerful results. However, the major challenge of in situ remediation is delivering the additives to the contaminated regions. How dense an injection matrix is necessary to reach the entire plume? Data that show the range of influence for each injection would help answer this question.

[*Response from Case Study Sponsor:* Figure 2-2 shows the monitoring and injection well network. Also, it is agreed that distribution of substrate is key for this technology. The goal at this site was to remediate only the hot spot of the plume rather than the entire plume. Currently, a three-well injection strategy is being used to deliver substrate to the entire hot spot.]

Finally, the graphs showing the fate of each compound over time illustrate the efficiency of the process, but the large scale (for contaminant concentration) makes it difficult to determine when the remediation goals—the respective MCLs—have been reached.

[*Response from Case Study Sponsor:* The remediation goals have not been reached at this site. When the time comes to demonstrate that this has been achieved, a more appropriate presentation of the data will be used.]

2.8.3 Mike Kavanaugh Comments

Project Scale and Purpose

This is an important case study because of the geologic conditions. The database is extensive, and the scientific caliber of the work is high. The pilot test conducted in 1999 led to the selection of the ISB technology as the designated remedy in the ROD. This the only site I am aware of where a DNAPL source area in a fractured environment has been targeted with ISB technology.

Site Conceptual Model

The SCM is well developed qualitatively, but the definition of the source area is rather vague: "Within the core is a very small residual source area." There is no discussion of "small." Also, there is no discussion about matrix diffusion and the possibility of a long-term source of TCE. In the next paragraph, the discussion focuses on the sludge that has been injected over the last 20 years, which contains large amounts of TCE. Presumably, the organic sludge is also providing some organic materials to serve as electron donors for the site. Again, neither pathways nor receptors are discussed in detail, so it is not possible to understand the nature of the risks at this site. Since it is a CERCLA site and has a ROD, this information is probably available but was not presented in the case study. I would like to have seen some calculations on the estimated mass of TCE present in the source area, and some discussion of the dimensions of the "source area." Also, it is not clear if TCE might have migrated to much greater depths at the site.

[*Response from Case Study Sponsor:* Text was clarified to state that the residual source area is estimated to occur to a radius of about 100 feet from the injection well TSF-05 and that this sludge occurs primarily in the upper 100 feet of the aquifer. The text also mentions that some organic material was present in the sludge that probably drove the limited dechlorination to *cis*-DCE that was present at the site prior to bioremediation operations. In terms of the amount of TCE injected into the aquifer, the estimates range from 350 to 35,000 gallons of TCE.]

Remediation Goals

The RAOs have been established in the ROD. The most relevant to the performance of the in situ technology is restoration of the aquifer by 2095, defined as achieving MCLs for TCE and other COCs. Presumably, this RAO will be measured through monitoring from specific compliance wells. While it is possible that MCLs will be achieved in some portions of the aquifer, restoration seems unlikely. Monitoring in discrete intervals is likely to miss significant aquifer zones that may have no flow but still contain TCE that will remain a long-term source to the aquifer. It is implied that flux will be measured and possibly used as a metric, but this is not explained very thoroughly.

[*Response from Case Study Sponsor:* The TAN TCE plume has undergone extensive characterization, and much of the data were not presented explicitly in this summary. For example, a four-year multilevel sampling program was performed, and one important conclusion from this effort was that no previously uncharacterized zones of high TCE flux are present in the aquifer, including zones that would be considered "no-flow" zones. The sampling pumps were placed at discrete intervals where contaminant concentrations are expected to be highest.]

Bioremediation Performance Monitoring

An extensive database is available for this case study. In addition to a wide range of analytes, including those needed to assess the effectiveness of natural attenuation, various molecular techniques have been applied at this site to confirm the presence of the appropriate microbial species to carry out the reductive dehalogenation process. This is good scientific work, but translation of these data into a quantitative framework that will allow estimates of duration of the cleanup necessary to assess the likely life-cycle cost of the remedy is lacking.

[*Response from Case Study Sponsor:* Based on the uncertainty of the estimates of TCE disposed of in the aquifer, estimates of cleanup times range over two orders of magnitude, depending on the assumptions, making this calculation not very useful.]

Effect on the Source Area

The authors of this study claim that the injection of lactate and subsequent microbially mediated processes enhanced the bioavailability of TCE, which has resulted in the issuance of a U.S. patent. These claims are not quantified here. There is support for the conclusion that the rate limiting step in remediating source zones is the dissolution step and not the microbially mediated reactions. This seems to be supported by their data.

This of course is the critical issue. What rate of dissolution can be achieved with this technology? The case study states a sixfold increase using whey powder compared to water dissolution only. Other field studies (Cape Canaveral, Ft. Lewis) have indicated enhanced dissolution by factors of 2–10. Lab studies by Joe Hughes and others indicted even higher values. I have not done a careful assessment of these claims, but I think there is plenty of potential for exaggeration of the effectiveness of the technology regarding the increased rate of dissolution. This issue certainly deserves careful attention by the panel. From a mass transfer perspective, the rate of dissolution is proportional to the difference between effective aqueous solubility and the hypothetical interfacial concentration. ISB drives this interfacial concentration to zero, thus increasing the rate of mass transfer, hence, rate of dissolution. Whether the solubility increases due to a surfactant or cosolvent effect still seems speculative to me. I would need to see more laboratory investigations to confirm this because I think field data are not easily interpreted.

The statement "ultimately resulting in reduction of the remediation time frame at TAN" sounds like a marketing statement to me. I need data to demonstrate that this in fact has been achieved. Also, this was not the RAO of interest. The RAO of interest was whether restoration can be achieved. The authors state that the data "suggest" that MCLs have been achieved, but they have not shown this. Rebound is a real issue that has not been discussed.

[*Response from Case Study Sponsor:* The quantitative data on dissolution enhancement appear in a separate paper: Macbeth, T. W., L. O. Nelson, J. S. Rothermel, R. A. Wymore, and K. S. Sorenson, Jr. 2006. "Evaluation of Whey for Bioremediation of Trichloroethene Source Zones," *Bioremediation Journal* **10**(3): 115–28. These studies, along with recent results from an Environmental Security Technology Certification Program (ESTCP) demonstration project, show an enhancement factor of approximately 5–6. Of course, this may not result in a reduction in remediation time frame by the same factor. This is an area of active research and debate among the remediation community. Regarding the achievement of MCLs, while some wells have aqueous concentrations of contaminants that are below detection, clearly this site has not met RAOs at this time. Continued operations are required because the residual source is still present. At some point in the future, once certain compliance goals have been met (as described in the summary), then a "rebound study" might be appropriate where donor injections are stopped and contaminant concentrations monitored to determine whether source material still contributes mass to the groundwater.]

Cost Information

Not presented.

Summary

This is a very important case study. As it stands, the authors claim "success" without really showing that the RAOs are likely to be achieved. The time frame is 2095 or nearly 100 years. The data clearly show significant mass removal via biodegradation, but is this sufficient to achieve the RAO? Not certain. I look forward to further discussions on this site, especially regarding the volume of injections required, the frequency of injections required, and the issue of removing TCE that may have accumulated in inaccessible portions of the aquifer where no flow occurs.

2.8.4 Tom Sale Comments

Applicability Across the United States

- EISB (via addition of an electron donor) potentially has wide applicability.
- The geologic setting of interbedded basalt flows occurs widely throughout the northwest United States and in other parts of the world. The work also may be relevant to other geologic settings, including fractured rock settings where the matrix has low porosity (e.g., granite).
- Note performance in fractured media with high matrix storage (e.g., limestone) could be quite different.
- It may not be applicable for sites with large DNAPL bodies with high saturation.
- Care is needed at sites where there is a potential for physical displacement of contaminants (e.g., DNAPL) through injection, adverse mobilization of metals, or negative impacts from elevated total organic carbon (TOC) in groundwater.

Sufficiency of Site Characterization

- A geologic cartoon characterizing the geologic architecture and best estimates of hydraulic conductivity and porosity would be most helpful. In addition, estimates of seepage velocities, porosity, and hydraulic conductivity in relevant units would be helpful.
- The best available estimate of the volume of sludge and the mass of TCE injected would be helpful. This gets to the question of whether the observed depletion is significant relevant to the release.
- An estimate of the pore volume of the target would be helpful. The issue here is the potential for contaminant displacement via delivery of lactate or whey.
- Information regarding the geochemical status of the target prior to treatment would be useful. To what degree was natural attenuation already addressing risk posed by the release?

[*Response from Case Study Sponsor:* A plan view figure showing well layouts is provided as Figure 2-2, and information on the parameters that the reviewer mentions were added. Also, the estimated volumes of TCE disposal and a brief description of prebioremediation redox conditions were added.]

Goals

- Measurable—Yes, given large time
- Realistic—Yes. I'm confused by the combination of 10^{-4} risk-based goals and MCLs. I thought MCLs were based on 10^{-6} risk levels. Are there different risk levels for different contaminants? If so, why?
- Attainable—This is to be determined.

[*Response from Case Study Sponsor:* Both MCLs and risk levels are included in the RAOs because of the presence of radionuclides that do not have MCLs.]

Utility and Value-Added of Monitoring Approaches

- Overall, the monitoring seem appropriate given the physical setting (rock).
- Why was chloride not measured? Increases in chloride might provide a basis for estimating the mass of chlorinated solvent that was degraded.
- Relying solely on aqueous samples provides limited insight as to the effect of the treatment on sorbed contaminants and or DNAPL.
- Were there any adverse effects of carbon addition (mobilization of metal, high TOC in groundwater)?

[*Response from Case Study Sponsor:* Several parameters were measured during the field evaluation phase of the project that were dropped for long-term operations. One of these parameters was chloride, which was dropped because background levels were too high to distinguish any increase from TCE degradation. Also, metals and radionuclides were monitored to assess mobilization, and results showed that none were mobilized beyond the treatment zone.]

Magnitude of Enhanced Dissolution

- A summary table describing the injection activities (start stop volume, flow rates, concentrations) would be helpful.

- The most convincing statement is that aqueous concentrations at TAN-D2 have remained below MCLs in the absence of any measurable electron donor. This is promising. Unfortunately, it is not clear to me that this demonstrates enhanced dissolution (it is not clear what was present at TAN-D2 in the first place).
- Is there spatially variable treatment in the target? A statement regarding uniformity of treatment would help resolve the efficacy of the treatment.
- Ideally, it would be nice if there was another basis for demonstrating treatment (chloride mass balance, soil cores, etc.). I recognize that neither of these may be practical.

[*Response from Case Study Sponsor:* The injection strategies used at the TAN site have changed many times over the course of operations. Because of this, addition of a table presenting injection parameters would make the case study summary unmanageable. The discussion of well TAN-D2 was removed from the case study summary because the level of explanation required is not appropriate for a project summary of this nature. Also, the authors agree that other metrics for demonstrating treatment effectiveness are desirable but not practical for this site.]

Applicability of Costs to Other Sites

I strongly urge the authors to address costs. Both cost and time to complete play a major role in resolving the utility of a technology.

Overall Assessment of Project

- What impresses me most with this project is the fractured rock (low matrix porosity) setting. The prevailing opinion is that little can be done with solvents in fractured rock.
- The complexity of this site makes it difficult to know whether substantive progress toward risk reduction or reduced site care cost has been achieved.
- The time frame to resolve whether this technology works at any given site is a challenge. Both the number of required injections and the period of monitoring seem uncertain. This seems to constrain analysis of site management of cost or planning of future land use.
- The authors might want to consider what they see as the optimal niche for this technology.
- This is an important piece of work.

3. PILOT-SCALE EVALUATION USING BIOAUGMENTATION TO ENHANCE PCE DISSOLUTION AT DOVER AFB NATIONAL TEST SITE CASE STUDY SUMMARY

The presentation associated with this case study, given by Carmen Lebrón, Timothy McHale, David Major, and Michaye McMaster at the forum on March 28, 2006, is included on the CD accompanying this document. The reviewers for this case study were Tom Sale, Alex Naugle, Mary Jo Ondrechen, and Tom Early.

3.1 Project Scale and Purpose

This project was a pilot-scale demonstration completed to validate the effects of biological activity on enhancing dissolution of an emplaced PCE DNAPL source. The field demonstration was conducted at the DNTS in Dover, Delaware, which has five hydraulically contained sheet pile cells. In July 2001, a group of researchers from the University of Wyoming (UW) and

Oregon State University (OSU) released 100 L of PCE as a DNAPL into the vadose zone and the saturated zone (50 L to each area) of Test Cell #1 at the DNTS. The UW/OSU research focused on noninvasive techniques to map DNAPL source zones but did not attempt to remove mass from the test cell. NFESC and Geosyntec Consultants team then conducted a bioaugmentation demonstration using the PCE released in the test cell. During the demonstration, the test cell was flushed at a constant groundwater velocity, and a number of test phases evaluated the rate of DNAPL removal and the extent of VOC treatment. Each phase was operated for sufficient duration to establish a near "steady state" rate of DNAPL removal under each of the different operating conditions (i.e., under enhanced extraction conditions, under biostimulation with sodium lactate and ethanol conditions, and under biostimulation plus bioaugmentation conditions).

The primary objectives of the demonstration were as follows:

- to enhance the dissolution rate (flux rate) of a DNAPL source via enhanced biological activity (bioaugmentation)
- to demonstrate that enhanced biodegradation is an effective means of containing a high-concentration source zone by rapidly degrading the dissolved-phase plume emanating from the source zone
- to validate the performance of the technology at field scale
- to provide valuable operational data to guide future applications of this technology

This demonstration used PCE as the primary DNAPL in a porous-media groundwater system. The study approach consisted of laboratory tests and a field-scale pilot test to demonstrate that bioaugmentation can stimulate complete dechlorination to a nontoxic end product and that the mass flux from a source zone increases when biological dehalorespiration activity is enhanced through nutrient (electron donor) addition and bioaugmentation.

The results of the laboratory experiments have been published and summarized elsewhere (Sleep et al. 2006). The focus of this case study is to present data from the field-scale pilot test.

3.2 Site Conceptual Model

3.2.1 Location

The field demonstration was conducted in a controlled-release test cell located at DNTS (formerly known as the Groundwater Remediation Field Laboratory [GRFL] National Test Site) within Dover AFB (Figure 3-1), which is located 3 miles southeast of Dover, Delaware. DNTS is designed to support the needs of researchers developing and demonstrating technologies for the cleanup of soil and groundwater contaminated with fuels and solvents. DNTS was located at Dover AFB because of the hydrogeologic environment combined with a history of innovative technology demonstrations and a favorable regulatory climate. DNTS covers approximately 3.5 acres in an unused, maintained open area in the northwest corner of the base. The St. Jones River and residential housing are located off base to the west of the site. Directly east of the site is a soccer field and running track. To the north is the Dover AFB boundary, and to the south is an open field with an electrical transformer station. Since the primary focus of DNTS is the demonstration of technologies to remediate DNAPLs, DNTS maintains the capabilities (i.e., has

a valid permit) to conduct contained releases of DNAPLs into the water table aquifer. A plan and cross-section view of the test cell are presented in Figure 3-2.

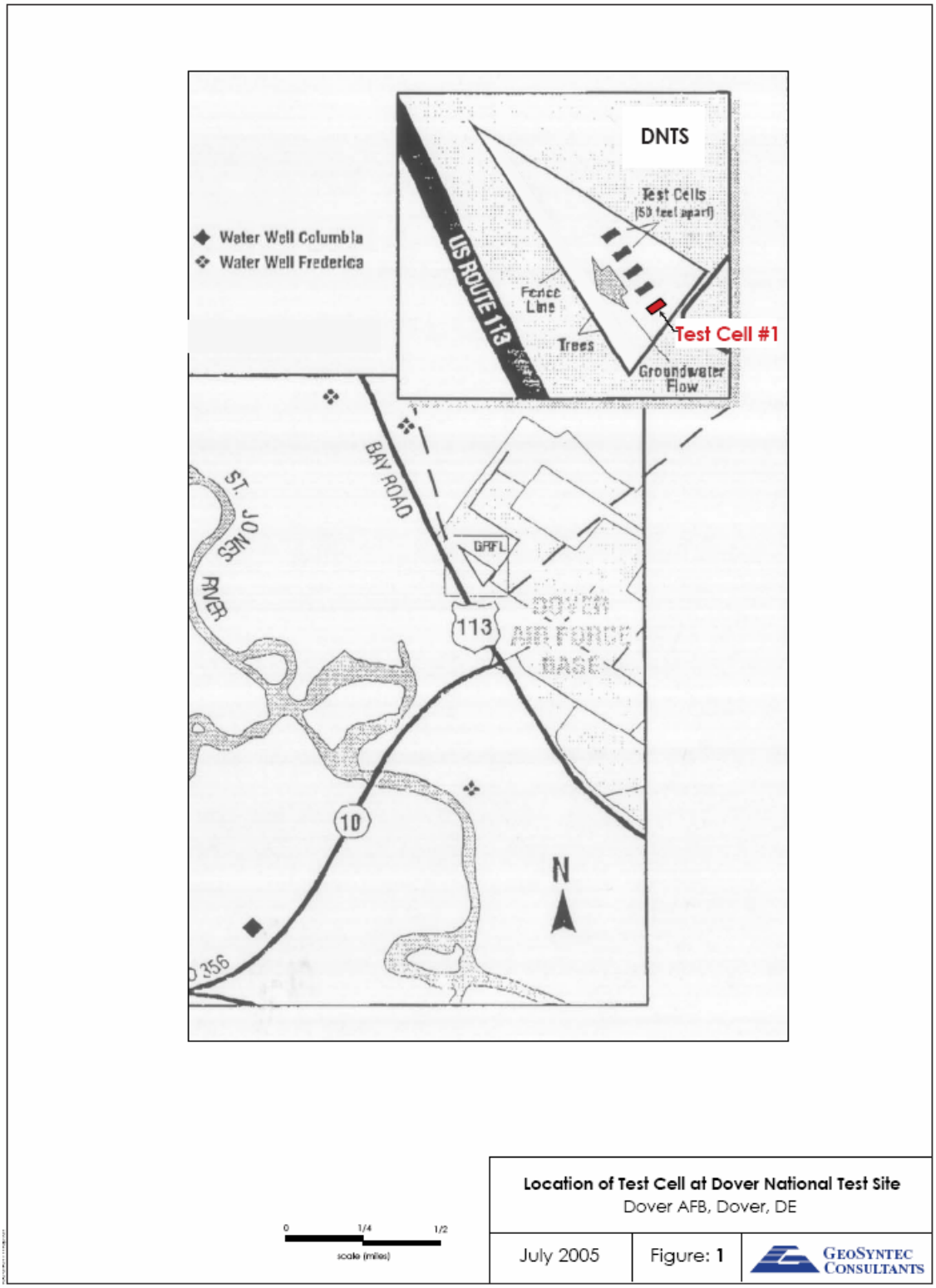


Figure 3-1. Location of test cell at Dover National Test Site.

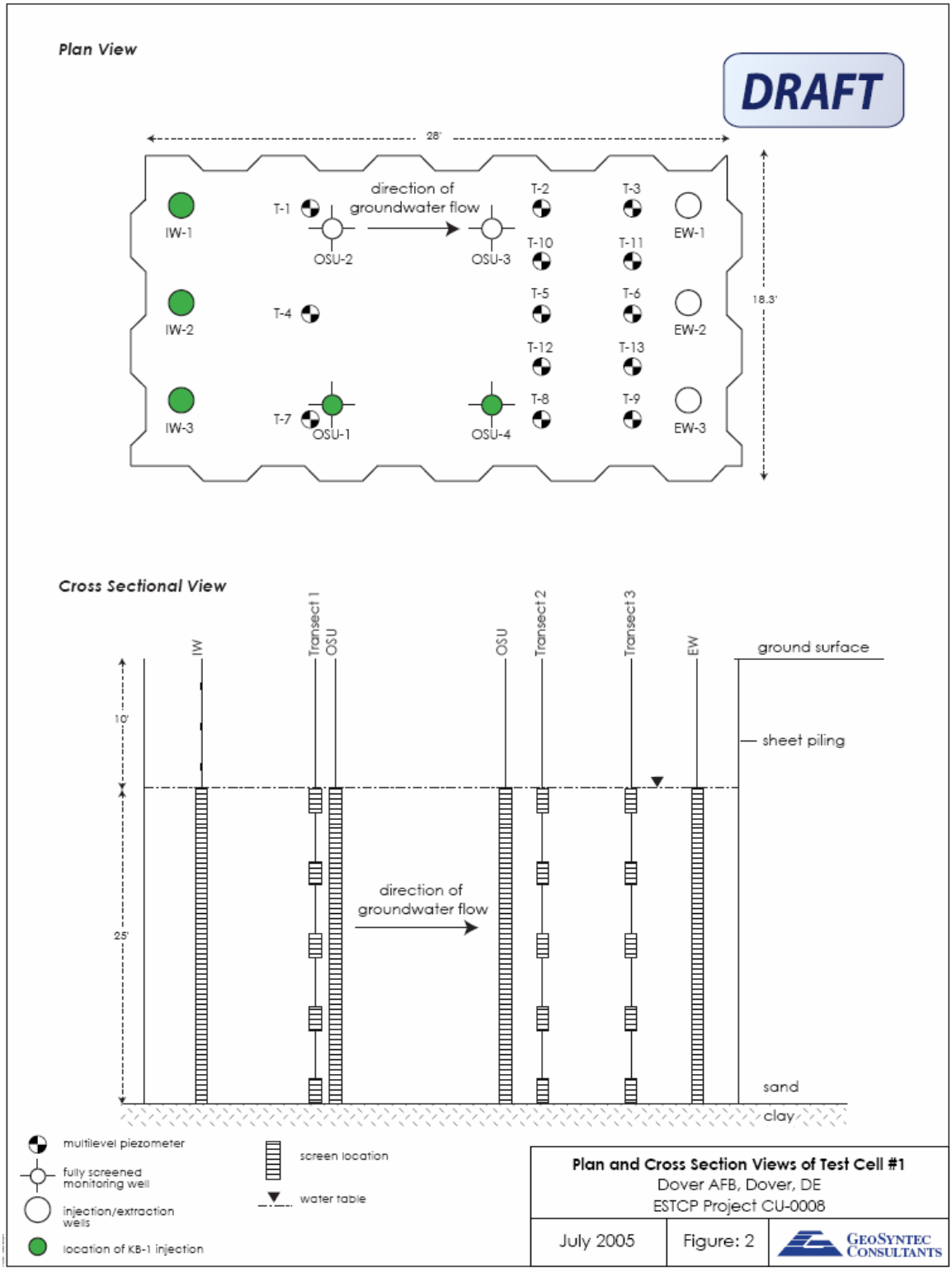


Figure 3-2. Plan and cross-section view of Test Cell #1.

3.2.2 Environmental Setting and Geology

Dover AFB is generally level with little topographic relief. The surface elevation ranges 10–35 feet above mean sea level. The area has a continental type of climate that is marked by well-defined seasons. January is the coldest month with an average daily high of 42.5°F and an average daily low of 25.3°F. July is the warmest month with an average daily high of 88.9°F and an average daily low of 68.0°F. Average annual rainfall is 44.37 inches, generally evenly distributed, with May being the wettest month (5.16 inches) and October the driest (2.59 inches).

Dover AFB is underlain by sediments of Cretaceous to present age, forming a wedge of sediments which thickens to the southeast. The Pleistocene Columbia (1 million years ago) and Lynch Heights (0.5 million years ago) formations form a water table aquifer in the area. Generally, these formations are composed of medium to fine sands with gravely sand, silt, and clay lenses. The Columbia Formation is characterized by a fining-upward sequence of silty, poorly sorted sands. The Lynch Heights Formation overlies the Columbia Formation and is composed of a coarsening upward sequence of silty sands. Discontinuous clay lenses are common in the Lynch Heights Formation, with occasional gravely sand lenses. Underlying the Columbia Formation is the upper unit of the Calvert Formation (Miocene). This unit generally consists of gray, firm, dense, marine clays with thin laminations of silt and fine sand. The thickness of this unit ranges 20–28 feet beneath the base of the Columbia Formation. The Frederica aquifer is a 22-foot-thick sand unit within the Calvert Formation. Beneath the upper sand unit is a middle silt and clay unit with a thickness of greater than 80 feet.

3.2.3 Hydrogeology

The primary water-bearing unit in the area of the DNTS is the Columbia aquifer, which forms a water table aquifer overlying the Frederica, Cheswold, and Piney Point aquifers (confined aquifers). Analyses of water-level data collected during pumping tests conducted in the Columbia suggest that the hydraulic conductivity of the formation is in the range of 3×10^{-3} to 1×10^{-2} cm/second. Pumping tests at the GRFL suggest that the hydraulic conductivity of the unconfined Columbia aquifer ranges from 2.8×10^{-3} to 1.2×10^{-2} cm/second.

Groundwater from the Columbia aquifer is generally soft, slightly acidic, and characterized by low dissolved-solids content. High iron content and low pH are the only natural characteristics that commonly require treatment (Johnston 1973). The underlying Calvert Formation is composed of marine, estuarine, and delta plain silty clays and forms an aquitard to the unconfined Columbia aquifer. Beneath Dover AFB, the aquitard thickness ranges 18–28 feet, averaging of 22 feet. The estimated range of the vertical hydraulic conductivity of this unit is 2.7×10^{-8} to 1×10^{-7} cm/second. Included in the Calvert Formation is the Frederica aquifer, which is a thin, confined zone composed of fine sand that lies approximately 66–88 feet bgs.

Regional water supply aquifers in the Dover AFB area include the Piney Point, Cheswold, Frederica, and Columbia aquifers. The top of the Cheswold is approximately 175 feet bgs at Dover AFB and is separated from the Frederica aquifer by approximately 87 feet of silty clays of the Calvert Formation. The top of the Piney Point aquifer is approximately 334 feet bgs at Dover AFB and is separated from the Cheswold aquifer by approximately 87 feet of silty clay.

3.2.4 Contaminant Distribution within the Test Cell

Previous experiments at the test cell have included an in situ co-oxidation study of chlorinated solvents during bioventing of petroleum hydrocarbons. The chemicals added were JP-4 jet propellent (as a light, nonaqueous-phase liquid [LNAPL]), toluene, xylene, PCE, TCE, and chlorobenzene (dissolved in the LNAPL). This test was completed in 1996. It is estimated that 99 kg total hydrocarbon, 1.75 kg total BTEX, 40 g TCE, less than 115 g PCE, and 40 g of chlorobenzene remained after seven months of bioventing (removed only 5.7% of the total mass of contaminant). The placement of the LNAPL within the vadose zone is unlikely to impact the DNAPL PCE since JP-4 can serve as an electron donor for biodegradation. The impact of the existing chemicals in the test cell was assessed during Phase 1 of the demonstration, and the residual VOCs were not considered detrimental to the goals of the proposed pilot work.

3.2.5 Preliminary Test Cell Investigation

A soil investigation was completed to assess the distribution and extent of contaminants present within the test cell prior to the controlled DNAPL release. Soil samples were collected from eight boreholes within the test cell in March, April, and May 2001 for GC analysis of priority pollutants and xylenes. These samples were also analyzed for JP-4 using a modified Method 8015B.

A total of six VOCs were detected in the soil samples collected from the test cell (PCE, TCE, ethylbenzene, toluene, o-xylenes, and m,p-xylenes). At three locations, TCE was present below the water table at concentrations ranging from 75–220 µg/kg. All other VOCs were detected in samples collected from the unsaturated zone. JP-4 was detected at two locations within the unsaturated zone (9.5 and 11 feet bgs). In general, the presence of JP-4 coincided with the detection of VOCs.

3.2.6 DNAPL Release

The DNAPL release was conducted by the Bradford group from UW in July 2001. A total of 100 L of pure-phase PCE was released into injection wells installed in the vadose zone (screened 4–5 feet bgs) and the saturated zone (screened 12–13 feet bgs). The saturated zone injection point is located directly above a course-grained/fine-grained sand boundary, and it was expected that it would form a zone of DNAPL accumulation with a high volumetric saturation above the boundary; however, a final report by this group was never provided.

3.2.7 Site Improvements for ESTCP Enhanced Dissolution Experiment

Injection, extraction, and monitoring well installation was completed during several consecutive field visits concurrently with the soil borehole investigation. Three injection, three extraction, and four fully screened monitoring wells were installed in March, April, and May 2001, and a series of soil samples was collected for laboratory analysis. Thirteen multilevel piezometers were installed in October 2001 without additional soil investigation activities. All fully screened wells and multilevel piezometers were developed in February 2002 following the completion of the aboveground recirculation system.

3.2.8 Infrastructure and Operation of the Test Cell

The recirculation system consisted of five major elements: flow control, aboveground treatment, electron donor addition (as required by phase), groundwater reinjection, and data acquisition and control. Control of the extraction and injection of groundwater within the test cell was necessary to simulate a natural aquifer system. Three 0.13-gallon bladder pumps with air pressure control manifolds and a 60-gallon air compressor were used to extract and discharge the groundwater into a 1000-gallon polyethylene settling tank. The bladder pumps were expected to deliver a combined flow of 1 gpm into the settling tank. A Grundfos Redi Flow III variable-speed transfer pump that allows for remote control of the injection flow rate transferred the groundwater within the settling tank through the aboveground treatment system and into the three injection wells. Through the use of the variable speed control, an injection flow rate of approximately 1 gpm was projected.

Aboveground treatment of the extracted groundwater consisted of two granular activated carbon (GAC) drums in series to prevent the injection of VOC-contaminated water into the test cell. This setup was later decreased to one GAC drum due to on-site water treatment regulations as directed by state environmental officials.

A multichannel, variable-flow peristaltic pump with computer input terminal (chemical feed pump) allowed for the automated injection of electron donor to the test cell during the biostimulation and bioaugmentation phases of the demonstration.

Remote control of the extraction, transfer, and chemical feed pumps was accessed through a data acquisition and control system. The system consisted of an on-site laptop computer with modem and digital subscriber line and CITEC software to control all of the inputs and outputs of the equipment. The data acquisition system was programmed to record system data on an hourly basis and save to a data file at the end of each day. A second program averaged the hourly readings over the entire day and incorporated them in a summary data file.

The initial testing of the recirculation system required a stepwise testing procedure to ensure that all equipment was functioning as intended. The extraction pump air solenoid emergency shutoff, bladder control modules, flow elements, level alarms, and discharge piping were the first set of units to be tested. Calibration and confirmatory testing of the extraction well flow meters and optimization of the bladder pump extraction rates was time-consuming. The injection system flow meters were calibrated, and the remote control settings for the biostimulation system were edited as required. For enhanced safety, high-level alarms were wired to an automatic dial-out system in all aboveground secondary containment areas.

3.3 Remediation Goals

Goals were provided in Section 3.1. As previously described, the test was operated in five phases. Table 3-1 summarizes the duration and composition of each phase. The details of each phase are discussed below in the results section.

Table 3-1. Summary of operating conditions and sample events

EVENT	Date	Total Days	Days Since ED Addition	Days Since KB1 Addition	Event / Comments
Phase 1 (Start Up and Tracer Test 1)	26-Mar-02	0	---	---	Tracer Test Preparation
	27-Mar-02	1	---	---	Conduct chloride breakthrough test (monitor total extracted water with auto sampler)
	11-May-02	46	---	---	Start bromide breakthrough test - monitor at all sample points on selective schedule
	24-May-02	59	---	---	End of bromide tracer test.
Phase 2 - Establish Baseline Condition	1-Nov-01	---	---	---	Test Cell is sampled for DHE and DGGE characterization.
	6-May-02	41	---	---	Baseline snap shot sample round - 6 to 8 May 2002. Collected VOCs, SCIA, bromide, chloride and field parameters
	25-Feb-03	336	---	---	Final phase 2 snap shot sample round - 25 to 27 February 2003. Collected: VOCs, SCIAs, VFAs, DHGs, molecular, anions, dissolved and total metals
Phase 3 - Biostimulation	5-Mar-03	344	0	---	Electron Donor addition begins (average donor: Na-Lactate 225 mL/day and Ethanol 475 mL/day)
	16-Jul-03	477	133	---	Final phase 3 snap shot sample round - 16 to 17 July 03. Collected: VOCs, SCIAs, VFAs, DHGs, molecular, anions
Phase 4 - Bioaugmentation	18-Jul-03	479	135	0	Add KB-1 to Test Cell (11 L to IW-1, -2, -3, OSU-1 and -4). 340 mL ethanol added to OSU-1 and -4 prior to KB-1 injection. Na-Lactate discontinued. Ethanol addition continued.
	4-Mar-05	1074	730	595	Electron donor addition discontinued.
Tracer Test 2	4-Mar-05	1074	730	595	Bromide tracer test preparation
	25-Mar-05	1095	751	616	End of bromide tracer test.
Phase 5 - Post-Bioaugmentation	11-Mar-05	1081	737	602	EW and IW Total Sampled for VOCs, DHGs and VFAs and field Parameters.
	26-May-05	1157	813	678	Circulation system shut down at the end of final Phase 5 sample event. Field demonstration completed.

3.4 Bioremediation Performance Monitoring

Figure 3-2 shows the test cell site plan with the locations of the multilevel monitoring wells, fully screened monitoring wells, injection wells, and extraction wells. The evaluation of the effectiveness of biologically enhanced dissolution of the PCE DNAPL was based on the results of groundwater sampling and analysis. The analytical results from samples collected from the extraction wells on a weekly basis were used to develop the schedule for the detailed snapshot rounds for each phase of the demonstration. Groundwater samples were collected on multiple occasions following system installation; during the tracer tests; prior to electron donor addition; and before, during, and following bioaugmentation. These samples were analyzed in both the field and the laboratory depending on the specific parameter being measured. Table 3-2 lists the analytical sampling schedule for each sampling location, the analysis performed, and the analytes reported. Prior to sample collection, the groundwater parameters (pH, DO, ORP, and temperature) were measured with a flow-through cell and handheld meters. Details regarding field measurements and sample collection methods laboratory methods for the analysis of site soil and groundwater samples can be provided upon request.

Table 3-2. Summary sampling schedule

Analysis	Analytes Reported	Sample Location	Schedule
VOCs	PCE, TCE, cis-DCE, VC, Ethylbenzene, Benzene, Toluene, o,m,p-Xylene	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Weekly, Snap Shot Sample Rounds Weekly, Snap Shot Sample Rounds Snap Shot Sample Rounds Snap Shot Sample Rounds
DHGs	Ethene, Methane, Ethane	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Bi-monthly[1], Snap Shot Sample Rounds Bi-monthly[1], Snap Shot Sample Rounds Snap Shot Sample Rounds Snap Shot Sample Rounds[2]
VFAs	Lactate[3], ethanol	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Bi-monthly[1], Snap Shot Sample Rounds Bi-monthly[1], Snap Shot Sample Rounds Snap Shot Sample Rounds Snap Shot Sample Rounds[2]
Anions	Cl^-, Br^-, PO_4^{-3}, NO_2^-, NO_3^-, SO_2^{-2}	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Bi-monthly[1], Snap Shot Sample Rounds Bi-monthly[1], Snap Shot Sample Rounds Snap Shot Sample Rounds Snap Shot Sample Rounds[4]
SCIAs	PCE, TCE, cis-DCE, VC	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Snap Shot Sample Rounds Not Analyzed Not Analyzed Snap Shot Sample Rounds[5]
DHC-PCR	Dehalococcoides ethenogenes	Extraction Wells Injection Water Fully Screened Wells Multilevel Piezometers	Snap Shot Sample Rounds Not Analyzed Snap Shot Sample Rounds Not Analyzed

Notes:
VOCs- volatile organic compounds
DHGs - dissolved hydrocarbon gases
VFAs - volatile fatty acids
SCIAs - stable carbon isotopic analysis
DHC-PCR - dehalococcoides ethenogenes 16s RNA polymerase chain reaction
1 - bi-monthly sample collection started in April 2004
2 - DHGs collected from select multi-level sample locations T-1, 2, 3, 7, 8, 9, 11, 12 at all depths
3 - lactate concentration includes degradation products propanoate and acetate
4 - anions collected from all multi-level sample locations
5 - SCIAs collected from select multi-level sample locations T-4, 5, 6, 10, 13 at all depths

3.5 Effect on the Source Area

No previous remedial activities were completed to treat the source. During the study it became apparent that there was nonaqueous-phase PCE suspended in the unsaturated zone. An SVE system was operated to extract and calculate this mass to evaluate the potential total mass in the saturated zone. However, we know that SVE removal was incomplete. Partial mass removal estimates are being calculated. It is known that there was 50 L (or 50% of the mass released to the saturated zone). The following describes the different operating stages that were assessed over the operational period.

Phase 1, startup and shakedown, included tracer testing using chloride and bromide to determine flow paths and velocities within the test cell. Phase 2, baseline operation, was operated for 15

months to evaluate the effect of flushing the DNAPL source with groundwater in the presence of the indigenous microorganisms of the test cell. This phase required a substantial amount of time due to the relatively young age of the DNAPL source and the length of time required to reach a steady-state condition typical of industrial source zones. Mass discharge from the extraction wells decreased substantially over the months of August to October 2002. During this time, two of the three extraction wells were increasingly impacted by silt buildup within the bladder of the pump. Therefore, the groundwater samples collected over this time period represented the contribution of only one of the extraction wells. With the pumps repaired in November and groundwater recirculation continued, the mass discharge increased to pre-August levels and then decreased again to lower levels in February 2003.

The high mass discharge observed early in Phase 2 up to the post extraction well repair was likely due to the high surface area of the mobile PCE stringers present within the test cell. The treatment rate established in the last two months of Phase 2 is likely representative of a more stable DNAPL mass. It is noteworthy that regardless of the operational status of the extraction wells, the ratio of each chlorinated ethene to the total ethenes in the groundwater remained constant, with PCE representing 99.8% of the total ethenes present (Figure 3-3). The very low concentrations of other chlorinated ethenes detected in samples from the extraction wells and multilevel piezometers collected during Phase 2 suggest that, in the absence of a suitable electron donor, the indigenous microbial community was not capable of dechlorinating the PCE DNAPL. This hypothesis is corroborated by the results of the stable carbon isotopic analysis of samples collected over this time period (Figure 3-4).

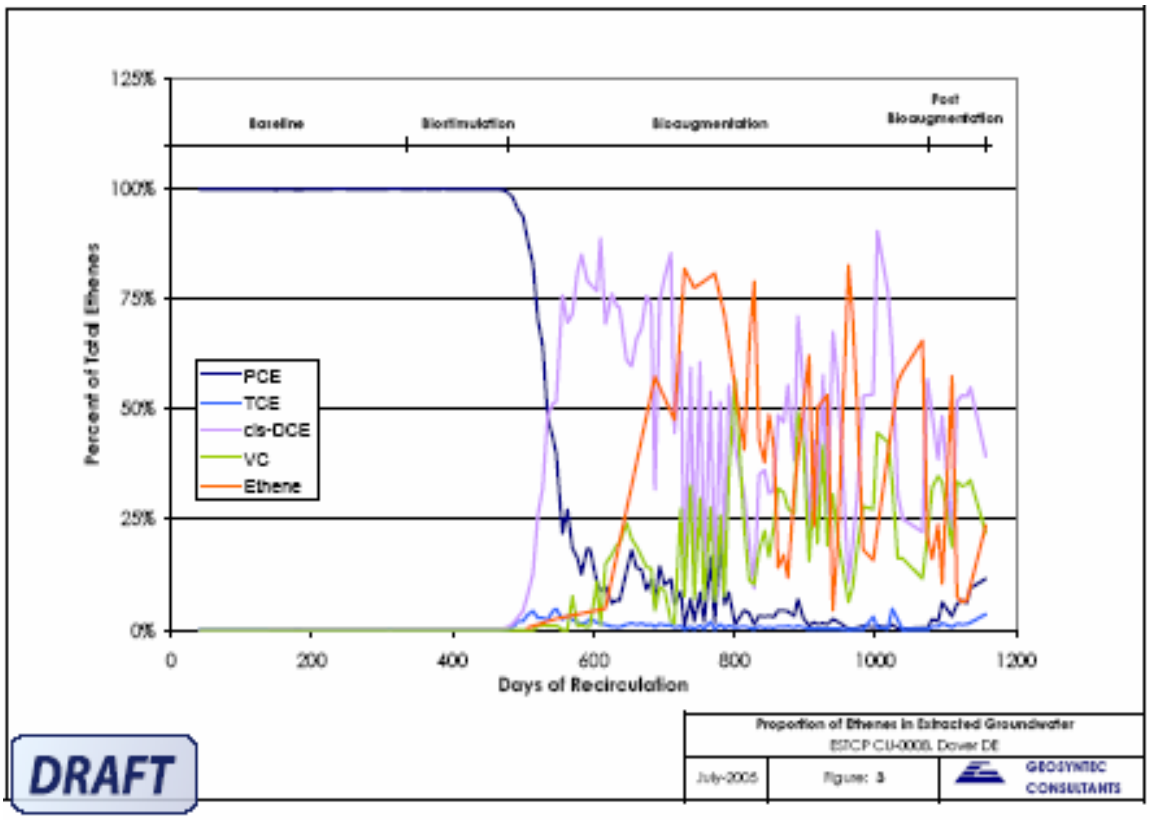


Figure 3-3. Proportion of ethenes in extracted groundwater.

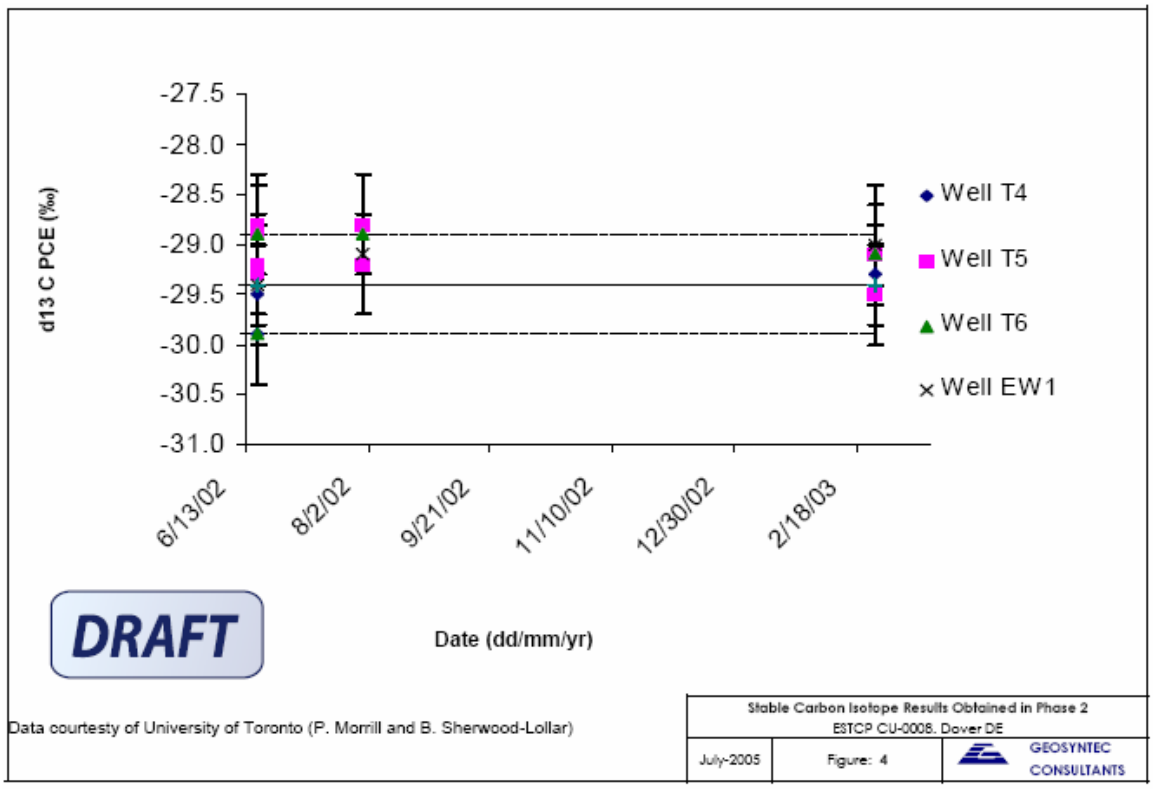


Figure 3-4. Stable carbon isotopic analysis.

During the second phase of this study, the stable carbon isotope values of the dissolved PCE were always within the standard analytical error (±0.5% as shown with error bars and dashed lines) of the isotope value of the pure-phase PCE (solid line). If the dissolved PCE had been significantly biodegraded, the isotope values of the PCE would have become more positive than that of the pure-phase PCE. The fact that the isotope values of the dissolved PCE remained within the standard analytical error of the isotope value of the pure-phase PCE supports the concentration data, suggesting that in the absence of a suitable electron donor, the indigenous microbial community was not capable of dechlorinating the PCE.

In Phase 3, biostimulation with the addition of a pair of electron donors (sodium lactate and ethanol) was operated for a period of five months. On 5 March 2003, the treated groundwater was amended once daily with a combination of ethanol and sodium lactate equal to three times the calculated stoichiometric demand of the test cell. The purpose of adding electron donor to the injection water was to increase the activity of the indigenous microorganisms and attempt to stimulate complete dechlorination of the PCE. The relatively short duration of this operational phase was based on the comparison of analytical results reported in previous studies of the Dover aquifer and the results of the laboratory experiments completed at the University of Toronto (Sleep et al. 2006), which showed there was very little dechlorinating activity exhibited by indigenous microorganisms. The mass discharge from the extraction wells remained relatively stable over the electron donor addition phase, confirming the results of lab tests. The dominant chlorinated ethene within the extracted groundwater continued to be PCE (99% of total ethenes), with low estimated concentrations of TCE and *cis*-DCE (Figure 3-3).

On 18 July 2003, 60 L of KB-1™ was injected into five locations within the test cell (Figure 3-2). This was the only KB-1 addition to the test cell during the demonstration. Phase 4, bioaugmentation with KB-1 and continued electron donor addition, was operated for a period of 20 months. As expected, the mass discharge of VOCs from the DNAPL increased with time and averaged a rate of approximately 100 mmol/day (Figure 3-5). The calculated mass discharge from the extraction wells decreased during August to December 2003, while the dominant chlorinated ethene detected in groundwater samples changed from PCE (86% in August 2003) to *cis*-DCE (55.8% in December 2003). Note: These data are uncorrected for recent conservative tracer/groundwater velocity estimate results (see below).

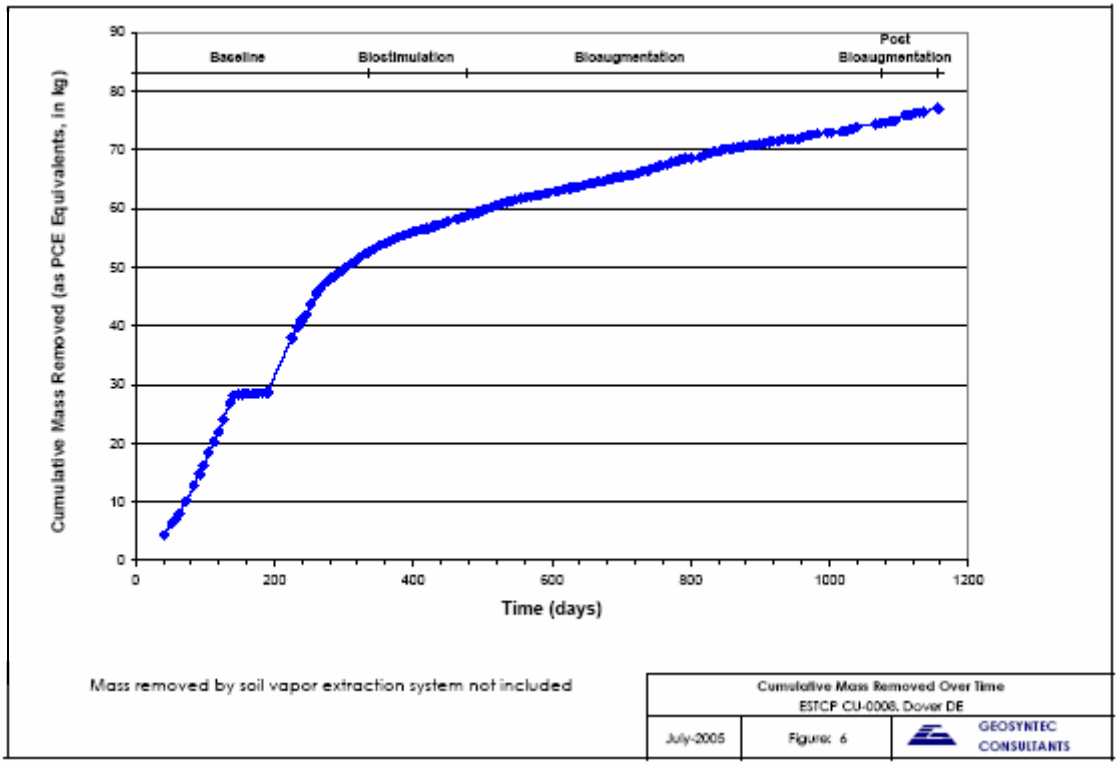


Figure 3-5. Cumulative mass removed over time.

Phase 5 (Post-bioaugmentation) began in late February 2005 (electron donor addition was terminated, but groundwater recirculation continued). During this phase the production of ethene within the groundwater increased significantly and the percent of *cis*-DCE decreased to 16% in May 2005. By May 2005, ethene represented 70% of the total ethenes in the extracted groundwater. The lower than expected mass discharge from the extraction wells may be a function of preferential partitioning of the dechlorination products back into the DNAPL source. The system was shut down (i.e., recirculation stopped) on 23 May 2005.

3.6 Summary

The field component of the project was completed in May 2005. The overall goals of the project demonstration were met. Figure 3-5 shows the total mass extracted based on the mass collected at the extraction wells. It was estimated at the completion of the test that about 47% of the PCE mass remained in the test cell.

Given the longevity of the experiment and the observations in the test cell, a final tracer test was completed to corroborate field evidence of biomass fouling in the test cell. Figures 8a and 8b (see the presentation on the companion CD) show the estimated differences in flow between May 2002 (Phase 1) and March 2005 (start of Phase 5). Given the reductions in flow (biomass occlusion is suspected) during the electron donor stages, additional data evaluation will be investigated to determine whether mass flux estimates have been underestimated or overestimated using the tracer data obtained in 2002. Once this work is complete, additional results (mass flux over time and during each phase and snapshot sampling round) will be generated and will be available for inclusion to this review.

Important achievements include demonstrating the ability to degrade a PCE DNAPL source to ethene and obtaining significant information on the impacts to the microbial populations and corresponding isotope enrichments during biodegradation of a source area.

3.7 Available Resources

The following additional documents could be provided:

- ESTCP demonstration plan
- Progress reports
- Draft copy of ESTCP final technical report

3.8 References

Johnston, R. H. 1973. *Hydrology of the Columbia (Pleistocene) Deposits of Delaware: An Appraisal of a Regional Water Table Aquifer.* Bulletin No. 14. Newark, Del.: Delaware Geological Survey.

Sleep, B. E., D. J. Seepersad, K. Mo, C. M. Heidorn, L. Hrapovic, P. L. Morrill, M. L. McMaster, E. D. Hood, C. LeBrón, B. S. Lollar, D. W. Major, and E. A. Edwards. 2006. "Biological Enhancement of Tetrachloroethene Dissolution and Associated Microbial Community Changes," *Environmental Science and Technology* **40**(11): 3623–33.

3.9 Reviewer Comments

NOTE: When the reviewers call out figures in the following comments, they use the numbers for figures as presented at the Case Studies Forum, only some of which are included here (and numbered or renumbered to suit the context). Please refer to the forum presentation on the companion CD, which contains the full set of figures, numbered as called out by the reviewers.

3.9.1 Tom Sale Comments

Applicability across the United States

- This technology should be applicable in a wide range of physical settings.
- It may not be applicable for sites with large DNAPL bodies (e.g., large basal pools).

- Sites where physical displacement of DNAPL through injection, mobilization of metals, or elevated TOC in groundwater are concerns should be avoided.

Sufficiency of Site Characterization

This is well done. This project illustrates the benefits of working at simple sites where rigorous monitoring is feasible.

Goals

- Enhanced dissolution—Demonstrating this result is possible but not easy. Multiple factors can cause elevated aqueous concentration, and tracking mass remaining versus time is challenging.
- Containing high concentration plumes—Working within a sheet pile wall complicates analysis of whether the technology is a practical way to contain high-concentration plumes. The work seems to more practically demonstrate source depletion.
- Validate at a field-scale—This project goes a long way to achieving this end. The small scale of the demonstration and walls impose some limitations.
- Operational data—Yes, this is achieved.

Utility and Value-Added of Monitoring Approaches

- All of the monitoring seems helpful.
- Chloride production is not mentioned. It seems this could provide an independent check on estimated depletion of chlorinated solvents.

Magnitude of Enhanced Dissolution

- It appears that 100 L of PCE was released (~160 kg). Of this, Figure 7 suggests that approximately half was removed in produced waters as a dissolved phase. In addition, some PCE was removed via SVE. Is there an estimate of how much was degraded and how much remained at the end (May 23, 2005)?
- Inspection of Figure 7 does not indicate distinct increases in contaminant depletion with biostimulation or bioaugmentation. The primary evidence of the potentially enhanced dissolution with bioaugmentation is increased daughter products. It is not clear to me that there is strong evidence of a meaningful increase in the rates of DNAPL dissolution.
- End point soil cores and/or water quality data would help resolve whether substantial source depletion or reduction in potential contaminant flux from the source ("containing high-concentration plumes") was achieved.

Applicability of Costs to Other Sites

I strongly urge the authors to address costs. Both cost and time to complete play a major role in resolving the utility of a technology.

Overall Assessment of Project

- The authors have conducted a useful field study.
- The work clearly shows that bioaugmentation can enhance degradation of PCE.
- Unfortunately, it is not clear to me that the experiment demonstrates that biostimulation or bioaugmentation can meaningfully reduce potential risks or site care requirements.

3.9.2 Alec Naugle Comments

Project Scale and Purpose

Is the electron donor the same as the "nutrients"? The electron donors and nutrients used should be identified in the introduction.

Site Conceptual Model

- The write-up would benefit from inclusion of a cross-sectional figure showing the site geology described in the text in relation to the depth of the test cell. This information is described in geology and hydrogeology sections.

- What was the groundwater gradient that was simulated? How does it compare to a natural system in a similar hydrogeologic setting?

- Where in the test cell was the DNAPL injected? This location should be shown on Figure 2. Also, why inject half the DNAPL into the vadose zone?

- The write-up states that noninvasive techniques were used to map DNAPL distribution. Were the starting and ending locations of the emplaced DNAPL verified? If so, how? Was DNAPL ever observed in any of the piezometers or extraction wells?

Remediation Goals

- The statement that "the placement of LNAPL within the vadose zone is unlikely to impact the DNAPL PCE since JP-4 can serve as an electron donor…" seems to be right but for the wrong reason. For example, maybe the only reason JP-4 did not impact the PCE DNAPL is that there were no indigenous PCE-degrading microbes. Furthermore, it may well be that, once the bioaugmentation phase began, JP-4 did play a role as an electron donor. Who knows?

- The point of Phase 2 seems to be to allow an acclimation period for indigenous microbes in the presence of the emplaced PCE DNAPL. How is it known that 15 months is an adequate period "to reach a steady-state condition typical of industrial source zones"? My experience is that plumes at industrial sites are typically much older. Was there any analysis of microbial cultures and populations before the DNAPL was injected and at the end of the 15-month period?

- According to Table 3-2, Phase 1 included a tracer test to establish flow rates through the test cell. The results of this testing should be presented, particularly the groundwater velocity and gradient established with comparison to real-world scenarios.

- Figure 4 needs to be provided in color. Also, the x-axis in Figure 4 is in days since recirculation started, yet the write-up refers to dates, typically by month. I suggest the scale be changed to months since start-up or provide a separate figure.

Bioremediation Performance Monitoring

- Where in the test cell is the mass discharge rate calculated? Is this the same point where the percentages of chlorinated ethenes are determined? If not, are there any potentially negative implications?

- Phase 3 (biostimulation) lasted five months based on research from other sites that apparently showed there was little ability to stimulate indigenous organisms over some period of time. Exactly how long was this research carried out at the other sites? Is it possible that it's just a matter of time before indigenous organisms can be cultivated in a significant way? Discussion of this aspect would be helpful.

- Does running the groundwater through GAC have any effect on the natural or augmented microbial populations prior to injection? Was there any attempt to evaluate it, or is there any research on this?

Effect on Source Area

- Figure 6 shows a nearly 40% reduction of the mass discharge between Phases 2 and 3. Is this an artifact tied to the high mass discharge rate associated with flushing of the most mobile PCE during Phase 2? Was there any attempt to quantify the mass discharge rate at the end of Phase 2 so that a more reasonable comparison could be made with the Phase 3 rate shown in Figure 6?

- Please explain why the mass discharge rate declined from August to December 2003. The implication is that mass discharge rates rebounded after December 2003. Note: The monthly mass discharge rate for all phases of the test should be graphed to illustrate such changes.

Cost Information

None provided.

Summary

- It appears that bioaugmentation successfully degraded much of the PCE DNAPL to the ethane end point. However, it is not clear that there was any increase in the rate of PCE dissolution (flux rate) compared to Phase 3. Could this be because concentrations were initially already close to saturation levels? To what extent did solubility limits control biodegradation? Was there any attempt to optimize the groundwater velocity (up or down) to maximize the mass discharge rate for this geologic setting?

- One of the stated goals of this study was to demonstrate that enhanced biodegradation can be an effective containment measure by rapidly degrading the dissolved-phase plume. The results of this study demonstrate that significant biodegradation did occur. However, it is not clear that increased biodegradation of the dissolved-phase plume is an effective containment measure. If biodegradation increases the rate of DNAPL dissolution, then there is potential for additional plume mobilization. At the same time, "rapid biodegradation" must be evaluated in the context of available distance at the site that the plume could move before contacting a receptor, which is largely controlled by groundwater velocity.

3.9.3 Mary Jo Ondrechen Comments

Project Scale and Purpose

This is a pilot study wherein PCE was released to create a DNAPL source. This is simply a field demonstration to establish proof of principle.

Site Conceptual Model

The sponsor has provided a detailed description of the site and its features, including geology and hydrology.

Remediation Goals

The sponsor describes straightforward goals for this pilot-scale demonstration.

Bioremediation Performance Monitoring

The description of the monitoring is sufficiently detailed.

Effect on the Source Area

I note that different amendments were studied to attempt to accelerate the indigenous bioremediation. Monitoring data confirm that the indigenous population of microorganisms was unable to decrease PCE concentration significantly without augmentation. First ethanol and lactate were tried as electron donors. This combination does not appear to have a significant effect in promoting the biodechlorination. Then KB-1 was tried and appears to have been successful in promoting the first two steps of dechlorination (PCE to *cis*-DCE). It appears that after electron donor addition was discontinued, biodechlorination continued with significant, albeit incomplete, conversion.

Cost Information

No information was given.

Summary

Results of this study are encouraging. The sponsors have demonstrated that a significant fraction of PCE contamination can be converted into ethylene with KB-1 augmentation. Within the 1.5-year time frame of the KB-1 injections, about half of the PCE mass was degraded in the test cell. Questions: How frequent were the KB-1 injections? That is not clear from the summary. Generalization of these results seems to indicate that injections of KB-1, together with monitoring, over the course of a few years would be necessary for complete remediation of the chlorinated ethylenes. Is this cost-effective, and can it be scaled up to the entire site? What will be required to take the conversion to completion, i.e., *cis*-DCE and vinyl chloride converted into ethylene?

3.9.4 Tom Early Comments

Project Scale and Purpose

This is a pilot-scale R&D project focused on evaluating the efficacy of bioaugmentation to increase the dissolution rate and degradation of DNAPL (PCE) in a well-characterized, fully contained test cell. An extensive monitoring program is designed to document the dissolution/degradation processes and validate the remediation concept. Well-conceived and implemented projects of this type carried out under carefully controlled conditions have great potential for elucidating critical design features for future application at other sites.

Site Conceptual Model

The summary identifies several studies that preceded the biostimulation project. Apparently, there was a bioventing investigation in the mid-1990s in which a variety of organic contaminants was added to the vadose zone. Only 5.7% of the total mass was removed by bioventing. The case study summary indicates that no significant impact was anticipated, although no supporting information is provided. It is essential to ensure that previous investigations have not affected the outcome or interpretations of the current investigation.

It appears that the UW/OSU and NFESC/Geosyntec projects were done in a coordinated fashion. Injection, extraction, and monitoring wells were installed between March and May 2001; soil samples were collected at the same time. In July, 2001, UW released 50 L of PCE to both the vadose and saturated zones for a project where the objective was to image the DNAPL. When did UW/OSU conduct their DNAPL imaging work? Multilevel piezometers were installed in October 2001. The wells and piezometers were developed in February 2002. A timeline for these events would be helpful. Figures 4 and 7 contain some information related to baseline and biostimulation activities, but a comprehensive timeline is not provided.

Because DNTS has been the location of numerous R&D projects over the past ~10 years, extensive characterization data for the overall site must be available on the geology and hydrogeology of the subsurface above the clay confining zone (located at a depth of ~35 feet). Furthermore, I presume that the test cell used for this study underwent detailed characterization by UW and OSU during their investigations (what about for other studies?). That said, the case study summary does not provide much information on the lithologies (and their distribution) encountered in the test cell. It is not possible to get a good idea about vertical and lateral heterogeneities that will impact DNAPL distribution and preferential groundwater flow paths. The cross section in Figure 2 would be an ideal place to overlay lithologic information.

Information relevant to subsurface heterogeneities is available in a series of cross sections through the cell that illustrate the groundwater velocity at two time periods (May 2002 and March 2005) during the test, but they are discussed only briefly at the end of the summary. Referring to Table 3-1, it seems likely that the May 2002 measurements come from the first Br tracer test conducted during the baseline period of operation (after DNAPL release); the March 2005 measurements seem to correlate with the second tracer test (following bistimulation and bioaugmentation). These tracer tests, the associated figures (Figures 8a and 8b), and their interpretation were mentioned only within the context of biomass occlusion. It appears that these data had not been fully evaluated at the time the summary was prepared. This information is very

useful in getting some idea about pre- and post-test hydraulic heterogeneities that are related to lithologic and/or DNAPL/biological activity. Were soil samples taken to help understand the observed changes in velocities? As the UW/OSU project was focused on attempts to map the DNAPL, it would be helpful to know what they were able to accomplish, how their results correlated with observations in Figures 8a and 8b, and how it might have affected the design of this investigation.

The summary indicates that soil samples from eight boreholes were analyzed for contaminants prior to conducting the test. No information is provided as to the location of these borings, the depths from which samples were obtained, etc. How were the locations and sampling intervals related to the sites of PCE released by UW? Or to release sites from any earlier studies? A variety of VOCs were detected in the soil, but reference is made to a Phase 1 evaluation that concluded these contaminants would not interfere with the biostimulation investigation. It would be helpful to have additional information that supports this assertion.

The biostimulation project utilized the DNAPL (50 L of PCE) released below the water table by UW. Where was it released in the cell? The summary indicates that the depth of release was 12–13 feet BGS, but no information is given about the plan view location. Is there any information on the architecture of the DNAPL in the saturated zone? Is there any information as to whether or not any of the 50 L of PCE released to the vadose zone eventually drained into the saturated zone? Where were the two PCE release points located?

Remediation Goals

There are no specific remediation objectives. The goal of the investigation is to evaluate the efficacy of bioaugmentation to increase the dissolution rate and degradation of DNAPL (PCE) in a well-characterized, fully contained test cell. An extensive monitoring program was designed to document the dissolution/degradation processes and validate the remediation concept. This highly controlled, in situ test environment coupled with a robust monitoring program is well suited to meeting the project goal.

Bioremediation Performance Monitoring

Table 3-2 outlines an extensive monitoring program. A wide range of analytes, sample locations, and depths is indicated. Extraction well samples yield valuable information on mass flux of various analytes, whereas the piezometers provide information from which a quasi-three-dimensional picture of contaminant and other analyte distributions can be constructed. The fully screened monitoring wells will yield some type of average analysis depending on the production of each lithologic zone penetrated by the well. These results might be interesting (and less costly) than sampling the multilevel piezometers, but I believe they are less useful than information obtained from discrete intervals in several transects. The carbon isotope data can provide useful confirmation of contaminant degradation and is appropriate for this type of R&D study. However, I question whether it should be considered as a standard procedure for routine remediation projects.

The experimental design permits the measurement of mass flux of various contaminants and other analytes. This provides very important performance information but is an approach that

applies to only a fully contained test cell. Mass flux measurements in a normal field setting are possible but require a different methodology.

No information is provided on the number and timing of the snapshot sample rounds. Referring to Figure 5, it is inferred that three such sample rounds occurred between June 2002 and February 2003. Were there others?

Effect on the Source Area

The summary notes that UW released 50 L of PCE to both the vadose and saturated zones in the test cell. No information is provided that addresses the possibility that some of the PCE released in the vadose zone drained into the saturated zone. Therefore, it is possible (likely?) that the starting amount of DNAPL below the water table was between 50 and 100 L. Furthermore, no information addresses the distribution of DNAPL in the saturated zone. Did a significant quantity pool on top of the confining clay or other low-conductiviy lenses? This would be useful and potentially important information. The summary does mention that SVE was used to attempt to remove residual DNAPL from the vadose zone. It is noted that this attempt was "incomplete," but no further information is provided.

The carbon isotope data obtained during Phase 2 are cited as evidence of the lack of microbial degradation of PCE. However, no similar data from later stages where degradation is occurring are presented for comparison.

Data collected during Phase 3 (biostimulation) confirm that little PCE degradation occurred during this phase.

Phase 4 (bioaugmentation) involved injection of KB-1 (not described or referenced) and electron donors. Figure 7 shows the cumulative mass removed (as equivalent mass of PCE) during the course of the field test. One can clearly see the approach to steady state near the end of Phase 2 that appears to stabilize during Phase 3 (biostimulation). Rough calculations made from the graph in Figure 7 agree with the results for mass discharge during Phase 2 and 3 as presented in Figure 6. However, it is difficult to reconcile the cumulative mass removal curve during Phase 4 (bioaugmentation) in Figure 7 with the results shown in Figure 6. If anything, this segment of the curve in Figure 7 indicates a lower daily average mass extraction during Phase 4 (compared to Phase 3), not higher as shown in Figure 6. If true, then the impact of the bioaugmentation, while clearly leading to accelerated microbial degradation of PCE, has not resulted in an increase of DNAPL solubility and may even have led to a decrease in the total mass flux. It certainly is possible that my evaluation of these figures is in error, but I cannot reconcile data from these two figures for Phase 4.

Cost

No cost information provided.

Summary

What steps were taken to control infiltration from precipitation in the test cell? Is it not likely that any infiltration will dissolve and carry down to the water table various contaminants remaining in the vadose zone? What is the likely magnitude of this effect?

The conclusion that 47% of the original mass of PCE in the cell remained after the test concluded is puzzling. The cumulative mass removal curve in Figure 7 suggests that an equivalent of about 77 kg of PCE was removed. This is ~48 L, close to the 50 L originally place in the saturated zone. I assume that the 47% figure also includes the 50 L of PCE place in the vadose zone less the amount removed by SVE. If so, obviously SVE was not very successful.

4. LAUNCH COMPLEX 34 AT CAPE CANAVERAL CASE STUDY SUMMARY

The presentation associated with this case study, was given by Eric Hood, David Major, Jacqueline Quinn, Sam Yoon, and Arun Gavaskar at the forum on March 28, 2006, is included on the CD accompanying this document. The reviewers for this case study were Mike Kavanaugh, Alex Naugle, Mary Jo Ondrechen, and Nancy Kinner.

4.1 Project Scale and Purpose

LC34, a launch facility at the Kennedy Space Center, is the site of historic releases of TCE, which is present in the subsurface as a DNAPL. TCE was used in launch operations, which continued up until 1969. The large source zone is partially located below the Engineering Support Building (ESB) at LC34 (Figure 4-1). Up to 40,000 kg of TCE is present in the aquifer below LC34, suggesting that centuries will be required to restore groundwater using intrinsic remediation processes.

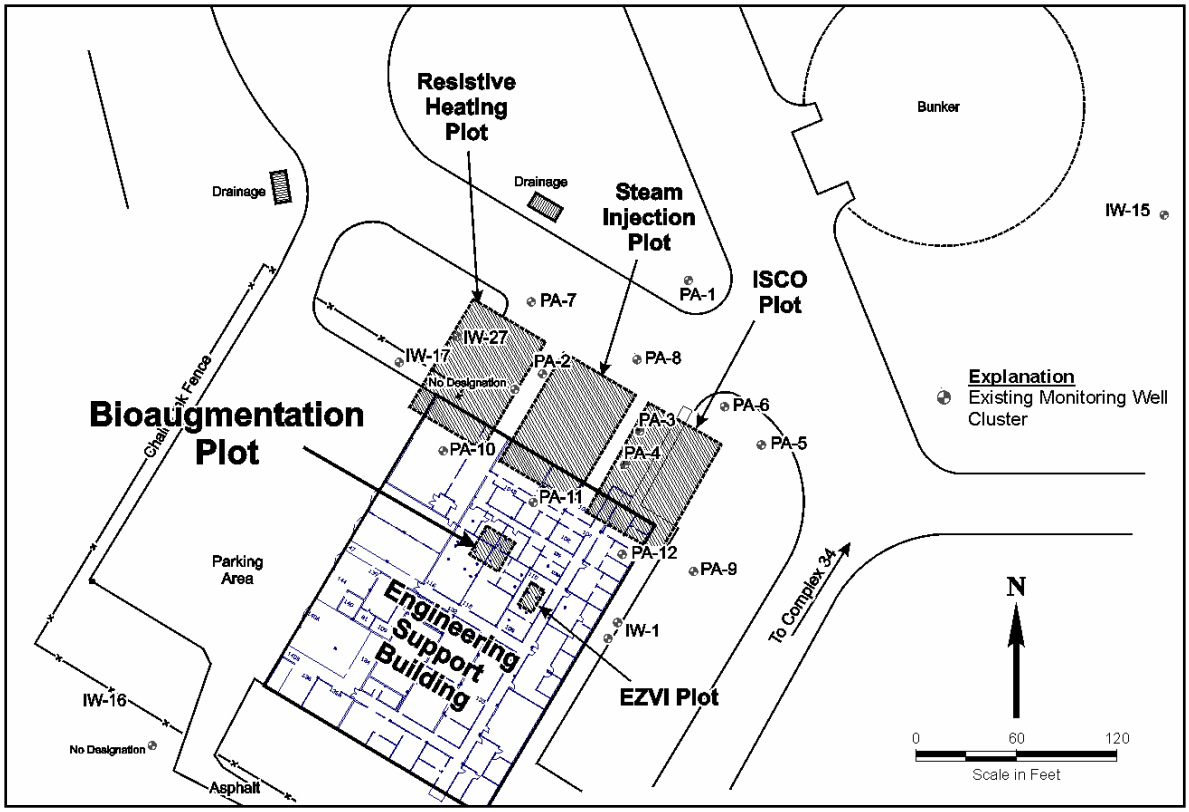


Figure 4-1. Bioaugmentation test plot location at LC34, Kennedy Space Center.
(*Source:* Battelle 2004)

A demonstration of EISB of TCE was initiated May 2002 in a test plot located within the ESB. The small test plot was contained entirely within the much larger source area at LC34. The biodegradation mechanism of interest was reductive dechlorination (Figure 4-2). Reductive dechlorination is the most common biodegradation mechanism for TCE and other chlorinated alkenes (i.e., *cis*-1,2-DCE and VC) in groundwater and can result in complete dechlorination to ethene, a nontoxic degradation product.

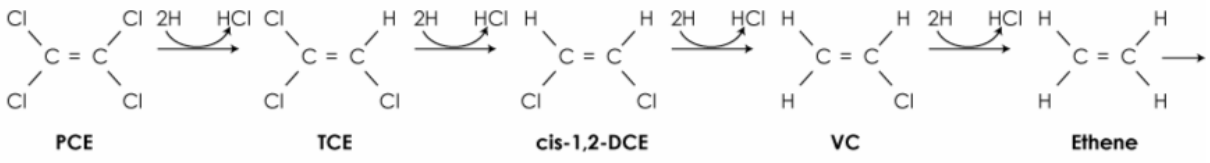


Figure 4-2. Pathway for reductive dechlorination of tetrachloroethene and trichloroethene.

4.2 Site Conceptual Model

The demonstration was conducted in a shallow, unconfined aquifer at LC34, Kennedy Space Center. As shown in Figure 4-3, the unconfined aquifer is subdivided into three distinct lithologic subunits. The target depth interval (from the water table at ~5 feet bgs to 26 feet bgs) was entirely within the upper sand unit, which consists of medium- to coarse-grained sand with beds of crushed shells. The underlying sediments are believed to be less permeable. Recharge of the aquifer is through the infiltration of precipitation, and, as a consequence of the limited topographic relief, groundwater velocities at the site are low (1–10 feet/year).

Concentrations of total dissolved solids in groundwater are as high as 2120 mg/L with about 285 mg/L of sulfate. Groundwater pH is near neutral with an alkalinity of ~400 mg/L (as $CaCO_3$). Sulfate and TCE are the dominant electron acceptors. Measurements of the groundwater ORP suggest that redox conditions (76–171 mV) in the surficial aquifer are above the range commonly associated with reductive dechlorination (AFCEE 2004).

Under intrinsic conditions some TCE is partially biodegraded through reductive dechlorination although this process appears to be electron donor–limited. Although an indigenous *Dehalococcoides* organism is present, the dominant degradation product under intrinsic conditions is *cis*-DCE, which constitutes 5% of the total chloroethenes (molar basis) although trace concentrations of VC are also present.

4.3 Remediation Goals

The goal of the study was to complete a carefully controlled evaluation of the performance of EISB in a source area containing DNAPL; however, the study was completed purely as a research effort and was not an integrated component of the LC34 remediation program.

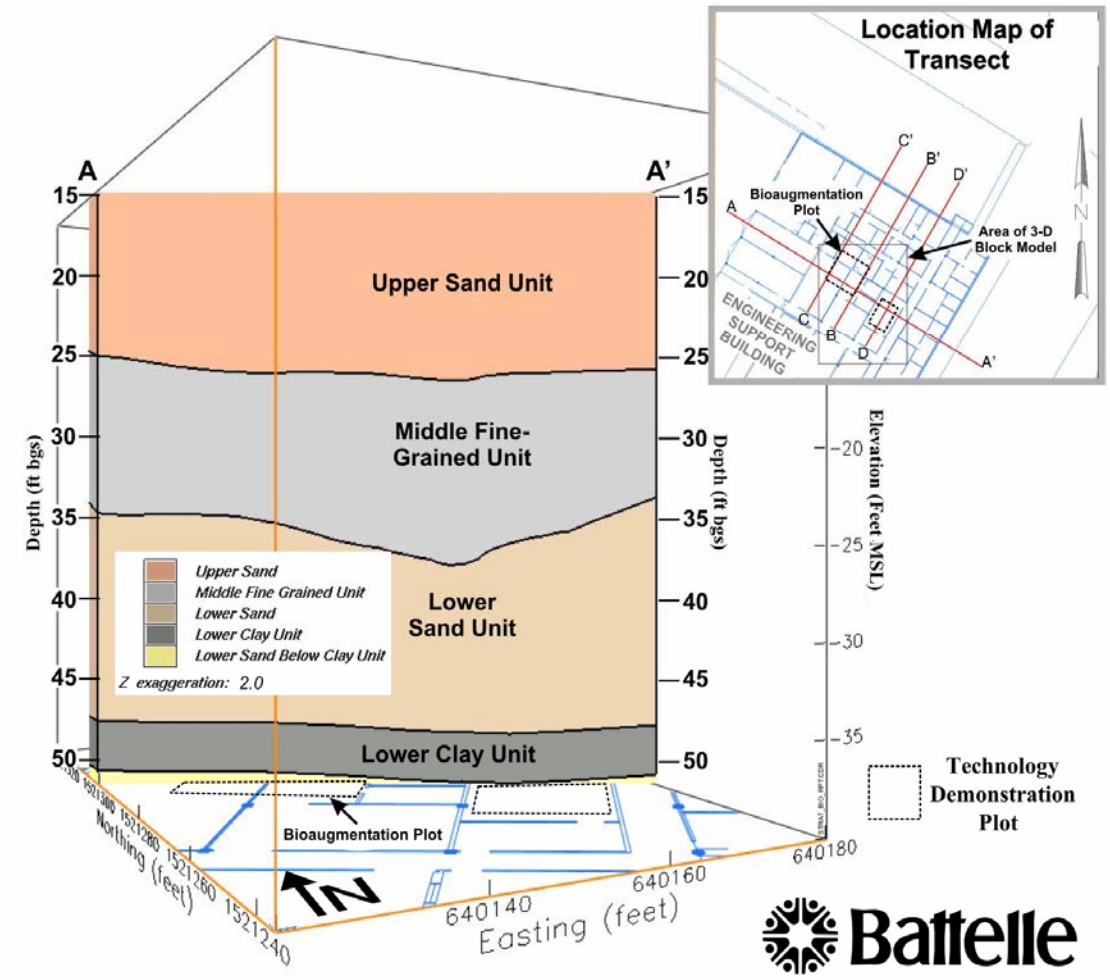


Figure 4-3. Geologic cross section (NW to SE) through the bioaugmentation test plot.
(*Source:* Battelle 2004)

4.4 Bioremediation System Construction and Operation

As shown in Figure 4-4, the treatment system consisted of a test plot equipped with a network of injection, extraction, and monitoring wells. During the study, groundwater was continuously recirculated from the extraction wells to the injection wells at 1.5 gpm through the test plot. Based on the results of tracer testing, the average residence time within the test plot was 24 days. Three phases of the study were completed, including recirculation of unamended groundwater, recirculation of electron donor–amended groundwater, and bioaugmentation with recirculation of electron donor–amended groundwater. Groundwater was recirculated during the initial baseline phase for 184 days. During the biostimulation phase (108 days), ethanol (520 mg/L) was used as an electron donor. The electron donor concentration was based on providing a fourfold excess of the stoichiometric electron donor demand exerted by sulfate and TCE, the principal electron acceptors in groundwater, and insufficient to enhance TCE removal via cosolvency. At the start of the bioaugmentation phase, the test plot was amended with 40 L of KB-1 (SiREM, Guelph, Ontario) divided equally between the three injection wells. As during the biostimulation phase, electron donor was added during the bioaugmentation phase (294 days).

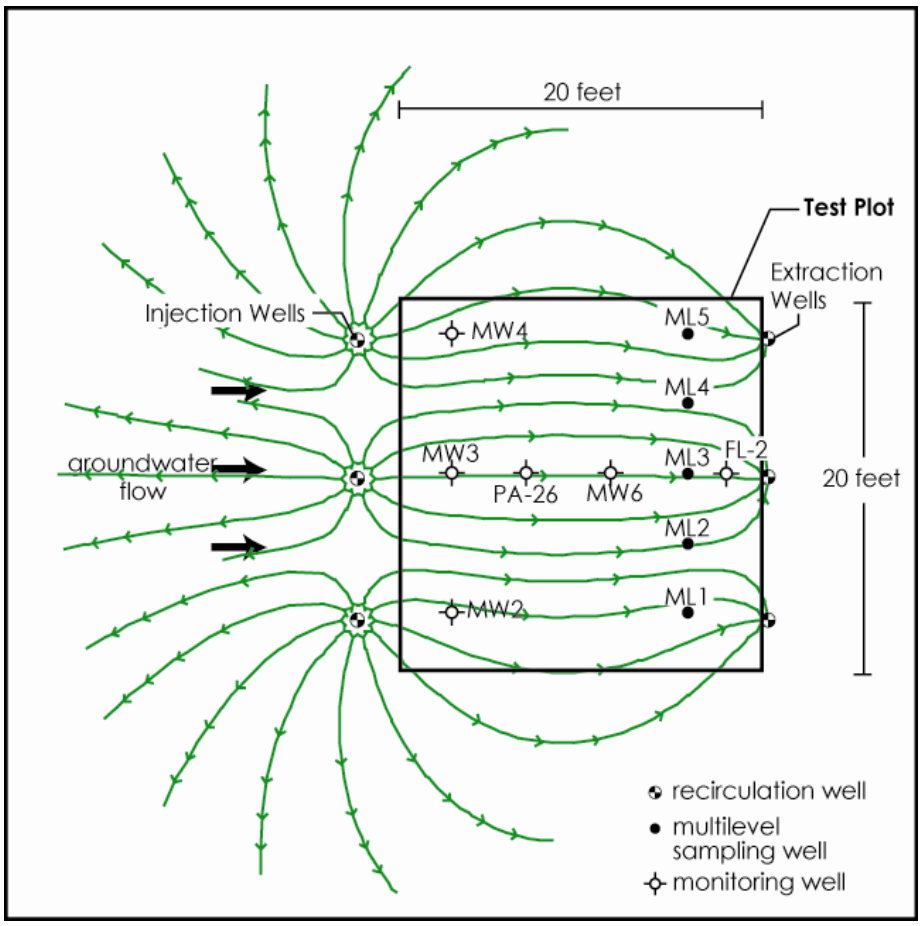


Figure 4-4. Layout of bioaugmentation test plot, including extraction and injection wells.

4.5 Bioremediation Performance Monitoring

Pre- and post-demonstration geochemical parameters are presented in Table 4-1. In general, groundwater in the test plot was anoxic and reduced, with detections of both dissolved iron and manganese. After study completion, test plot groundwater was significantly more reducing (lower ORP). The large decrease in sulfate concentration was indicative of sulfate-reducing conditions, commonly associated with reductive dechlorination (AFCEE 2004).

The results of chloroethene/ethene monitoring are presented in Figure 4-5. The initial TCE concentration was 1220 mg/L. The addition of electron donor and bioaugmentation resulted in significant TCE dechlorination and the accumulation of *cis*-DCE and VC. The final TCE concentration was 0.239 mg/L, corresponding to a 99.98% reduction in concentration. During electron donor addition, *cis*-DCE was the principal degradation product although gradual increases in the concentrations of both VC and ethene were observed. Rapid dechlorination to ethene occurred only following bioaugmentation of the test plot with KB-1. By the end of the demonstration, ethene was the dominant degradation product. The methane concentration during the baseline phase was 0.004 mg/L. During electron donor addition, methane concentrations did not increase until after the onset of ethene production (final concentration 0.137 mg/L), suggesting that the chloroethene concentration was sufficient to inhibit methanogenesis.

Table 4-1. Summary of test plot geochemical parameters during the study for monitoring well PA-26

Parameter	Unit	Groundwater standard	Pre-demonstration	Post-demonstration
pH		Not applicable (NA)	6.5 to 6.7	6.4 to 6.7
Oxidation-reduction potential	mV	NA	+76 to +171	-301 to -191
Dissolved oxygen	mg/L	NA	0.7 to 1.0	0.2 to 0.7
Conductivity	mS/cm	NA	0.15 to 0.21	0.20 to 0.28
Calcium	mg/L	NA	109 to 140	50 to 538
Magnesium	mg/L	NA	10 to 18	33 to 49
Alkalinity	mg/L as $CaCO_3$	NA	390 to 463	469 to 847
Chloride	mg/L	250	125 to 246	278 to 344
Manganese	mg/L	0.05	0.074 to 0.213	0.195 to 1.31
Dissolved iron	mg/L	0.3	7.5 to 31	0.4 to 17
Total dissolved solids	mg/L	500	898 to 1220	1320 to 3060
Biological oxygen demand	mg/L	NA	<12.0	38.0 to 104
Total organic carbon	mg/L	NA	31 to 235	140 to 1,050
Potassium	mg/L	NA	146 to 279	51 to 69
Sodium	mg/L	160	32 to 58	69 to 80
Phosphate	mg/L	NA	<3.0	<0.5 to 1.2
Sulfate	mg/L	250	100 to 172	1.2J to <3.0

(*Source:* Battelle 2004)

4.6 Effect on the Source Area

Pre- and post-demonstration soil samples (70 and 64 samples, respectively) were collected for TCE analysis. In the pre-demonstration samples, bulk TCE concentrations as high as 8327 mg/kg indicated the presence of DNAPL within the test plot. Statistical analysis of these data indicated that >98% of the total TCE mass (including sorbed, aqueous, and nonaqueous-phase TCE) was removed from the test plot during the demonstration. In the post-demonstration data set, it was evident that there were significant decreases in bulk TCE concentration (with numerous nondetect samples, detection limit <0.3 mg/kg) through the treatment zone and in parts of the underlying silty sand zone.

In August 2005 (two years following the conclusion of the study) additional groundwater samples were collected from the test plot. The results of this monitoring event indicated that dechlorinating activity was sustained despite the absence of further electron donor addition. Ethene remained the dominant degradation product, and TCE was detected in only one of four groundwater samples. However, the total ethenes concentration was lower than that previously observed by about two orders of magnitude. In the absence of significant dilution effects, this result suggests that there is a loss of ethene from the system. One possible degradation mechanism for ethene is anaerobic oxidation to CO_2 under sulfate-reducing and methanogenic conditions (Bradley and Chapelle 1999, Dolfing 1999).

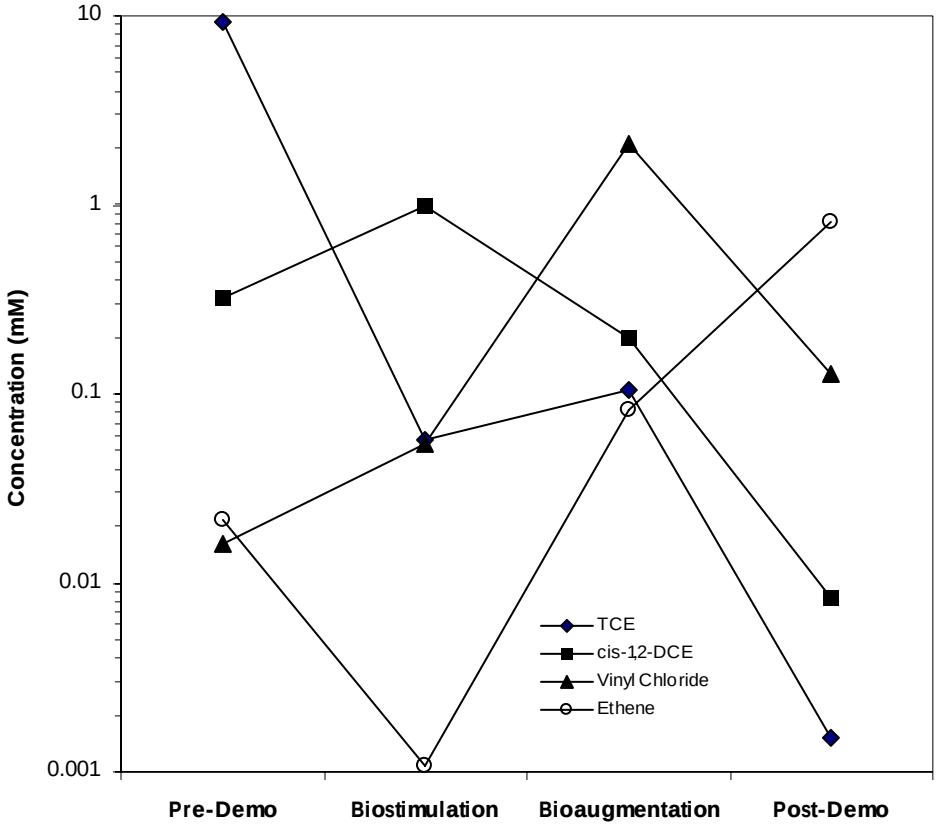


Figure 4-5. Summary of chloroethene and ethene monitoring data for monitoring well PA-26. (Data from Battelle 2004)

4.7 Cost Information

Since this was a research study using a recirculation system with a very high level of data collection, the operational costs are not representative of an EISB system at a typical field site. A cost analysis comparing the cost of EISB to the cost of groundwater extraction and treatment is presented in Battelle (2004).

4.8 Summary

In contrast to the prevailing consensus that EISB is not relevant to source zone remediation, the results of this study demonstrated that rapid and complete dechlorination occurred in the presence of very high initial chloroethene concentration (TCE 1220 mg/L). The study resulted in the removal of >98% of total TCE mass from the test plot. The continued decrease in chloroethene concentrations for two years following the completion of the study suggests that the activity was sustained in the absence of continuous electron donor addition.

4.9 References

AFCEE (Air Force Center for Environmental Excellence). 2004. *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents*. Brooks City-Base, Tex.

Battelle. 2004. *Demonstration of Biodegradation of Dense, Non-Aqueous-Phase Liquids (DNAPL) through Biostimulation and Bioaugmentation at Launch Complex 34 in Cape Canaveral Air Force Station.* Florida Final Innovative Technology Evaluation Report prepared for the U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Superfund Innovative Technology Evaluation Program.

Bradley, P. M., and F. H. Chapelle. 1999. "Methane as a Product of Chloroethene Biodegradation under Methanogenic Conditions," *Environmental Science and Technology* **33**(4): 653–56.

Dolfing, J. 1999. "Comment on 'Methane as a Product of Chloroethene Biodegradation under Methanogenic Conditions,'" *Environmental Science and Technology* **33**(13): 2302–03.

4.10 Reviewer Comments

4.10.1 Mike Kavanaugh Comments

Project Scale and Purpose

This is a well-documented case study. The applicability of the data to other sites is uncertain given the very low (~2 feet/year) groundwater velocities and the large VOC mass in the source area (>40,000 kg of TCE). Data clearly show the ability of EISB to remove mass.

Site Conceptual Model

The SCM focuses on geochemistry but provides little in the way of quantitative discussion of source area, mass in source area, architecture of DNAPL (pool, residual?), and whether TCE may have migrated to deeper zones. The study in that sense is quite restricted and does not address the larger issue of complete site remediation. This is understandable given that the project is a demonstration project, but to assess the performance of the technology, one has to consider all site-related issues, such as overall remedial goals and risks posed by the site.

Remediation Goals

As a research project, goals are to demonstrate "effectiveness" of technology. I think it was a mistake not to have quantifiable goals, however.

Bioremediation Performance Monitoring

The focus of study was demonstrating reductive dehalogenation and an increased rate of dissolution using ethanol as the electron donor. Since ethanol acts as a co-solvent and presumably increases the solubility of the TCE, it is not clear whether the observed enhanced dissolution is due to the ethanol or due to the microbial reactions or to surfactant-like materials exuded by the microbial population, as others have suggested.

Effect on the Source Area

The Superfund Innovative Technology Evaluation (SITE) EPA analysis, which I have not seen, suggests that >98% of the mass was removed. No data are provided on what the initial mass estimate was, so this conclusion can't be verified. Of course, 2% of 40,000 kg TCE will still result in TCE levels well above MCLs. Again, we have a case study demonstrating the effectiveness of the EISB technology to remove significant mass, but we are not able to

determine whether this is sufficient to achieve RAOs such as restoration to MCLs and how this might compare to other remedial options.

Cost Information

I haven't reviewed the conceptual cost data in the report.

Overall Summary

This is a limited case study and cannot be used to determine whether this is the appropriate technology for DNAPL source zone treatment because of the limited goals of the study. The study is very useful, however, in confirming that ISB can be applied in source zones and that high concentrations of TCE do not inhibit this consortium of microbes. How to translate this information into closure strategies at DNAPL impacted sites is left unresolved.

4.10.2 Alec Naugle Comments

Project Scale and Purpose

- The summary provided by Geosyntec Consultants indicates that 40,000 kg TCE exists in the subsurface at the site but does not mention that the plot area where the testing was conducted only contains 18 to 47 kg, 2.6 kg of which may be DNAPL.

- The introduction in the write-up should do a better job explaining that the testing was performed on a small (22 × 22 foot) portion of the source area.

- This study did not attempt to evaluate the effect on mass flux (dissolution rate) from the source zone as other studies have done. It seems like this test plot would have provided an ideal setup for that kind of evaluation. Why was an evaluation of the effects of bioaugmentation on mass discharge rate not performed?

Site Conceptual Model

- The Battelle report does a good job describing the SCM and site characterization and also provides a very good executive summary explaining the purpose and testing methods. Key components of the methods are the use of statistical tools (interpolation, kriging) to evaluate TCE mass removal and that soil data were the primary basis for the evaluation.

- Many figures in the Battelle report show groundwater maps for a much larger area than the test plot. It could be made a bit more clear in the summary or introduction why this is the case.

Remediation Goals

Was there any attempt to quantify the degradation rates during bioaugmentation and after the demonstration ended using groundwater data?

Bioremediation Performance Monitoring

- In the post-demonstration soil sampling, several sample results are listed as NA, zero, and ND in Table 5-1 from the Battelle report. It appears that several of the NA's in the Upper San

Unit were co-located with pre-demonstration samples that had relatively high TCE levels (559 mg/kg, 961 mg/kg, etc.). How were the NA and ND results handled by the statistical methods? What does a zero mean? In Figure 5-1, the post-demonstration results show several values listed near 1 mg/kg and several listed as 0.0001 mg/kg. Do these correlate with the NA's and the ND's? The handling of NA's and ND's and use of a zero value could bias the statistical results in a way that downplays the actual post-demonstration distribution of TCE. Please discuss.

- In the Battelle report, what is the point of Table 5-3? Most of the wells listed in this table are far beyond the boundaries of the test plot and the effects of the biostimulation and bioaugmentation. Therefore, it seems distracting to include columns for "during biostimulation" and "during bioaugmentation" as if those tests could have any effect on the wells farther away.

- Figure 5-5(a) shows that no groundwater samples were collected from the wells within the plot before the biostimulation period. Why? This would have been an ideal period to establish a baseline condition. Furthermore, the data in Figure 5-5(d) are too sparse (only three data points) to support the contour map as drawn. This does not seem like a serious attempt to evaluate the post-demonstration TCE degradation using groundwater data.

- My understanding of this demonstration project is that the 22 × 22 plot area was hydraulically contained using injection wells upgradient and extraction wells downgradient. However, it seems that several groundwater figures are relying on data from wells far outside the plot area. How can the maps in Figures 5-5(d) through 5-8(d) be drawn using only three data points from within the plot?

- Why was a five-month biostimulation period selected? How is it known that five months is enough time?

- Does running the groundwater through GAC have any effect on the natural or augmented microbial populations prior to injection? Was there any attempt to evaluate it or is there any research on this?

Effect on Source Area

No comments.

Cost Information

No comments.

Summary

Results from well PA-26, located in the center of the plot, seem to show that the biostimulation phase resulted in buildup of DCE and VC (Figure 11a). However, with introduction of the KB-1, the end product appears to be significant ethane (Figure 11b). It would be interesting to evaluate the TCE mass reduction based on the groundwater concentration data within the plot area.

4.10.3 Mary Jo Ondrechen Comments

Project Scale and Purpose

In the summary the sponsors did not comment on whether the present approach may be applicable to other sites across the country. However, although this is a research-scale project, it does appear to be a not uncommon case of TCE groundwater contamination.

Site Conceptual Model

I note that I did not receive Attachments A and B. The summary does not provide any information about the range, size, shape, concentration, and concentration gradients of the plume. The SCM as expressed in the summary is not adequate.

Remediation Goals

The expressed goals are very general. Therefore, it is not possible to comment on whether they are measurable, realistic, and achievable.

Bioremediation Performance Monitoring

The description of the monitoring is very sketchy. Therefore, I am unable to comment.

Effect on the Source Area

The results reported in the summary are encouraging. The sponsors report significant reduction of TCE levels and complete dechlorination (conversion to ethylene). However, my questions are as follows: How large was the test site relative to the entire site? What was the configuration of the electron donor injection relative to the rest of the site? What was the geometry of the sample collection? Where did sampling take place relative to the injection site(s) and in relation to the rest of the site?

Cost Information

This was a research study, and cost projections would not be applicable to a more typical remediation situation.

Summary

In general, the results are very encouraging. However, in the absence of details, I would be cautious about generalization to other DNAPL remediation situations. I wonder how extensive is the entire site relative to the test plot and can the process be scaled up to clean up the entire site? I note that this is a site with permeable soil and "limited topographic relief," which means that it does not have the large number of tiny pockets of DNAPL, a feature that is common in the sites that are most difficult to clean up.

4.10.4 Nancy Kinner Comments

Project Scale and Purpose

The introduction was very detailed and provided enough site characterization material to assess how the approach could be used at other sites with similar stratigraphic and hydrologic

parameters. There seemed to be some discrepancy between the manuscript and SITE report. For example, the manuscript states that the ORP was generally reducing in the surficial aquifer (<-100 mV) (p. 6 of 33), while the SITE report (p. 17) states that ORP ranged from +54 to +171 mV there). Another example appears with respect to the groundwater TOC data (<3 mg/L in manuscript [p. 6 of 33] and 31–235 mg/L on p. 21 of the SITE report). The higher TOC suggests more reducing conditions would be present (agreeing with the <-100 mV). What is the source of this TOC?

Site Conceptual Model

The degree of site characterization is extensive. Except for some of the discrepancies noted above, the model of the upper sand unit before treatment is good. Figure 1 in the manuscript is not as clear as Figure 2-2 in the SITE report with respect to the perspective the team wants to show. It would help to have a conceptual model with concentration profiles for a section view to complement those with plan views. Can the Br^- tracer test, used to obtain the flow pattern in Figure 2 (manuscript), be used for a section view of the flow? Can one interpret the trajectories in Figure 2 to mean that under the injection/extraction regime, the water moved through the plot in ~10–15 days? The results of the tracer test are key to understanding the biostimulation and bioaugmentation phases. Therefore, spending more time on this discussion would be valuable. Was this in the SITE report? Perhaps I overlooked it. How does the SCM after remediation starts change for biostimulation and bioaugmentation? These models are not shown. How does this compare with what the Br^- tracer site indicated about recirculation and residence time?

Remediation Goals

The goals for this project are somewhat different because it was a research project, but the SITE report does address regulatory issues of concern in one of the later chapters. The quality control section of the SITE report also makes understanding detection limit and recoveries very easy. The project is somewhat compromised by the proximity of the emulsified, zero-valent iron demonstration and the small volume in which significant contamination remained at the site.

Bioremediation Performance Monitoring

The monitoring in this study was much more comprehensive than in the other studies reviewed (most likely because this was a SITE demonstration). For example, a microcosm study was performed prior to the demonstration. Carbon isotope monitoring on a limited basis could have been helpful in establishing biodegradation rates. However, it would have been fairly expensive to get rate data with isotopes and may not have been justified. It appears that molecular analysis was done in some cases before and during the demonstration. It also appears that analysis for KB-1, as opposed to the native community, was not attempted for the June 2002 samples. This is unfortunate as the role that KB-1 played is less clear (e.g., did KB-1 predominate in the aquifer after injection and during the conversion of c-DCE to ethene, or did something occur during the KB-1 injection to stimulate the native community of dehalorespirers to affect this transformation?).

The limited amount of background data presented hampers interpretation of the results. It is difficult with only one preinjection event to understand the baseline variability in CVOCs and other concentrations in the plot and therefore to determine the extent of transformation that occurred, especially during biostimulation.

Effect on Source Area

The team does not explain the choice of ethanol as the organic carbon source. Is it because of the co-solvent properties? What role did co-solvent extraction with ethanol potentially play in the removal of TCE from the soil? How did in situ ethanol concentrations compare to those used in co-solvent washing? What role, if any, did the salinity play in the microbial process? Could it have inhibited biodegradation of TCE? Did the biofouling treatment change the microbial regime?

The data in Figure 3 and some of the other graphs (Figures 5-5 through 5-8 in the SITE report) can be seen as a progression through time in the plot (especially if Figure 3 is rearranged so that MW-3 → PA-26 → MW-6→ FL-2). Can this information, perhaps combined with the pore volume information, be used to determine degradation rates to compare with the microcosms and the literature? In Figure 3, for MW-3, why does the TCE concentration appear to be very low during the baseline period?

Table 2 shows biomass from 2×10^5 to 3×10^5 cells/mL, while the text (on p. 15 of 33) suggests an order of magnitude change. Which is correct? There also is a question regarding the maximum sulfate concentration of 11 vs. 5 mg/L (Table 5 vs. text).

Under the reducing conditions created, the team expected more CH_4 production but suggested that inhibition was the result of high chlorethane concentrations. Could ethanol have had an effect too?

For the mass flux/discharge estimates, how was the dilution effect at the multilevel sampling well closest to the plot edges taken into account?

Was there any indication that the CVOC contamination was driven into the middle stratigraphic unit by the treatment? Was the datum on the cores carefully controlled (a change of 5 feet in Figure 6 could account for some of the changes in concentration of TCE associated with the soil)?

In Table 1, the $t_{1/2}$ should be reported with ± values as the tests were replicated. In the microcosms, it also appears that ethene was produced in 154 days without KB-1 addition. Judging from the biostimulation timeline (October 23 to February 6), the period was <154 days. Could bioestimation alone have worked given enough time? The period February to April for the bioaugmentation effect is very short. It is unfortunate that the next event is October (six months later), and no KB-1 results are available. All of this makes the effects of biostimulation alone vs. bioaugmentation difficult to separate. Table 5-3 (p. 45 SITE report) also suggests that the time allotted for the phases may have been a factor.

Cost Information

This was fairly detailed in the SITE report and may be useful elsewhere, except that the number of cores etc. may be unrealistic for a nonresearch-based project.

Summary

Most of my questions regarding the study are listed above. The key questions are those regarding (1) the hydraulics denoted with the Br^- tracer, (2) the effect of ethanol as an electron donor vs. co-solvent vs. methanogensis inhibitor, and (3) the adequacy of the length of time for each phase and the ability to separate the biostimulation vs. the bioaugmentation effects.

5. DEMONSTRATION OF ENHANCED BIOREMEDIATION IN A TCE SOURCE AREA CASE STUDY SUMMARY

The presentation associated with this case study, given by Fred Payne at the forum on March 28, 2006, is included on the CD accompanying this document. The reviewers for this case study were Jeff Marqusee, Lenny Siegel, Mike Kavanaugh, and Tom Sale.

5.1 Project Scope and Purpose

ARCADIS began practicing enhanced reductive dechlorination more than 12 years ago, after observing the sequential dechlorination of TCE at the site of an in situ reactive zone treatment for hexavalent chromium. During our early reductive dechlorination efforts, we observed what we called a "surfactant effect," in which sharp increases in dissolved-phase solvent compounds occurred in association with high carbohydrate loading rates. We limited the application of reductive dechlorination to dissolved-phase contamination until we could determine whether it was possible to control the release of solvent stored in sorbed and nonaqueous-phase storage in source zone aquifer materials. In 2001, we published case study data (Payne et al. 2001) that suggested the possibility of manageable desorption and dissolution, while pointing to the development of electron donor fermentation products as a likely causative agent for the enhanced dissolution and desorption. Since that time, we have extended the application of enhanced reductive dechlorination into DNAPL-bearing PCE and TCE source zones, with promising results.

This case study is drawn from a demonstration project undertaken at a private-sector site in the United States. The client agreed to allow use of the project data for consideration by ITRC, on the condition that they remain anonymous and that no site-identifying characteristics be disclosed in the data. We selected this case study for presentation at ITRC because the data collection intensity was very high relative to most commercial-scale technology applications and the project has been under way long enough (nearing three years) for its effects to be evident.

The case study facility is the site of a PCE DNAPL release that likely occurred more than 20 years ago. A groundwater extraction system has been in place for more than 15 years. The study unit is ~9 m thick and covers an area of ~19,000 m^2. Aquifer permeability is generally low, and groundwater migration is believed to be limited to a stratum <2 m thick in the lowermost portion of the study zone. The study site is described more completely below.

The site provided a valuable testing ground because the generally low aquifer permeabilities limited fluid movements and the groundwater containment system provided protection against mobilization of contaminant, if that were to occur. The objectives of the demonstration were to determine the following:

- Can complete reductive dechlorination be established at a site containing DNAPL PCE through carbohydrate-driven biostimulation?
- Does the reductive dechlorination process draw nonaqueous-phase mass out of the formation (either sorbed mass or nonaqueous-phase liquids)?
- Are the attainable source mass reductions sufficient to cause a commensurate decrease in the long-term due care costs for the site?

In the case study summary that follows, we present a few key elements of our rationale for the use of carbohydrates to induce desorption and dissolution of nonaqueous mass and to support dechlorination metabolism. We then summarize the SCM and provide a synopsis of the injection and monitoring program that is nearing its conclusion. Finally, we summarize the observed contaminant concentration patterns that were observed in groundwater monitoring wells, extraction wells, and a number of the carbohydrate injection wells. Appendix 2, included on the companion CD to this document, is a database extract of the raw data, providing a more extensive record of groundwater chemistry and system operations.

5.2 DNAPL Source Zone Treatment Strategy

When chlorinated alkenes such as PCE and TCE are released to an aquifer, a large fraction of their masses often resides in the nonaqueous-phase components of the formation—sorbed-phase and nonaqueous-phase liquids. The reductive dechlorination process has access to only the dissolved-phase fraction of these solvents, and its successful application relies on its ability to draw nonaqueous-phase solvent mass into solution. Many researchers suggest that electron donor should be metered to provide molecular hydrogen at a pace that just satisfies the dehalogenating bacteria demands. We believe that this approach overlooks another critical function of the electron donor supply: the generation of co-solvents and biosurfactants that support the desorption and dissolution of nonaqueous contaminant mass. Figure 5-1 shows a number of metabolic pathways that can form when highly fermentable carbohydrate is injected into an aquifer to support reductive dechlorination. In addition to at least four mechanisms of hydrogen formation, there are numerous sources of co-solvent production that reduce the interfacial tension between groundwater and break down the physical-chemical barriers that isolate solvent source masses from the aqueous phase.

We have found that when carbohydrate is supplied at rates that generate a carbon-saturated microbial community over a 100-day span of groundwater travel from the injection zone, we can reliably generate large increases in the molarities of dechlorination products, relative to pretreatment dissolved-phase concentrations. Figure 5-2, for example, provides extended data from a case study presented initially in Payne et al. (2001) and shows the general pattern we observe when carbohydrate is used to support enhanced reductive dechlorination.[1] The observation point in Figure 5-2 is located approximately 100 days downgradient from a line of carbohydrate injection wells that are dosed every 4–8 weeks with a dilute molasses solution. The injections began on Day 0, and dissolved organic carbon (represented by TOC on the graph) initially reached the downgradient well at high concentrations.

[1] The data is presented in our standard operational assessment format for reductive dechlorination, placing critical operating parameters (pH, TOC, methane, VOCs, ethene, and ethane) in a single composite graphic.

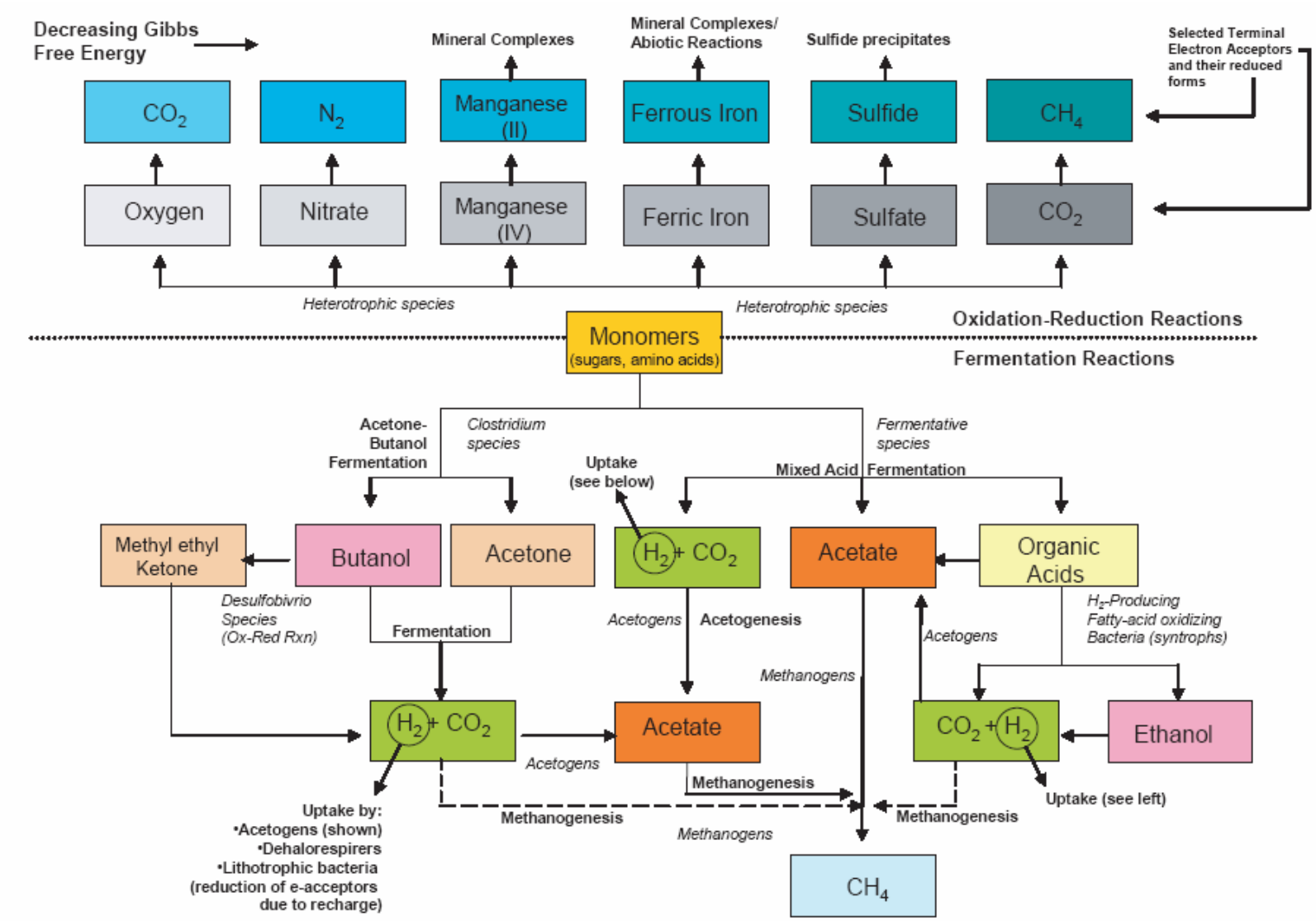


Figure 5-1. Interacting metabolic pathways in the enhanced reductive dechlorination process. Pathways represented by dashed lines are limited at typical aquifer temperatures. (Adapted from Brock and Madigan [1991] and Schink [1997]).

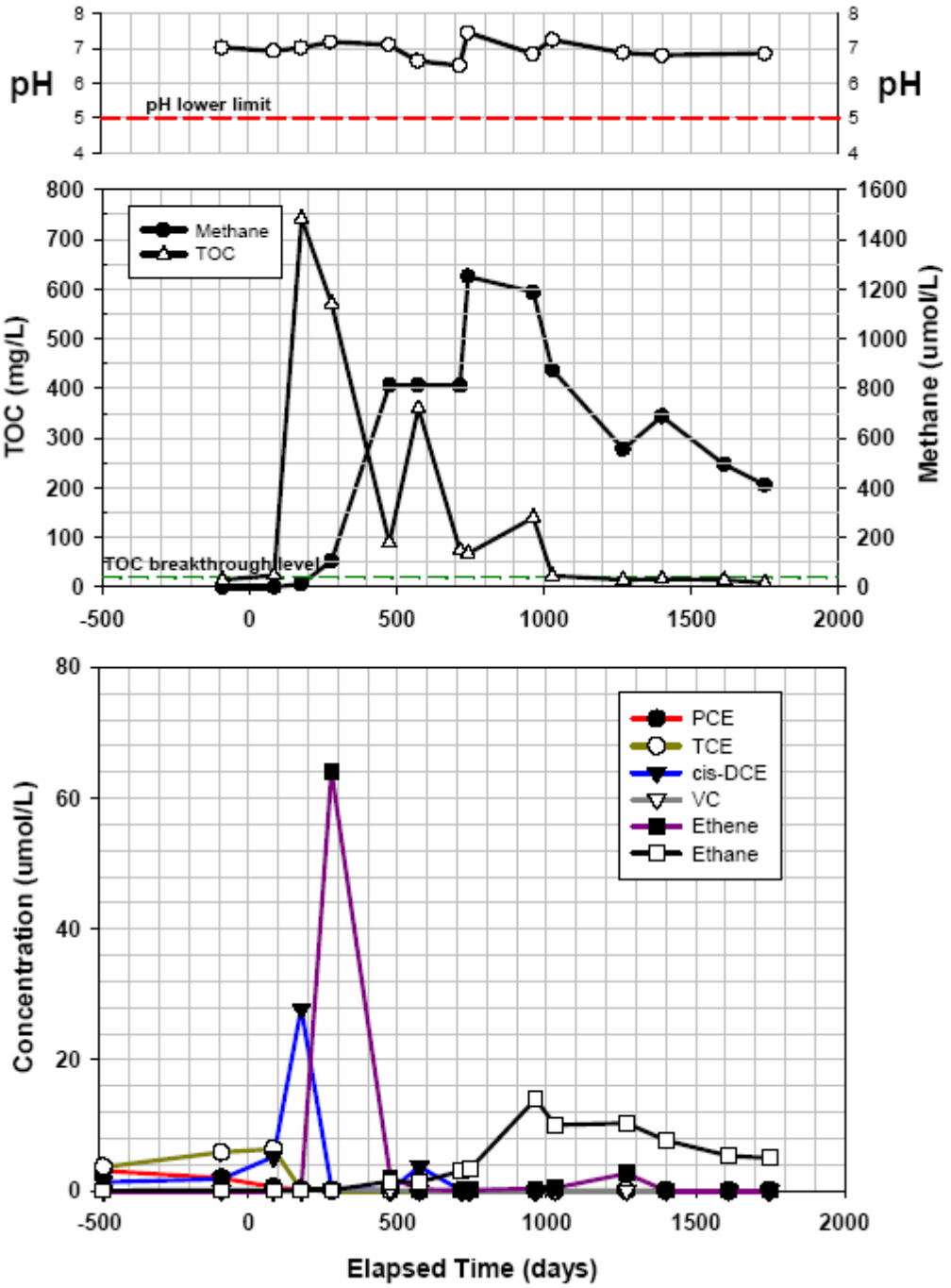


Figure 5-2. Results of enhanced reductive rechlorination applied to a PCE and TCE sorbed-phase source mass. (Results initially reported in Payne et al. 2001.)

As microbial populations increased in response to available carbon, TOC reaching 100 days downgradient gradually declined. After approximately six months, the contaminant mass was converted to mostly *cis*-DCE, and by nine months, PCE, TCE, *cis*-DCE, and VC were below detection, completely converted to ethene and ethane. During the dechlorination process, the total alkene concentration increased from 10 to 65 µM, the result of large-scale desorption of nonaqueous solvent mass from aquifer soils located between the injection line and the

observation point. We believe that this concentration increase is indicative of desorption and dissolution of nonaqueous mass and that these processes are enhanced by fermentation products generated in parallel with the reductive dechlorination metabolism.

5.3 Bioremediation System Construction and Operation

The site remediation program began in 1989 with limited excavation at the spill location. An extraction well system and vacuum-enhanced recovery system preceded the enhanced reductive dechlorination system.

Extraction wells. A line of extraction wells was installed to provide groundwater containment and protection against off-site contaminant migration (Figure 5-3). The system has operated since 1989, with groundwater extraction rates ranging 5,000–31,000 L/day/well during the first two years of the demonstration study.

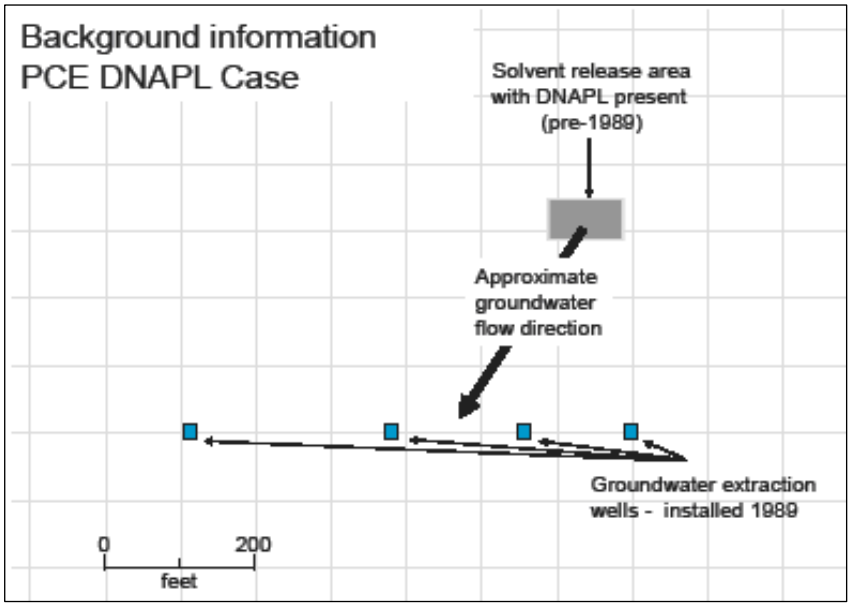


Figure 5-3. PCE DNAPL case study layout.

Vacuum-enhanced recovery. A vacuum-enhanced recovery (VER) system was operated at the source location for a short period, but no significant nonaqueous-phase liquid recovery was observed. The two VER wells were taken out of operation prior to the start of this study, for which they were used as groundwater monitoring wells (VER-1 and VER-2). The PCE DNAPL treatment demonstration program consisted of a monitor and injection well construction phase, followed by three years of carbohydrate injections, during which intensive groundwater sampling was conducted at 10 monitoring wells, 23 injection wells, and the 4 extraction wells.

Monitoring well network. Ten wells were used only for groundwater monitoring during the demonstration project, as shown on Figure 5-4. In the source area, the former VER wells, VER-1 and VER-2, were used for monitoring. Monitor wells MW-1 through MW-3 were constructed in the middle portion of the injection well layout, and monitor wells MW-4 through MW-8 were constructed ~100 feet upgradient of the line of extraction wells.

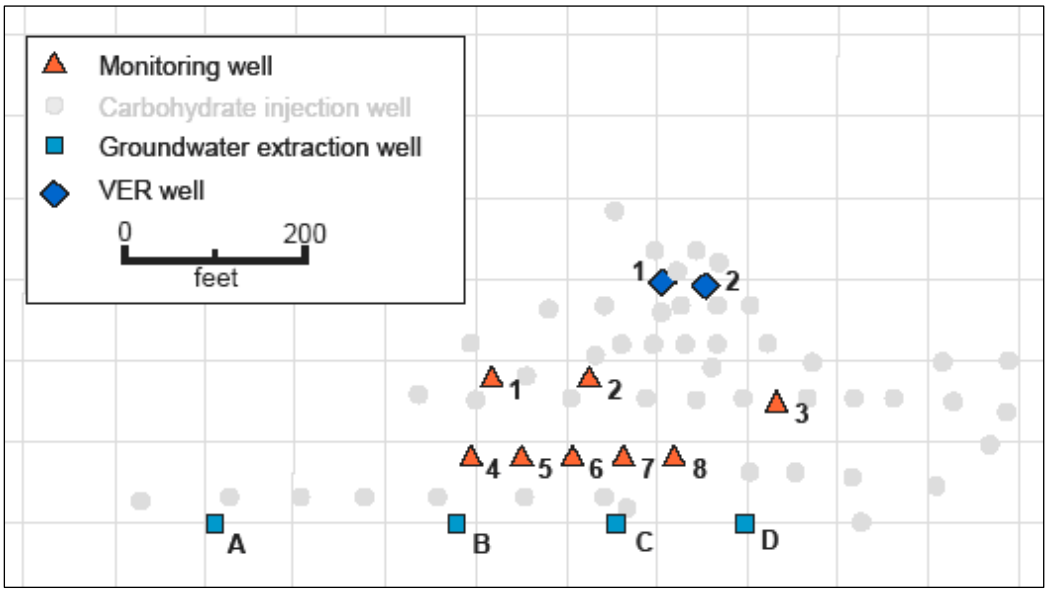


Figure 5-4. Location of groundwater extraction wells (A–D), monitoring wells (1–8), and VER wells (1–2, also used for monitoring), and carbohydrate injection wells (circles).

Injection well layout. We use two electron donor injection approaches to develop a reductive dechlorination zone in a DNAPL source area. In moderate- to fast-flowing groundwater systems, we generally establish lines of donor injection wells perpendicular to groundwater flow and allow the natural groundwater movement to carry the donor and its fermentation products through the treatment area. Alternatively, in slow-flowing groundwater systems, it may be more effective to develop an injection grid to achieve complete coverage of the targeted area. Although the site has a groundwater extraction system located immediately downgradient of the treatment zone, groundwater velocities are believed to be quite slow in the unconsolidated groundwater at the site. Therefore, the project team elected to install a grid-type injection well network. Figure 5-5 shows the locations of 47 injection wells that were constructed for this project (Wells 11, 46, and 47 were not used).

Injection process. A 10% molasses solution (TOC = 45,000 mg/L) was used as the carbohydrate source for injections. The target volume was 500 gallons for each well, repeated at 8-week intervals. Before each injection event, field crews collected basic water chemistry data from each injection well, including field parameters (pH, ORP) and samples for laboratory analysis of TOC. Fourteen of the injection wells were also sampled for full VOC chemistry at quarterly intervals, and nine other injection wells were sampled for full VOC chemistry at less frequent intervals. Intervals between injections were lengthened in wells that retained high TOC levels between injection events. The field crews also added sodium bicarbonate to neutralize some wells that showed pH drops[2] in a practice that was discontinued. The injection history for each well is recorded in Appendix 2 (see companion CD), the full raw dataset.

[2] This practice was discontinued, as it is unlikely to have the desired effect and we now believe it is not necessary to manage pH so closely at the point of injection. If pH excursions occur at points more than 30 days downgradient from the injection zone, action is required.

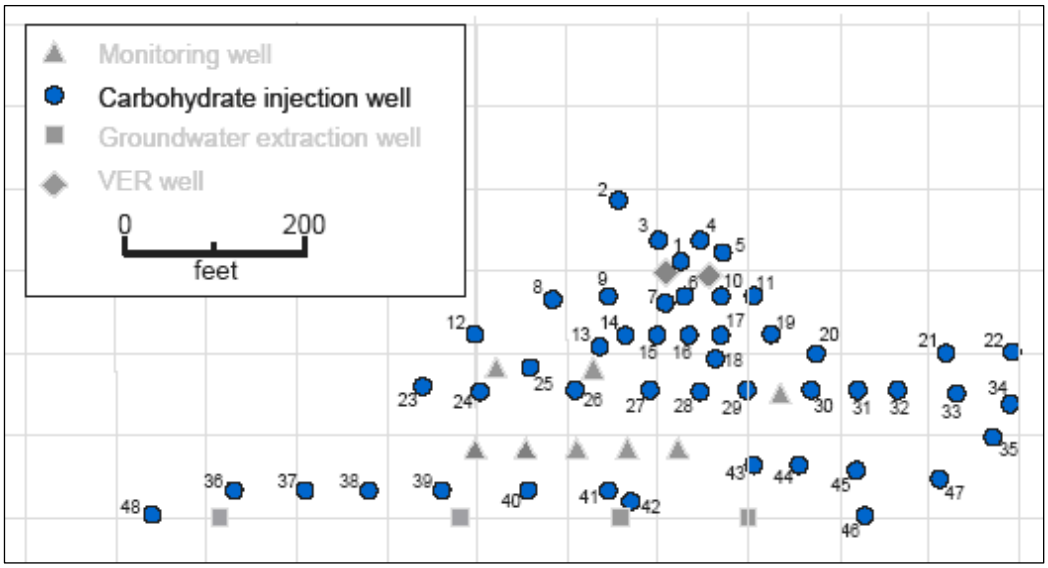


Figure 5-5. Location of carbohydrate injection wells, with monitoring (triangles and diamonds) and extraction (squares) wells shown in gray.

5.4 Effects on the Source Area

This project generated a very large dataset and, because the system is still operating, final analysis of the information has not been completed. Appendix 1 (see companion CD) provides detailed graphical summaries of each monitoring well and the four groundwater extraction wells. Appendix 2 (see companion CD) provides the raw data for all injections and groundwater monitoring results. We will focus our discussion on selected monitoring and injection wells and a summarization of extraction well yields.

We will address the most challenging of the overall project objectives first: Are the attainable source mass reductions sufficient to cause a commensurate decrease in the long-term due care costs for the site? There is ample evidence in the literature indicating complete cleanup of DNAPL source zones is not a sensible objective (e.g., National Research Council 2005). However, in some cases, we think it will be possible to reduce mass flux from the source zone to a level that can be addressed by natural attenuation processes, achieving acceptable contaminant levels at the site perimeter. Figures 5-6 and 5-7 show the impact of the source treatment demonstration on the extraction well system yield to date (detailed data for each extraction well during the study period is shown in Appendices 1 and 2 (see companion CD). A surge in total alkenes (largely dechlorination products) was observed in each extraction well following startup of the ERD process. Concentrations peaked one year into the treatment program and have now fallen to levels near or below pretreatment levels. These data suggest that a mass flux reduction has occurred; however, it is too early to determine whether the reduction will persist after the carbohydrate injections are finished or the reduction will be sufficient to allow natural attenuation.

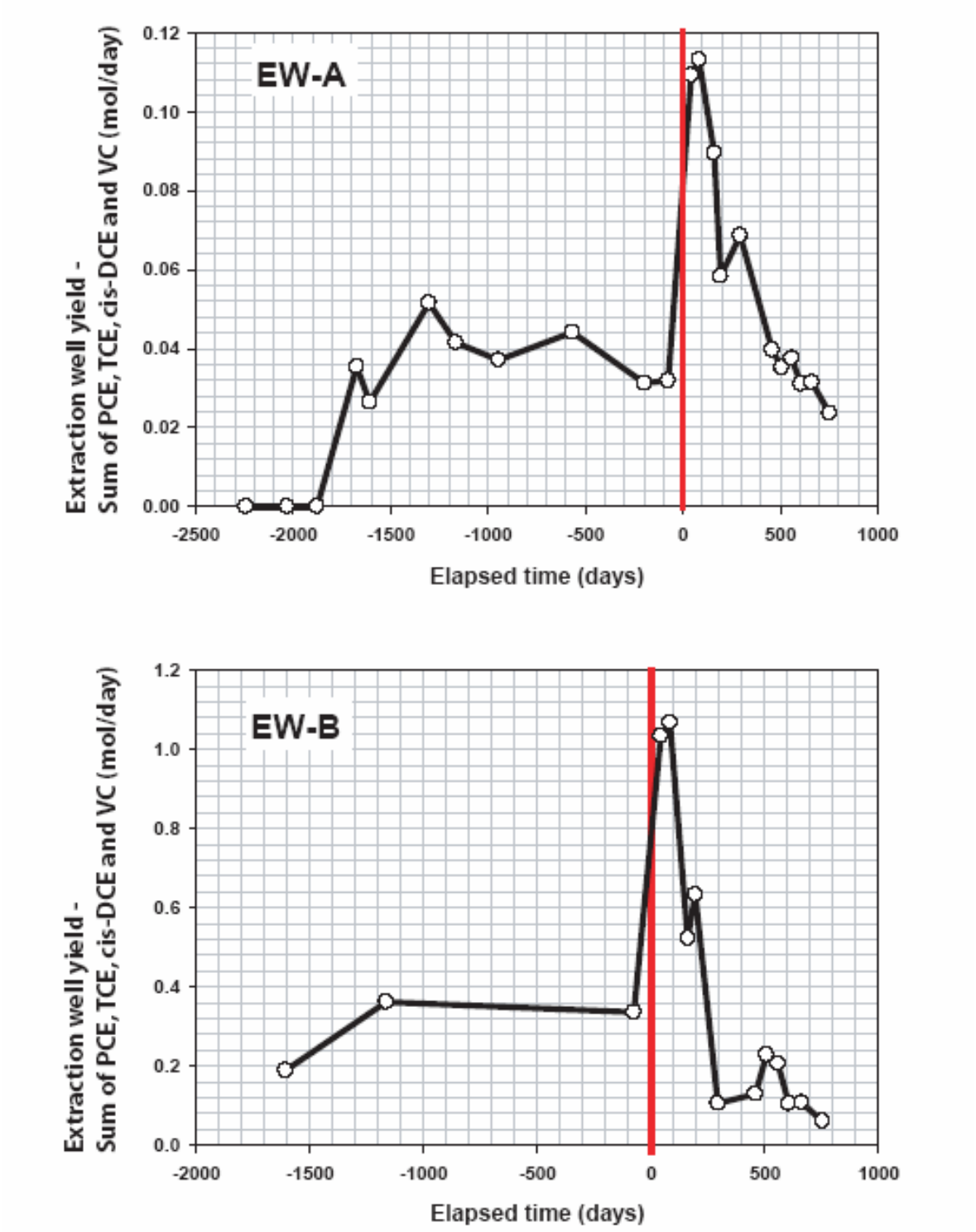


Figure 5-6. Impact of ERD source zone application on chlorinated solvent recovery in the groundwater containment system—extraction wells A and B.

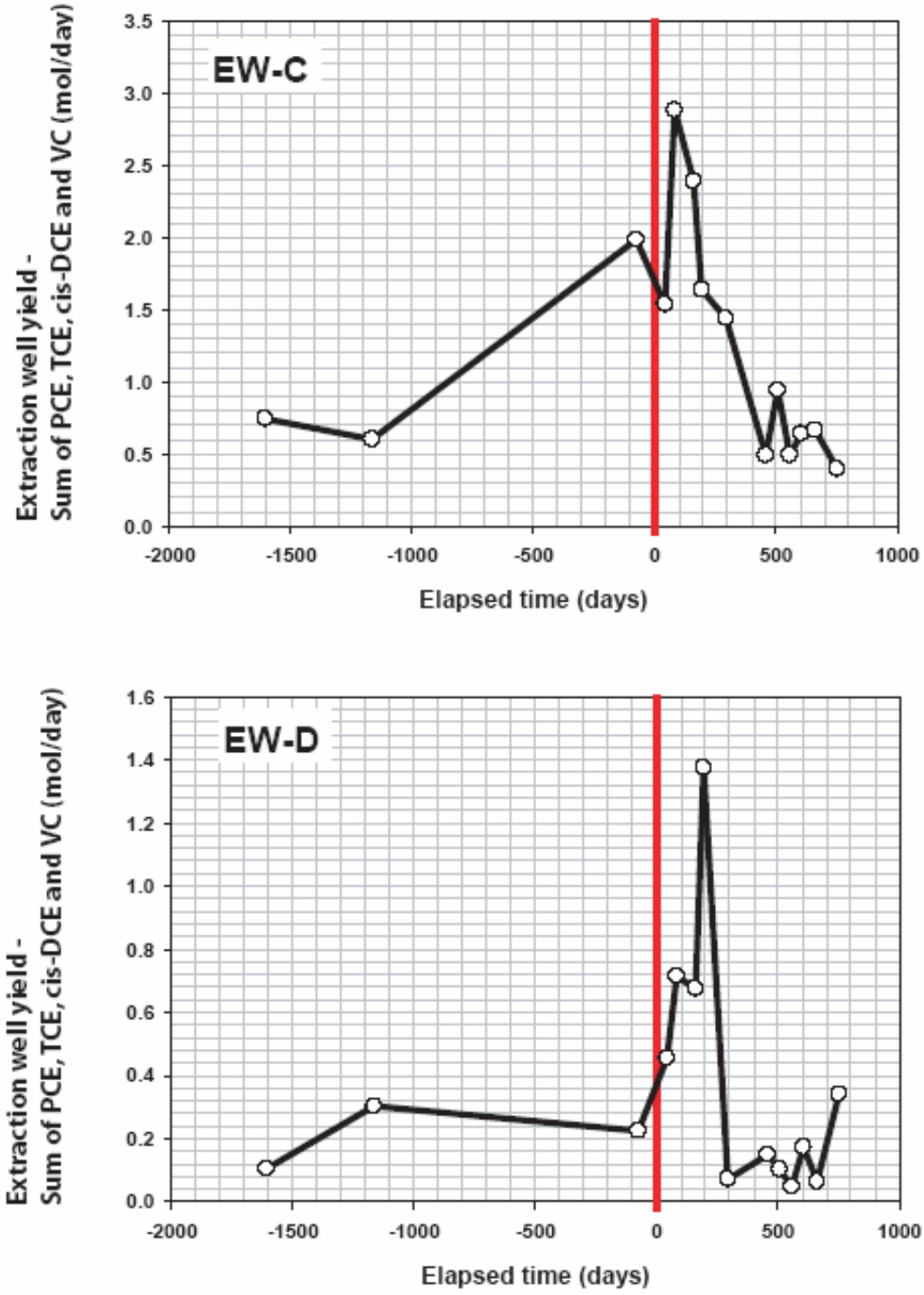


Figure 5-7. Impact of ERD source zone application on chlorinated solvent recovery in the groundwater containment system—extraction wells C and D.

Evidence that the other project objectives have been met is much stronger. Answering the first objective: Can complete reductive dechlorination be established at a site containing DNAPL PCE through carbohydrate-driven biostimulation? Evidence from across the site shows clearly that, yes, complete dechlorination through ethene and ethane can be achieved through biostimulation at a PCE DNAPL site. For example, MW-2 (Figure 5-8 and Appendix 1) began with a pretreatment 30 μM PCE. *Cis*-DCE and VC peaked at 100 and 90 μM, respectively, while *cis*-DCE and VC now total 70 μM and ethene plus ethane total 170 μM. Numerous other examples of complete dechlorination (ethene and ethane production at levels exceeding pretreatment PCE molarities are shown in Appendix 1). Despite these positive results, the dechlorination process is not complete in the study area, as the molarities of *cis*-DCE and VC remain high relative to the levels that might be required to achieve a natural attenuation closure for the site.

Answering the second objective: Does the reductive dechlorination process draw nonaqueous-phase mass out of the formation (either sorbed mass or nonaqueous-phase liquids)? We found extreme examples of the desorption-dissolution process at this site (combined with complete dechlorination). In MW-1, for example, the pretreatment PCE level was less than 0.5 μM, while ethane levels are now approaching 14 μM (Figure 5-9 and Appendix 1).

The monitoring wells VER-1 and VER-2 provide an assessment of treatment progress in the core of the spill zone. In each of these wells (Figures 5-10 and 5-11, respectively, and Appendix 1), very large increases in total alkenes have been observed, and the production of ethene indicates the dechlorination metabolic pathway is reaching its end point. However, each of these wells also indicates that there is a large amount of source mass remaining that was not available in aqueous phase until the carbohydrate injections were started.

Process results from the injection wells are much more favorable than in neighboring monitoring wells, as would be expected. Appendix 1 (see companion CD) provides graphical results for many of the injection wells that were sampled frequently, and Appendix 2 (see companion CD) provides all the raw chemistry and operational data for the entire group of injection wells.

5.5 Cost Information

The client has not elected to make cost information available.

5.6 Summary

This demonstration program provides encouragement that large amounts of nonaqueous solvent can be brought into the reductive dechlorination treatment process by dissolution and desorption. We feel that the capacity to attack nonaqueous mass is a prerequisite for any effective treatment of DNAPL source zones. For this site, the demonstration program has not yet convinced us that the ERD technology can economically reach a natural attenuation end point. Further, because the site geology is relatively unfavorable, it may be quite difficult to reach all the contaminant mass, regardless of the expenditure of time and effort.

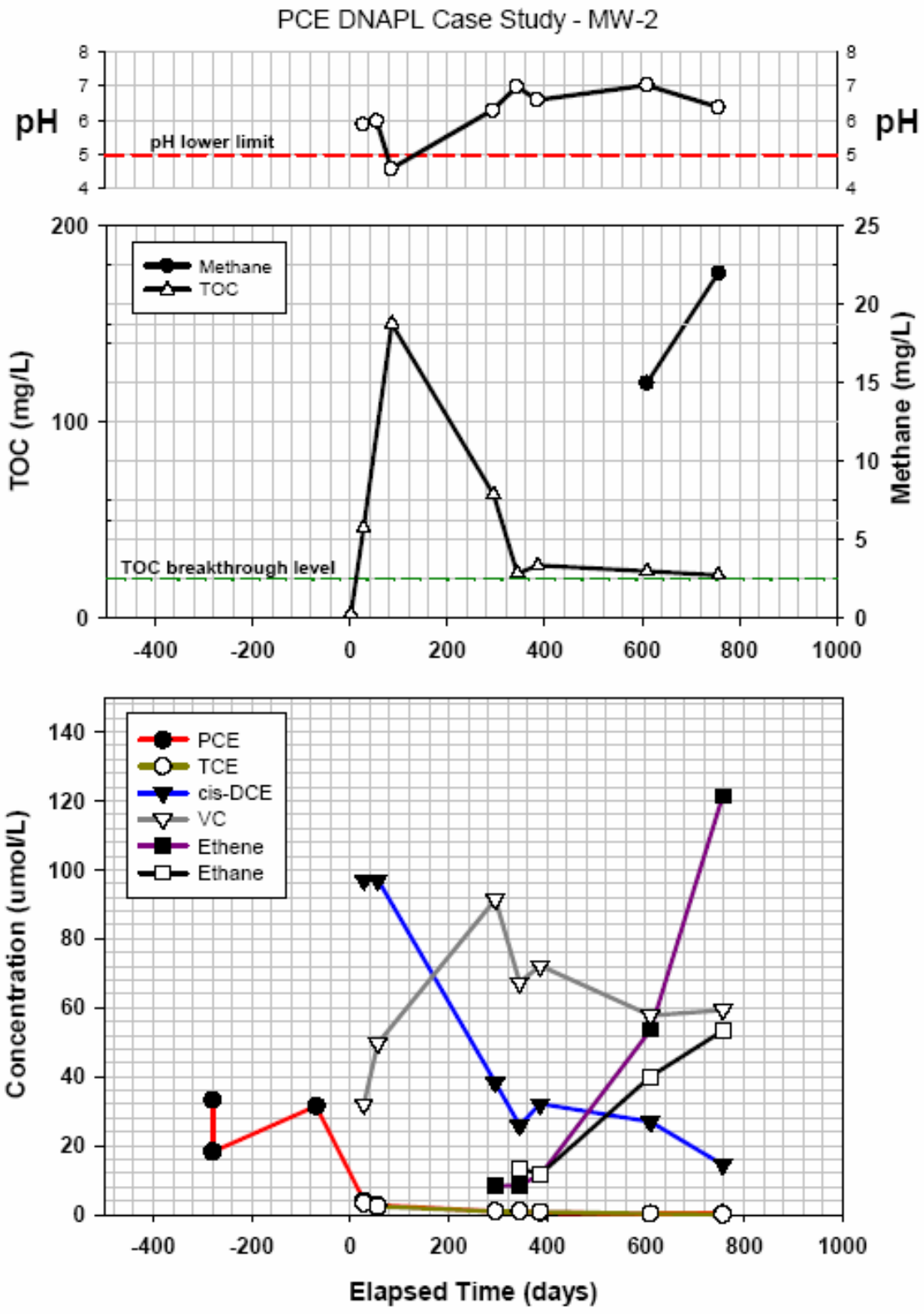


Figure 5-8. Enhanced reductive dechlorination results at MW-2.

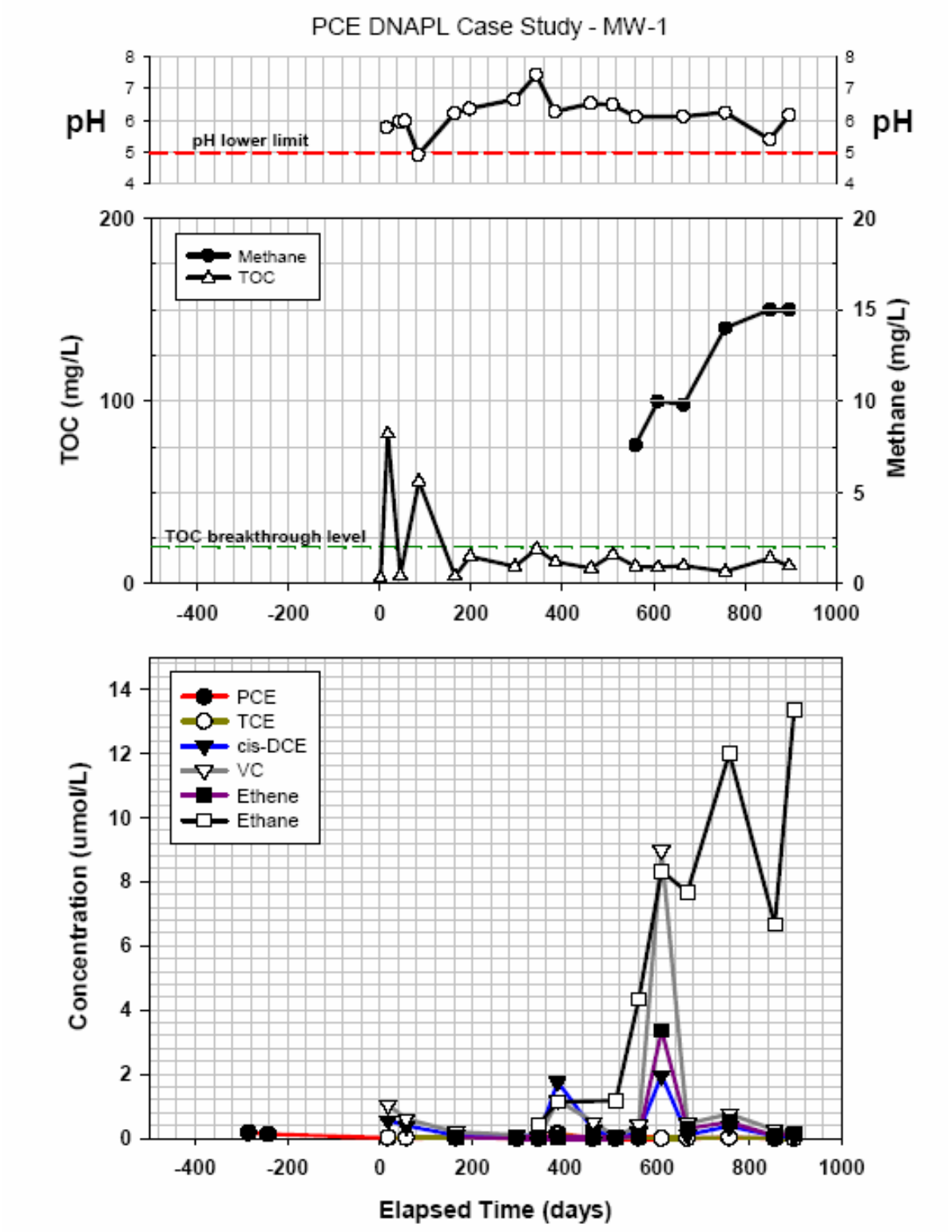


Figure 5-9. Enhanced reductive dechlorination results at MW-1.

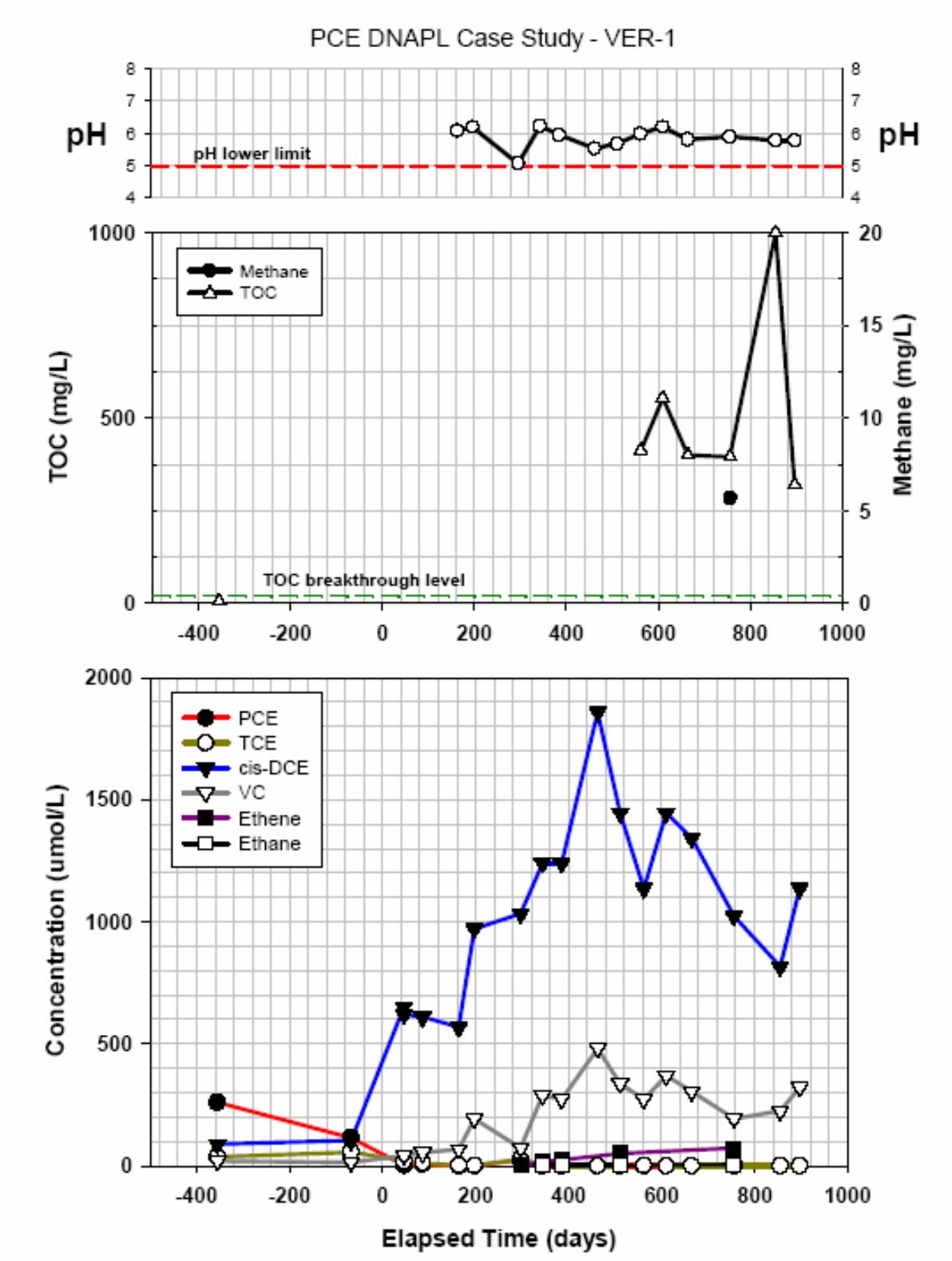


Figure 5-10. Enhanced reductive dechlorination results at monitoring well VER-1.

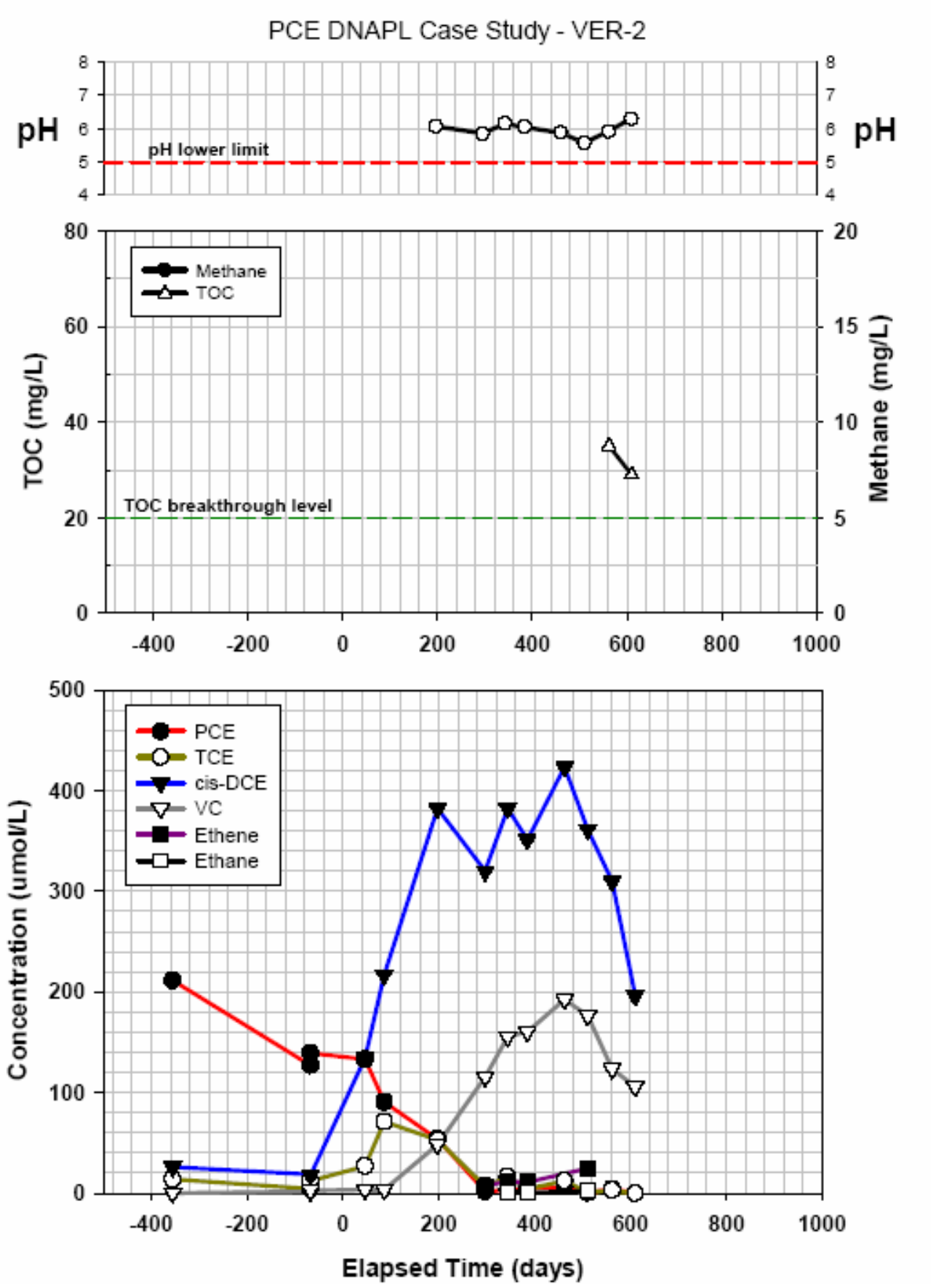


Figure 5-11. Enhanced reductive dechlorination results at monitoring well VER-2.

5.7 Additional Resources and References

Additional Resources (provided on companion CD)

- Appendix 1—Graphical results for all monitoring wells and for injection wells that were selected for chemical analysis
- Appendix 2—Raw data for all monitoring and injection wells, including injection volumes and composition

References

Brock, T. D., and M. T. Madigan. 1991. *Biology of Microorganisms*. Englewood Cliffs, N.J.: Prentice Hall.

National Research Council. 2005. *Contaminants in the Subsurface: Source Zone Assessment and Remediation*. Washington, D.C.: National Academies Press.

Payne, F. C., S. S. Suthersan, F. C. Lenzo, and J. S. Burdick. 2001. "Mobilization of Sorbed-Phase Chlorinated Alkenes in Enhanced Reductive Dechlorination," in *Anaerobic Degradation of Chlorinated Solvents, Proceedings of the International In Situ and On-Site Bioremediation Symposium* **6**(2): 53–60.

Schink, B. 1997. "Energetics of Syntrophic Cooperation in Methanogenic Degradation," *Microbiology and Molecular Biology Reviews* **61**: 262–80.

Suthersan, S. S., and F. C. Payne. 2005. *In-Situ Remediation Engineering*. Boca Raton, Fla.: CRC Press.

5.8 Reviewer Comments

5.8.1 Jeff Marqusee Comments

Project Scale and Purpose

The Arcadis study appears to be a typical PCE plume in a shallow, unconsolidated aquifer of low permeability and shallow hydraulic gradients. This is typical of many commercial sites and many of the smaller DOD sites. Information from this site should be applicable to many other sites in the country.

Site Conceptual Model

Insufficient information has been provided about the site. It would be helpful to put all the wells on a clear map with the results of pre- and post-treatment concentration contours. This information should be available. Information on the groundwater flows is discussed only very qualitatively. What are the natural gradients? What are the natural groundwater and contaminate velocities? What are the flow conditions under the induced flow from the extraction wells? What is the capture zone of the extraction wells? Without some of this information it is very difficult to understand what is going on at the site.

Remediation Goals

The demonstration has three well-defined and clearly stated goals. The first one is relatively easy to answer; the second two can be answered but are more difficult to assess.

Bioremediation Performance Monitoring

The sampling is interesting but limited to concentration measurements. Additional analysis would be of utility. Even presentation of a broader suite of groundwater parameters would be helpful.

Effect on the Source Area

First, I reject the assumption of this question. Increased dissolution is important but not the sole issue. As I will discuss below, they clearly have data that show complete dechlorination is taking place within the source zone. The information in support of the other goals is very tenuous at best or needs much greater analysis to support.

Cost Information

None provided.

Summary

This is an interesting demonstration, but the analysis to date and the structure of the treatment make it difficult (but not impossible) to draw conclusions. Below are some issues that need to be recognized or addressed (in no particular order).

- They clearly demonstrate that biostimulation alone is capable of supporting full dechlorination in the source area (Figures 5-10 and -11).
- Most of the injection wells for the treatment are clearly outside the source zone. Thus, this is both a source and plume treatment.
- The claim that the production of biosurfactants or co-solvents during anaerobic dechlorination play an important role in the increased desorption or dissolution is not substantiated by any data presented here. I would be interested in any published literature that supports that claim.
- A detailed analysis of both the monitoring and extraction well data in light of the site's flow patterns is needed to support any change in dissolution. The large amount of methane formation may be shifting the flow pattern.
- The observed large increase in chlorinated ethenes in the extraction well is short-lived (Figures 5-6 and -7), but the source zone seems to have a continuing robust dechlorination going on (Figures 5-10 and -11). What is the explanation for these observations?
- Why is so much ethane being generated?

5.8.2 Lenny Siegel Comments

Much of the information under review is beyond my technical expertise, so I'll focus on those areas where I believe I can be most helpful. In general, the results of the three case studies I reviewed—Test Area North, Portland Dry Cleaner, and the Arcadis PCE Site—are impressive. The prospect of accelerating the remediation of VOCs is particularly important to the

communities with which I work, not just because of the long-term savings and increased potential for reuse, but because the traditionally slow pace of remediation often means continuing exposures through the vapor intrusion pathway.

It always bothers me when the identity of a site under study remains confidential. Not only is there rarely a justification for concealing information about contamination, but it also eliminates any chance for independent confirmation of findings. Furthermore, I don't even know whether it's appropriate to ask about the impact of treatment on vapor migration.

I think this report does a good job of explaining the roles of desorption and dissolution.

The placement of multiple monitoring wells among the injection points appears well-suited to determine how well the molasses solution moved through the subsurface. Of the three sites that I am reviewing, this is the most thorough evaluation.

It would be helpful if some of the graphs showed VOC concentration in the unit (parts per billion or micrograms per liter) normally used for health standards and remediation goals.

The report states that *cis*-DCE and VC remain at concentrations too high to move directly to natural attenuation at this site, but there is no estimate whether the continuing injection of additives is ever likely to reach that point.

5.8.3 Mike Kavanaugh Comments

Project Scale and Purpose

This is a full-scale application over an expected source area of about 19,000 m^2. A grid pattern of electron donor injection wells was used. The goal is to reduce the duration of the pump-and-treat operation currently in operation as an hydraulic containment technology. Advantages of this site: over three years of operational data, DNAPL is apparently confined to a thin stratum (not convinced that is the case), low groundwater velocities, and location of DNAPL reasonably well defined based on past history of operations. Depth to groundwater <6 feet (1.5 m).

Site Conceptual Model

Minimal information was provided on pathways or potential receptors at the site. Thus, risk issues cannot be addressed. Source area conceptual model seems limited; no discussion of vertical migration pathways; and potential for PCE to penetrate weathered bedrock. This seems like a large oversight, although mass flux from this unit may be quite low. No discussion of estimated mass in source area or preremediation mass flux from source. This could be presented based on mass removed by pump and treat.

Remediation Goals

Stated goal is "reduction of mass flux" for several source areas, but there is no discussion of how this metric will be measured or estimated. Authors provide lots of data from individual monitoring wells and as well as data from injection wells. Significant mass removal seems to be occurring especially in the injection wells, but there is no attempt that I can see to estimate mass flux or estimate the actual mass removed. I haven't looked too closely, but for the injection

wells, showing significant removals in the wells says little about what is going on in the formation. This is especially important in this case study because of the apparent low permeability of the source zone itself. It is unclear how much dilution is occurring due to injections, for example.

Bioremediation Performance Monitoring

An extensive data set was provided which with some effort may provide useful information on performance assessment. However, no metrics are discussed beyond statements about the extent of dechlorination in most of the wells. The authors state that "Despite these positive results…levels remain high relative to levels that might be required to achieve MNA closure," but what these levels are needs to be stated. There is a failure to connect mass flux to "levels" required for natural attenuation. The data do support the hypothesis at least qualitatively that the ERD process increases the release of DNAPL from the formation. I can't judge whether their hypothesis of increased solubility due to a suggested surfactant effect is valid, but the data do show a significant amount of mass being destroyed. Unfortunately, no attempts are reported at any mass balances, which, although difficult to do and fraught with uncertainties, are essential to form a basis for assessing overall performance in comparison to cost.

Effect on the Source Area

No reports on reduction in mass flux, but plenty of data to show significant dechlorination.

Cost Information

None provided.

Summary

This has the potential to be a useful case study for wider application of this technology, but because few quantitative assessments have been performed, no flux estimates are provided, and no mass balances are attempted, it is not possible to provide an assessment of benefits versus costs for this technology. The authors seem to state that all the effort may not be justified because it is "quite difficult to reach all the contaminant mass." One is tempted to say, "So what's new?" I would expect to see a more quantitative comparison to justify the expenditure of the application of the technology. Clearly, significant mass is removed, but this does not appear to be sufficient to reduce the duration of the pump-and-treat system. Thus, in summary, the case study is unable to provide a basis for determining whether and how this technology should be applied to source area DNAPL remediation where a containment strategy is already in place.

5.8.4 Tom Sale Comments

Applicability across the United States

- This technology should be applicable in a wide range of physical settings.
- It may not be applicable for sites with large DNAPL bodies (e.g., large basal pools).
- Sites where physical displacement of DNAPL through injection, mobilization of metals, or elevated TOC in groundwater are concerns should be avoided.

Sufficiency of Site Characterization

Enough information is presented to review the data.

Goals

The goal seems vague. No specific time frame or end point concentrations are described.

Utility and Value-Added of Monitoring Approaches

- Why was chloride not measured? Increases in chloride might provide a basis for estimating the mass of chlorinated solvent that was degraded.
- Relying solely on aqueous samples provides limited insight as to the effect of the treatment on sorbed contaminants and or DNAPL. Were any soil cores collected?
- Were there any adverse effects of carbon addition (mobilization of metal, high TOC in groundwater)?

Magnitude of Enhanced Dissolution

- The hypothesis of generating cosolvents and/or biosurfactants is interesting.
- The best evidence for this seems to be in Figures 5-6 and -7.
- If enhanced dissolution is occurring the net effect is about one order of magnitude, and the duration of the effect is a few hundred days.
- Little difference between initial and final total CVOC in groundwater may indicate that the source has not been reduced significantly.

Applicability of Costs to Other Sites

I strongly urge the authors to address costs. Both cost and time to complete play a major role in resolving the utility of a technology.

Overall Assessment of Project

- The results clearly show that addition of a carbon source can facilitate reductive dechlorination of chlorinated ethenes.
- Furthermore, the data indicate that complete dechlorination can be achieved.
- Unfortunately, it is difficult to resolve whether substantive progress toward risk reduction or reduced site care cost has been achieved.

6. SOURCE AREA REMEDIATION AT A PORTLAND, OREGON DRY CLEANER SITE CASE STUDY SUMMARY

The presentation associated with this case study, given by Anna Willett, Steve Koenigsberg, Kevin Parrett, and Rick Gillespie at the forum on March 29, 2006, is included on the CD accompanying this document. The reviewers for this case study were Jeff Marqusee, Lenny Siegel, Tom Early, and Nancy Kinner.

6.1 Project Scale and Purpose

The Oregon Department of Environmental Quality is responsible for addressing groundwater impacts at an active dry cleaner facility located in a strip mall. ODEQ determined that maintaining current activities at the site required that an unobtrusive, semipassive remediation technology be used. Accelerated bioremediation using Hydrogen Release Compound within the plume and source area was selected as the remedial approach as it requires modest site access and minimal operation activity. A pilot test was conducted to determine whether this option is an appropriate remedy for the reduction of high concentrations of PCE and its daughter products in site groundwater.

HRC is an ester of glycerol (a three-carbon polyalcohol) and polylactate (a tetramer of lactic acid). Once injected into an aquifer, it slowly releases lactic acid. This lactic acid undergoes fermentation by indigenous microbes, generating dissolved hydrogen and a series of carboxylic acids (pyruvic, acetic, butyric, and propionic acids). As a result of the introduction of HRC, electron acceptors, like oxygen and nitrate, are consumed; the ORP is reduced; and dissolved hydrogen is generated. These processes create conditions favorable to reductive dechlorination of chlorinated ethenes. Because of the slow lactate release kinetics of HRC, electron donors and reduced conditions can be provided over an extended period of time (typically 12–18 months). In addition to the standard HRC, an extended-release, highly concentrated version of HRC (Hydrogen Release Compound–Extended Release, HRC-X®) has been used at the Oregon site. HRC-X is designed to treat source areas with residual DNAPL and has an anticipated lifetime of three to five years.

HRC was selected for a pilot test to determine whether the same basic approach could be used to treat both the source area and the plume. The limited accessibility of portions of the site, the documented success of HRC in stimulating the complete conversion of PCE to nonchlorinated end products, and minimal operation and maintenance requirements (sampling only) indicated that HRC was the most favorable technology for the site. Given the active use of this site, multiple injections and repeated site visits were considered too intrusive.

6.2 Site Conceptual Model

The site is a dry cleaning facility located in a strip mall in Portland, Oregon. The surrounding area is composed mainly of residential properties, with some commercial development. Several utilities (gas, electric, water, and sanitary sewer) run along the west (back) side of the strip mall. An investigation in 1999 revealed that dry cleaning contact water saturated with PCE (150,000 µg/L) and pure-phase PCE were probably discharged to a floor drain, which discharges to a utility trench. Leaks from the floor drain and the utility trench appear to have resulted in impacted soils and groundwater.

The soils consist of silty clay and silty sand. The depth to groundwater varies 4–7 feet bgs within the plume and 2–5 feet bgs in the source area. The seepage velocity is estimated at 0.3 foot/day (110 feet/year). Groundwater generally flows to the west but flows more to the southwest in the vicinity of the DNAPL pilot test area (Figure 6-1).

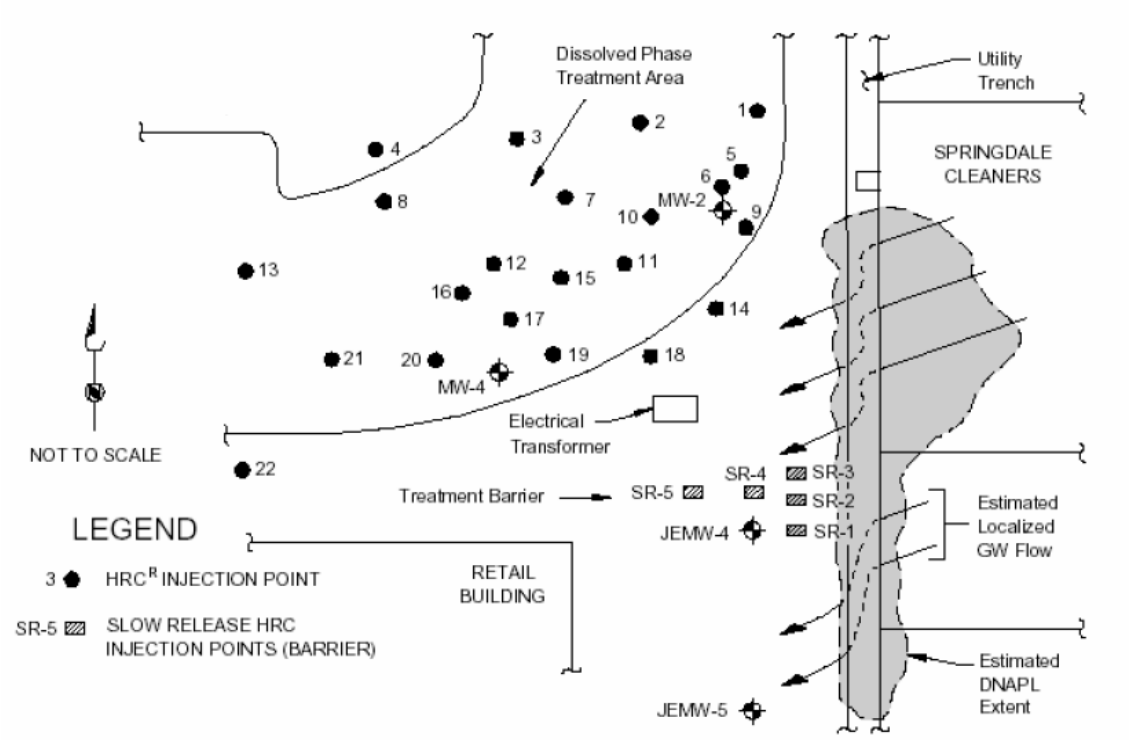


Figure 6-1. Springdale Cleaners site map.

The remediation area, shown in Figure 6-1, consists of a DNAPL-impacted area and an associated plume located down- and crossgradient from the DNAPL area. Within the DNAPL area wells (JEMW-4 and JEMW-5), VOC concentrations were as high as 120,000 µg/L of PCE, 8,300 µg/L of trichloroethene (TCE), and 740 µg/L of *cis*-DCE. The dissolved-phase plume concentrations (e.g., wells MW-2 and MW-4) were as high as 7,000 µg/L PCE, 480 µg/L TCE, and 130 µg/L *cis*-DCE. VC was not detected, indicating a potential "stall" in reductive dechlorination at *cis*-DCE.

6.3 Remediation Goals

The site consists of a dissolved-phase plume and a source area where PCE concentrations in groundwater indicate the presence of DNAPL. Successful remediation requires that both areas be addressed. ODEQ is both the regulatory agency and the client for this site.

A pilot-test approach was selected to determine the efficacy of HRC and HRC-X prior to full-scale application. The performance objective of the pilot test was to push HRC and HRC-X beyond their commonly accepted end points to determine length of performance, effectiveness over varying conditions, and cost of treatment. Specifically, the objectives of the pilot test were to determine the following:

- the effectiveness of HRC injection, as measured by the degree to which PCE degradation could be accelerated
- whether complete dechlorination (through ethene) of high concentrations of PCE is possible
- how long the effects of HRC application persist

- whether VOC concentrations would remain low after treatment

If the pilot test is considered successful, full-scale remediation is expected to be instituted. Remediation goals in Oregon are 10^{-6} risk level for carcinogens and a hazard index of 1. For PCE the practical remediation goal at the site is 5 µg/L.

6.4 Bioremediation System Construction and Operation

Within the dissolved-phase plume, 1900 pounds of HRC was injected via 22 injection points by means of direct-push technology. Injection occurred during the first few days of December 1999. This method consists of pushing a probe to the desired maximum depth of treatment and injecting the product under pressure as the probe is withdrawn. The treatment grid covered approximately 1200 square feet, with an aquifer injection vertical thickness of 22 feet. The application rate was 4 pounds of HRC per vertical foot. Within the DNAPL source area, 700 pounds of HRC-X was added via five injection points. The loading rate was 10 pounds per vertical foot. The location was next to the sewer line, so points were carefully located to avoid puncturing the line.

6.5 Bioremediation Performance Monitoring

6.5.1 VOC Data

As shown in Table 6-1, following addition of HRC to the dissolved-phase plume, the observed PCE concentration for HRC injection grid well MW-4 decreased from 340 µg/L to 22 µg/L after about one month. After 287 days, the PCE concentration in MW-4 was less than 5 µg/L and remained low (11 µg/L) after 1247 days. Following HRC injection, TCE and *cis*-DCE levels first increased and subsequently decreased over a period of 12 months. The concentration of *cis*-DCE increased from 230 µg/L to 904 µg/L before reaching 45 µg/L on day 372 and then ranging between 16 µg/L and 654 µg/L through day 1247. The *trans*-DCE concentration increased from 160 µg/L prebaseline to maximum concentrations of 543 µg/L and 420 µg/L after 8 and 372 days, respectively, before decreasing to 20 µg/L on day 1247. VC increased after nine months and peaked at 159 µg/L on day 553, demonstrating reductive dechlorination of *cis*-DCE and/or *trans*-DCE as well as the presence of a degradation pathway for VC. Observed ethene production was limited for MW-4.

As shown in Table 6-1 and Figure 6-2, the concentration of PCE reported for MW-2, located within the plume area grid, decreased from the baseline level of 7000 µg/L to 4210 µg/L after 37 days, to less than 50 µg/L after 372 days, and was 101 µg/L after 1247 days. TCE levels increased from the baseline level of 480 µg/L to 3550 µg/L before decreasing to less than 50 µg/L on day 372 and were 488 µg/L at day 1247. The concentration of *cis*-DCE increased from the baseline level of 130 µg/L to 7900 µg/L before decreasing to 672 µg/L on day 553 and 486 µg/L on day 1247. VC was initially at nondetect levels, increased to 1230 µg/L on day 287, declined to 145 µg/L on day 553, and was 110 µg/L on day 1247. Ethene was produced in MW-2 and ranged from 180 µg/L on day 287 to 43 µg/L on day 1247. The test was conducted longer than the typically longevity of HRC (12–18 months); thus, rebound of some of the daughter products (but not the parent compound) is not surprising and suggests that a second addition is justified.

Table 6-1. VOC concentrations

Well		Units	5/28/99 -186	12/8/99 day 8	1/6/00 day 37	2/8/00 day 70	3/7/00 day 98	6/15/00 day 198	9/12/00 day 287	12/6/00 day 372	6/5/01 day 553	3/6/02 day 827	8/29/02 day 1003	4/30/03 day 1247
MW-2 (dissolved area grid)	PCE	ug/L	7,000	818	4,210	4,180	3,360	3,870	635	<50	92	274	<10	101
	TCE	ug/L	480	1,190	1,460	1,480	825	3,550	1,580	<50	159	1,790	109	488
	cis-DCE	ug/L	130	542	677	1,010	2,350	2,050	7,900	1,370	672	1,210	1150	486
	trans-DCE	ug/L	93	381	141	86	100	145	323	300	130	135	112	140
	VC	ug/L	na	< 10	na	< 20	< 20	180	1,230	433	145	197	152	110
	Ethene	ug/L	na	< 10	< 20	< 20	< 20	67	180	na	101	71	112	43
	Acetic Acid	mg/L	na	129	87	100	72	223	198	270	266	3.8	113	24.3
	Butyric Acid	mg/L	na	< 1	< 1	15	10	138	149	266	297	< 1	20	37.9
	Lactic Acid	mg/L	na	623	84	42	4	388	299	334	64.6	< 1	< 1	< 1
	Propionic Acid	mg/L	na	< 1	207	195	138	320	292	386	277	< 1	20.1	23.1
	Pyruvic Acid	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	1.2	< 0.1	4.2	0.9	< 0.1	< 0.1	< 0.1
	Sulfate	mg/L	43	27	93	98	70	23	21	1	2.5	32.9	8.6	11.9
	Sulfide	mg/L	< 0.2	< 0.1	0.35	0.25	0.1	0.96	0.78	0.37	1.4	0.46	< 0.5	< 0.1
	Iron, diss.	mg/L	na	23	31	41.5	57	138	120	197	135	34.4	17.3	61.1
	Chloride	mg/L	8.9	13	14	< 0.5	12	13	17	28	na	na	na	na
	Mn, diss.	mg/L	na	na	4.22	4.64	11.6	11	10.4	18.6	na	na	na	na
	Redox	mV	na	-84.1	na	120	-6	na	na	na	na	na	na	na
MW-4 (dissolved area grid edge)	PCE	ug/L	340	648	22	26	26.6	4.5	< 5	< 5	17.8	65	1.0	10.6
	TCE	ug/L	180	926	621	534	380	17.5	12	< 5	74.4	306	2.2	122.0
	cis-DCE	ug/L	230	658	904	504	386	489	351	45.2	497	654	16.2	539.0
	trans-DCE	ug/L	160	543	468	232	140	174	302	420	144	41.4	6.2	19.6
	VC	ug/L	na	na	< 5	< 5	< 5	3	62	10.6	159	91.6	5.5	38.4
	Ethene	ug/L	na	< 10	< 20	< 20	< 20	< 10	40	na	< 8	19	11	< 10
	Acetic Acid	mg/L	na	< 1	23	17	22	106	13	24	<1	<1	<1	<1
	Butyric Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	<1	<1
	Lactic Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	<1	<1
	Propionic Acid	mg/L	na	< 1	17	10	11	208	2	12	<1	<1	<1	<1
	Pyruvic Acid	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1	<0.1	0.2	<0.1	<0.1
	Sulfate	mg/L	na	5	65	98	82	11	2	< 1	50.5	90.4	2.2	53.4
	Sulfide	mg/L	na	< 0.1	0.3	0.29	0.25	0.15	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Iron, diss	mg/L	na	11.2	20.3	8.41	11	42.5	32.9	43.4	32.7	4.61	na	19.2
	Chloride	mg/L	na	10	11	< 0.5	11	< 10	10	11	na	na	na	na
	Mn, diss.	mg/L	na	na	2.06	1.18	1.42	6.48	5.87	7.15	na	na	na	na
	Redox	mV	na	-108.4	na	-35	-7	na	na	na	na	na	na	na
JEMW-4 (source area dg)	PCE	ug/L	98,000	63,900	39,800	30,600	47,400	4,420	< 200	79.9	<250	<200	<200	<200
	TCE	ug/L	8,300	6,430	5,450	4,200	9,730	35,900	680	623	298	< 200	<200	<200
	cis-DCE	ug/L	740	871	608	580	1,330	37,900	73,700	91,400	43,900	38,400	54,700	53,500
	trans-DCE	ug/L	170	137	< 1	< 1	< 200	628	588	1,380	808	816	532	558
	VC	ug/L	na	na	< 1	< 1	< 200	< 100	< 200	366	9,510	9,690	4,060	4,900
	Ethene	ug/L	na	< 20	< 100	< 20	< 20	< 10	< 10	na	318	319	14	1,130
	Acetic Acid	mg/L	na	< 1	6	12	32	70	437	247	305	828	883	868
	Butyric Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	161	170	151	1,280	2060	2680
	Lactic Acid	mg/L	na	< 1	< 1	25	18	< 1	< 1	<1	<1	<5	<1	<1
	Propionic Acid	mg/L	na	< 1	< 1	< 1	14	199	828	560	352	549	597	682
	Pyruvic Acid	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.5	0.2	<0.5	< 0.1	< 0.1
	Sulfate	mg/L	na	6	2	3	< 1	1	< 1	1	<5	<1	<5	1.3
	Sulfide	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1	<0.1	<0.1	<0.1	< 0.5
	Iron, diss	mg/L	na	1.25	0.714	1.94	8.01	8.73	37.1	73	149	192	na	410
	Chloride	mg/L	na	24	20	23	31	80	120	91	na	na	na	na
	Mn, diss	mg/L	na	0.766	0.913	0.94	1.71	3.81	10.4	17.9	na	na	na	na
	Redox	mV	na	43.6	na	7	-43	na	na	na	na	na	na	na
JEMW-5 (source area cg 50 feet)	PCE	ug/L	120,000	60,600	39,000	63,700	51,400	40,600	87,300	108,000	132,000	121,000	66,300	74,000
	TCE	ug/L	4,600	5,630	3,630	5,590	3,860	8,010	7,660	9,850	4,020	3,130	5,340	4,500
	cis-DCE	ug/L	250	355	< 400	406	248	526	775	1,000	<500	<1000	<500	<500
	trans-DCE	ug/L	< 1	< 100	< 400	< 200	< 200	< 100	< 500	< 500	<500	<1000	<500	<500
	VC	ug/L	na	< 100	< 400	< 200	< 200	< 100	< 500	< 500	<500	<1000	<500	<500
	Ethene	ug/L	na	< 20	< 400	< 30	< 10	< 20	< 10	na	< 15	< 13	12	< 10
	Acetic Acid	mg/L	na	10	< 1	< 1	< 1	< 1	< 1	4	<1	<1	< 1	<1
	Butyric Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	< 2	<1
	Lactic Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	< 1	96.9
	Propionic Acid	mg/L	na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	<1	<1	500	<1
	Pyruvic Acid	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	46.7	< 0.1
	Sulfate	mg/L	na	9	6	6	6	5	5	9	11.4	10	7.9	6.5
	Sulfide	mg/L	na	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	<0.1	<0.1	< 0.1	< 0.1
	Iron, diss	mg/L	na	2.11	2.64	4.5	57	2.09	0.696	0.484	2.15	3.19	0.774	6.36
	Chloride	mg/L	na	24	23	26	25	23	25	22	na	na	na	na
	Mn, diss	mg/L	na	0.684	0.661	0.749	11.6	0.69	0.618	0.565	na	na	na	na
	Redox	mV	na	-22.6	na	-1	-58	na	na	na	na	na	na	na

na = not measured

As often is the case, *cis*-DCE reached concentrations greater than those of the parent compound, reflecting dissolution of the parent compound from the sorbed phase. If only dissolved-phase PCE had been converted to *cis*-DCE, the later would be present at approximately half the concentration of the former due to differences in molecular weight. The data from wells MW-4 and MW-2 show that degradation of the more toxic parent products, including sorbed-phase contaminants, is proceeding to completion to the nonchlorinated, nonregulated product, ethene.

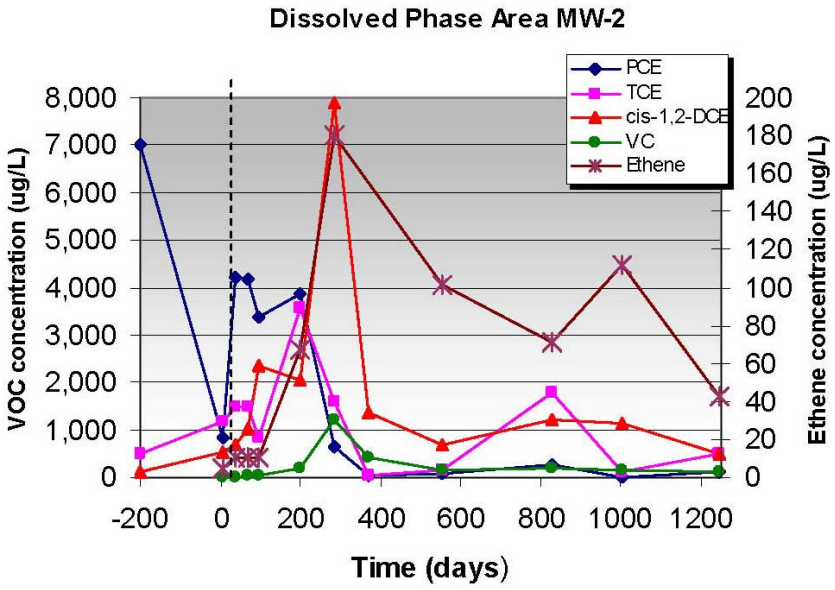


Figure 6-2. VOC concentration changes in the dissolved plume area.

As shown in Table 6-1 and Figure 6-3, a single addition of extended-release HRC-X was effective at achieving substantial treatment of the source (DNAPL) area. PCE concentrations in monitoring well JEMW-4, located immediately downgradient of the injection area, decreased within a short time after injection of HRC-X. A 95% decrease in PCE concentration was observed within 198 days of injection, with a 99.9% reduction achieved after one year. The TCE concentration increased from 8,300 µg/L to 35,900 µg/L at day 198 and then decreased to 298 µg/L at day 553 and to less than 200 µg/L at day 827 (a decrease of greater than 99.4% from the maximum concentration). PCE and TCE levels remained less than 200 µg/L after 1,247 days, indicating that rebound has not occurred.

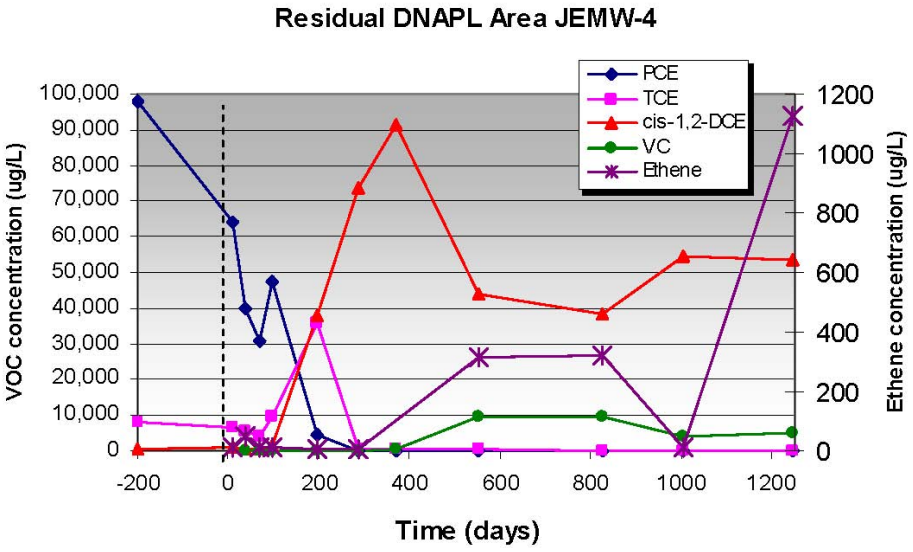


Figure 6-3. VOC concentration changes in the source area.

Here, *cis*-DCE increased from 740 µg/L to 91,400 µg/L on day 372 and then decreased to 38,400 µg/L on day 827. *Cis*-DCE then remained relatively constant throughout the remainder of the 1247-day test period. VC and ethene were not present above their detection limits prior to HRC addition but were observed at 9150 µg/L and 318 µg/L, respectively, on day 553 and were reported as 4900 µg/L and 1130 µg/L, respectively, on day 1247. There were minimal changes in VOCs following day 553, with parent compound concentrations remaining relatively low. The expected lifetime of HRC-X is three to five years. Continued reductive dechlorination may occur after the most recent monitoring event at 1247 days (3.4 years) after HRC-X injection, as suggested by the geochemical and metabolic acid data discussed below. The data clearly show that rebound of parent products has not occurred; it thus appears that sufficient electron donor was supplied to address the dissolved and sorbed phases of the parent compound, including that which may have been transported into the treatment area.

Well JEMW-5 is located within the source area and 50 feet crossgradient from the HRC-X treatment area (see Figure 6-1). Based on starting contaminant concentrations (Table 6-1) and the groundwater flow direction, JEMW-5 was similarly impacted as JEMW-4 but was not contacted with HRC-X or its breakdown products, as indicated from the geochemical and metabolic acid data discussed in the following sections. Thus, it serves as a contaminated reference/control for the contaminant reductions in well JEMW-4. Table 6-1 shows that, in contrast to nearly 100% reductions in parent products in JEMW-4, there was no overall change in PCE, TCE, or *cis*-DCE concentrations in well JEMW-5 during the pilot test period. No VC or ethene production was observed in JEMW-5.

6.5.2 Metabolic Acids

Upon hydration and contact with aquifer microorganisms, HRC and HRC-X release lactic acid, which is fermented to acetic, butyric, propionic, and pyruvic acids, as well as dissolved hydrogen. These organic acids and dissolved hydrogen serve as electron donors for reductive dechlorination. The total organic acid concentration can be used as a nonconservative tracer to indicate the influence of HRC and HRC-X on the aquifer geochemistry. Most often, lactic and acetic acids are initially observed in high concentrations, with butyric and propionic acids increasing over time. Butyric and propionic acids can be fermented to dissolved hydrogen and serve as "hydrogen storage" compounds.

Analysis for organic acid concentrations (Table 6-1) showed that elevated levels of electron donors were present at 553 days (1.5 years) post-injection in the dissolved plume area (MW-2) and 1247 days (3.4 years) post-injection in the source area (JEMW-4). Except for a few detections at the end of the monitoring period, no organic acids were measured in source area crossgradient well JEMW-5.

In the dissolved plume areas and specifically in well MW-2, lactic (632 mg/L) and acetic acids (129 mg/L) were detected by day 8 post-injection. Later, the total organic acid concentration rose to 1070 mg/L on day 198 and was maintained at similar concentrations through day 553, before decreasing to 85 mg/L on day 1247. Experience shows that reductive dechlorination is strongly favored when the total organic acids have concentrations greater than 80–100 mg/L; thus, HRC stimulated favorable conditions for reductive dechlorination in MW-2 for at least 18 months. Trends in organic acid concentrations in MW-2 are as follows:

- Lactic acid was observed at 623 mg/L on day 8, varied considerably, and declined from 65 mg/L on day 553 to less than 1 mg/L on day 827.
- Pyruvic acid was observed during the middle of the test at 1–4 mg/L.
- Acetic acid was observed at 129 mg/L on day 8 and at 266 mg/L on day 553, before decreasing to 24 mg/L on day 1247.
- Butyric acid was first observed at 15 mg/L on day 70, reached a maximum of 297 mg/L on day 553, and then declined to 38 mg/L on day 1247.
- Propionic acid was first observed at 207 mg/L on day 37, reached 386 mg/L on day 372, and declined to 23 mg/L on day 1247.

The total organic acid concentrations in MW-4 were much lower than those in MW-2, and they peaked in well MW-4 at 314 mg/L on day 198. This trend may reflect MW-4's location, which is on the edge and slightly downgradient of the HRC injection grid, while MW-2 is located directly in the injection grid. In MW-4, organic acids may be consumed in reductive processes at a similar rate as they are produced from HRC and transported to the well.

In JEMW-4, located in the source area, 25 mg/L of lactic and 12 mg/L of acetic acid were detected in the first 70 days post-injection. Total organic acid concentrations then increased to 269 mg/L (70 mg/L of acetic acid and 199 mg/L of propionic acid) on day 198 before rising steadily to 1426 mg/L on day 287 and 4230 mg/L on day 1247. These results are indicative of HRC-X's extended-release profile and highly concentrated nature. HRC-X was able to maintain total organic acid concentrations of 64–4230 mg/L for 1247 days (3.4 years) and may continue to maintain high concentrations past day 1247, when the most recent monitoring event occurred.

6.5.3 Geochemistry

Geochemical parameters, including dissolved iron and manganese, sulfate, and sulfide, demonstrated the creation of reducing conditions in wells impacted by HRC or HRC-X (Table 6-1). Iron(III) is used as an electron acceptor under anaerobic conditions and increases in dissolved iron [iron(II)] indicate the occurrence of biodegradation of the electron donors and the establishment of reducing conditions. Dissolved iron typically increases as electron donors are consumed and may decrease when electron donor substrates become scarce. Dissolved iron in well MW-2 increased from 23 mg/L on day 8 to 197 mg/L on day 198 and then decreased somewhat to 61 mg/L on day 1247, reflecting the cyclical pattern of HRC-stimulated organic acid production and consumption by biodegradation. Dissolved iron followed a similar pattern in well MW-4 (starting at 11.2 mg/L, peaking at 43 mg/L, and declining to 19.2 mg/L at day 1247), despite the relatively low organic acid concentrations during the monitoring period.

In well JEMW-4 in the source area, dissolved iron was measured initially at 1.25 mg/L and continually rose to 410 mg/L at day 1247. This pattern indicates that HRC-X has most likely not been depleted after 3.4 years of monitoring. In contrast, dissolved iron in well JEMW-5 remained, for the most part, below 10 mg/L, indicating a lack of electron donor in this well that is outside of the apparent influence of HRC-X.

Manganese responded similarly to iron. In all wells except JEMW-5, dissolved manganese concentrations increased until day 372, when monitoring of manganese was discontinued.

Another indication of reducing conditions is a decrease in sulfate and increase in its reduction product sulfide. Sulfate consumption and sulfide production imply the presence of sulfate-reducing bacteria, some of which are also capable of reductive dechlorination. However, reductive dechlorination is energetically favorable at a higher ORP value as compared to sulfate reduction, so the establishment of sulfate-reducing conditions is not a prerequisite for reductive dechlorination.

The sulfate concentration in MW-2 at the beginning of the pilot test was 43 mg/L. Sulfate decreased to 1.0 mg/L on day 372 and then increased to 12 mg/L at the end of the pilot study. During this time, sulfide levels increased from nondetect to 1.4 mg/L on day 553. Sulfide is typically rapidly depleted via dispersion, volatilization, or precipitation, so low, nonstoichiometric concentrations from sulfate reduction are expected. Trends in sulfate concentration in MW-4 were not clear, and no pattern was established during the pilot study, despite the presence of up to 98 mg/L of sulfate. The lack of sulfate reduction in MW-4 may be due to the moderate concentrations of electron donor, which appears to have created iron-reducing, but not sulfate-reducing, conditions. Similarly, sulfate concentrations in the source area wells, JEMW-4 and JEMW-5, were very low (<5 mg/L), and no consistent pattern was observed.

Increased levels of chloride are consistent with decreased VOC concentrations. Chloride levels in JEMW-4 increased to 120 mg/L on day 287 from less than 20 mg/L at baseline. These data indicate conversion of 120 mg/L of PCE to ethene, whereas the initial aqueous concentration of PCE was 98 mg/L. This result provides another indication that desorption and dissolution of residual DNAPL has taken place in the source area that was impacted by HRC-X. In contrast, chloride concentrations in well JEMW-5 remained at <25 mg/L for the duration of the pilot study.

6.6 Technology Cost

Costs are shown in Table 6-2 and do not include investigation, design (typically significantly less than for mechanical systems and partially offset by no-fee design assistance provided by Regenesis) and planning or preparation of agency documents prior to implementation. Costs are for installation and two years of monitoring. Reporting costs are based on typical consulting charges rather than ODEQ internal costs.

Cost estimates for HRC and HRC-X should be based on maintaining reducing conditions from 12–18 months and three to five years, respectively. This project was conducted as a pilot test. As such, the treated area was not as large as a full-scale injection. At this site, an initial full-scale injection could be 50% larger for the plume and eight times larger for the source area. Full-scale costs would thus be approximately $200,000 if no pilot had been conducted. Follow-up full-scale treatment, if required, could occur two to three years into the project and would cost approximately one-half to two-thirds the original installation costs, as some areas would not require further injections.

Table 6-2. Project costs

Installation cost	
Installation labor (3 days)[a]	$4,000
Injection points (3 days)	$8,000
Substrate HRC, HRC-X and shipping	$21,000
Baseline sampling	$5,000
Surveying	$1,000
Completion report	$5,000
Total installation costs[b]	**$44,000**
Annual operating costs[c]	
Mobilization	$2,000
Direct labor	$6,500
Sampling equipment and supplies	$2,000
Laboratory analysis	$12,800
Project planning and reporting	$12,000
Total annual operating costs	**$35,300**
Total installation and two years monitoring	**$114,600**

[a] Assumes 10 injection points per day (a large system may attain 15–20 injections per day).

[b] Does not include additional monitoring wells beyond those installed for contaminated area delineation. Two to four additional wells might be considered for a full-scale project, adding installation and sampling/analysis costs.

[c] Assumes eight wells sampled quarterly for VOCs, organic acids, gases, and inorganics.

6.7 Observations and Lessons Learned

In addition to demonstrating that HRC can address PCE plumes by accelerating reductive dechlorination, including formation of ethene, the pilot test demonstrated the ability of the extended-release HRC-X to remediate source areas over an extended time. Observations are as follows:

- HRC and HRC-X have been effective for 2.7 and 3.4 years, respectively, based on decreasing contaminant concentrations, the presence of organic acids, and changes in geochemistry.
- Parent compound (PCE and TCE) rebound has not occurred after an extended period.
- HRC addition was successful in overcoming an apparent *cis*-DCE stall 200–400 days after injection, supporting observations by others that addition of sufficient electron donor for an extended period of time can overcome the stall phenomenon.
- Desorption of parent compounds occurred with subsequent biodegradation.
- A second and full-scale addition of electron donor is required to reach MCLs.
- A full-scale addition is warranted and should occur over a wider area.
- Addition of HRC-X appeared to stimulate a larger mass reduction efficiency than did HRC, but HRC-X took a longer period of time to reach peak efficiency, as measured by organic acid release.

ODEQ is satisfied with the results of the pilot test and is continuing to monitor the site to determine how long HRC-X will remain effective. Full-scale addition has been postponed due to state funding limitations.

6.8 Reviewer Comments

6.8.1 Jeff Marqusee Comments

Project Scale and Purpose

Typical dry cleaning site.

Site Conceptual Model

So little real data are provided it is hard to tell. A map to scale with flow and concentration information would be helpful. The extent of information provided makes it impossible to assess the utility of this site as a case study. Note the Excel file sent was corrupted.

[*Response from Case Study Sponsor:* This was a real-life project, rather than an academic study. The degree of characterization for this project could be described as good in the real world of groundwater restoration projects. Boring logs, estimated seepage velocity, contaminant concentrations, and typical geochemical parameters were all available. Certainly more information could have been attained if ODEQ wanted to fund discrete vertical sampling, discrete transmissivity testing, tracer testing, etc. But in all reality, funding for these data collection activities is unavailable on 99% of the cleanups undertaken and reviewed by member states of the ITRC. Regulators are required to evaluate remedial alternatives without unlimited budget and within the confines of what is practical and affordable, particularly when the states themselves are funding the characterization.]

Regarding the utility of the site as a case history, this is one of clearest cases of a biological technology continually treating mass flux in a source zone available today. Additionally, this treatment was accomplished with a single injection event at an extremely affordable cost as documented by ODEQ. This should certainly serve as an important case history to those ITRC members and others interested in cost-effective treatments of real-world sites.

Remediation Goals

The goals are not linked to source zone treatment in any way. They have also not defined the point of compliance. The goals are more about HRC duration than anything else.

[*Response from Case Study Sponsor:* The goals were linked directly to treating the concentrations of chlorinated solvents present on the site in the DNAPL area. Regarding point of compliance, I assume that is far downgradient outside the study zone. The objective here was treating the DNAPL area.]

Bioremediation Performance Monitoring

Very limited data provided. General claims are made but not substantiated by any analysis.

[*Response from Case Study Sponsor:* HRC was injected; parent contaminant concentrations dropped dramatically in the nearby monitoring well of concern. Desorption of bound mass occurred in the injection zone and was also dehalogenated (indicated by daughter products present in excess of parent compounds). Near steady-state dechlorination has occurred within a residence time of about 5–10 days (based upon estimated seepage velocity) for a period in excess of 3.5 years with a single HRC-X injection. If someone would like to donate the radioisotopes and pay the analytical costs to further substantiate, we would be happy to grab the sample.]

Effect on the Source Area

No real analysis provided. HRC and HRC-X do promote dechlorination, but there has been no real analysis of other impacts.

[*Response from Case Study Sponsor:* The author does a nice job describing the relative concentrations of daughter/parent compounds, clearly indicating the desorption effect of enhanced biological activity.]

Cost Information

Cost of HRC is provided.

Overall Summary

Given the limited information provided and analysis done, it is hard to see how this is useful case study. See comments below.

- Provide data in micro-molar so mass balance can be easily seen.
- Without an assessment of the groundwater flow, the value of this study is limited.

[*Response from Case Study Sponsor:* See comments above.]

6.8.2 Lenny Siegel Comments

Much of the information under review is beyond my technical expertise, so I'll focus on those areas where I believe I can be most helpful. In general, the results of the three case studies I reviewed—Test Area North, Portland Dry Cleaner, and the Arcadis PCE Site—are impressive. The prospect of accelerating the remediation of VOCs is particularly important to the communities with which I work, not just because of the long-term savings and increased potential for reuse, but because the traditionally slow pace of remediation often means continuing exposures through the vapor intrusion pathway.

Have any of the structures (businesses or homes) been evaluated for vapor intrusion? If so, it would be useful to know if this project reduced exposures due to the vapor pathway. While this site worked well as a pilot test, would the technology be suitable for full-scale remediation, given the active use of the site?

[*Response from Case Study Sponsor:* Good point. No, to my knowledge no vapor intrusion monitoring was conducted at this site. Prior to implementing full scale, I would certainly recommend an evaluation of the potential for vapor intrusion impacts.

Is contamination confined to the upper aquifer?

Same comment as above: In locations where the degradation products of the original contaminant of concern are comparably toxic, it's important to establish a remediation goal that combines the exposures. For example, the decrease of TCE exposures below the MCL does not adequately measure the success of a remediation technology if the levels of VC are elevated above its MCL. It is possible that both concentrations would be, at some point, below the MCL but the cumulative exposure would nevertheless be unacceptable. In this case, the technology would still achieve the goals, but the goals should be more appropriately stated.

It's clear that substantial degradation occurred at the points of injection, but it isn't clear what the range of influence was for each injection. I was pleased to see a map of both injection points and monitoring wells, but I'm surprised that monitoring was so sparse.

Same comment as above: The large-scale (for contaminant concentration) makes it difficult to determine when the remediation goals—the respective MCLs—have been reached.

It would be helpful to compare the costs for this or a full-scale project using the same technology with two baseline approaches: pump and treat and MNA. Both should be priced to include long-term monitoring.

Do the people who conducted the study have an idea why there appeared to be a breakdown "stall" before treatment with the HRC compounds?

[*Response from Case Study Sponsor:* These are all good comments. According to the site characterization, the contamination was thought to reside only in the perched upper zone. Regarding the degradation of the parent products to produce daughters of comparable toxicity, I agree with this assessment. Clearly the HRC-X is pushing the parent compound through to ethene as evidenced by the ethene concentrations; however, budget constraints did not allow for ODEQ to install any wells downgradient of the subject well, which is only 5–10 days' residence time from the HRC-X injection points (according to the estimated seepage velocity). We assume from other experience that given the presence of ample electron donor that dehalogenation would continue downgradient of the subject well. Of course, it is uncertain at what rate this would occur without the wells to monitor from.

Regarding the "stall" seen before the HRC, no, we cannot say for certain why this was occurring.

What we can glean from this case study is that with a single, low-cost injection of HRC-X, rapid dehalogenation occurred in an area of known DNAPL for a period in excess of 3.5 years.]

6.8.3 Tom Early Comments

This project apparently took place at a site within an active strip mall with limited access and a requirement not to interfere with ongoing commercial activities. As a result, few monitoring locations were available, and the time interval for the actual injection of amendments needed to

be of limited duration and not require frequent, repeated application. For many commercial sites this is the real world.

It is my assumption that the objective of the case studies is to present examples where a thorough evaluation of the site before, during, and after treatment can be documented to assess the short- and long-term effectiveness of treatment. The assessment frequently involves application of rather detailed treatment and monitoring approaches beyond what will eventually be used when implemented on a routine basis. This systematic approach tends to be costly and time-consuming but eventually allows one to identify the most appropriate way to implement and monitor a technology on a routine basis.

Project Scale and Purpose

This is a pilot-scale project at a small site within a strip mall setting with limited access and a requirement not to interfere with commercial activities in the area. Use of HRC and HRC-X as amendments to stimulate biodegradation activity of PCE and its metabolites in both the source area and dissolved-phase plume generally appear to satisfy these conditions and is a reasonable option for many other sites. The types of monitoring used are appropriate and applicable to other sites.

Site Conceptual Model

More detailed site characterization data may be available, but the amount of information presented in the case study summary and supplemental material is rather brief and amounts to very limited information on lithologies, hydrology, and contaminant distribution. Nothing is provided on the lithologic heterogeneities of the subsurface, and the vertical and lateral distribution of contaminants is quite limited. Is there a confining layer at depth that limits potential downward migration of DNAPL? No information about soil contaminant levels is provided.

Only four monitoring wells are reported in the data table, and no information regarding the screened intervals and their relationship to the vertical distribution of contaminants is given. However, some information about two additional monitoring wells is included in the supplemental material. Where are they located? Do they add useful information to the study? Multilevel monitoring wells, which would help provide resolution to the vertical distribution of dissolved contaminants, apparently were not used at this site.

The site map is useful, and recognition of the importance of the buried utility trench as a DNAPL source area is very helpful. However, the presumed extent of DNAPL appears to be based on limited information. The concentrations of PCE in JEMW-4 and -5 appear to signal the presence of DNAPL at or very close to these locations. However, no soil boring data are provided. Are they available?

[*Response from Case Study Sponsor:* All good points raised here. Unfortunately, the characterization undertaken did not offer the information you point out. No information is available for the other wells mentioned. Wells are all screened in the upper perched zone (5–20 feet bgs). No soil data were provided, but as you mentioned, DNAPL is clearly present as evidenced by the dissolved chlorinated alkene concentrations.]

Remediation Goals

As this is a pilot-scale project, the goals focus on evaluating if HRC and HRC-X treatment can accelerate PCE degradation, result in complete dechlorination of PCE, and maintain sustainably low VOC concentrations after treatment (and document the persistence of the effects of HRC application) rather than attaining a specific concentration end point. In general, these goals are attainable, at least within the zones of influence around the four monitoring locations. The required analytical parameters can be measured.

However, as noted in the summary, one of the monitoring wells near the source area (JEMW-5) is outside of the zone of influence of injection sites for HRC-X. Therefore, it is only a baseline monitoring site that is not influenced by treatment. MW-02 lies near the upgradient limit of the zone of injection of HRC. The groundwater flow rate for the site is estimated as 110 feet/year. Should we expect the HRC to persist around MW-02 or be flushed from the system? The persistence of organic acids at MW-02 for >1 year suggests that this may not have occurred.

The number and locations of monitoring points is very limited and raises questions about the conclusions that can be made from results obtained from them. It should be noted that graphs for JEMW-3 and JEMW-6 are provided in the supplemental material but not located on the map or discussed in the summary. Their location and significance to this project is unknown.

[*Response from Case Study Sponsor:* Regarding the HRC persistence and the presence of organic acids in MW-02, this is to be expected. HRC remains in place after injection, continuing to release soluble acids for period of up to 18 months.

Regarding JEMW-3 and JEMW-6, both of these wells were outside the study area. JEMW-3 is south and downgradient from the "control" well JEMW-5. JEMW-6 is actually east (upgradient) of the impacted trench area under study.]

Bioremediation Performance Monitoring

The injection of HRC occurred at 22 locations using direct-push methods and occurred over a vertical thickness of 22 feet. The injection points appear to be relatively close together, and I assume that overlap of the zones of influence among nearest neighbors is expected. Depending on the details of lithologic heterogeneities, this may or may not be correct for some intervals but cannot be evaluated from the information presented as there are few monitoring wells in the treated plume area. In the source area, using the injection data provided it appears that a 14-foot-thick zone received HRC-X. No information is given to support how this interval was selected or how the HRC-X was vertically distributed.

Periodic monitoring of groundwater samples for the parent contaminant, PCE, and its reductive metabolites from before injection until several years post-injection provides very important data. Likewise, information on the presence of metabolite organic acids (electron donors) appears to be very useful for tracking the longevity of treatment effectiveness. This seems to be valuable information to support the period of activity of HRC and HRC-X.

The graphs for PCE and metabolites for JEMW-5 (untreated) illustrate that significant variations in the concentration of PCE occur over the extent of the monitoring period with no explanation

as to the cause being provided. It is possible that the injection of HRC and HRC-X resulted in lateral displacement of less-contaminated groundwater that might explain changes occurring around the time of injection, but other factors might be involved. Are there changes in groundwater levels and the direction of groundwater flow during the study period that might account for the variability? Are there other events occurring in the general area that might impact the flow?

The high concentration levels for *cis*-DCE in MW-2 and MW-4 are suggested as evidence that sorbed PCE was desorbed and degraded during treatment. While this may be a plausible explanation, it would be helpful to have support from the concentrations of natural organic matter or other sorbing materials in soil obtained from soil cores.

In terms of other geochemical parameters that were measured, it appears that the amount of dissolved iron supports the development of reducing conditions. However, it is curious that the concentration of chloride (an indirect measure of PCE/TCE/DCE/VC degradation) in MW-2, MW-4, and JEMW-5 ranges between ~10 and 28 mg/L (background?). Only in JEMW-4 are distinctly elevated chloride concentrations observed. Why do samples from MW-2 not exhibit higher chloride values when significant dechlorination reactions appear to have occurred?

[*Response from Case Study Sponsor:* Again, these are all good points. No significant changes in groundwater flow velocity or direction were noted. Other than the initial injection events, no other events other than the typical hydrogeologic cycle are thought to have impacted flow. Regarding chloride, I cannot explain why MW-2 samples do not exhibit higher chloride concentrations.]

Effect on the Source Area

There is only one well that appears to monitor the impact of HRC-X treatment on the DNAPL source (JEMW-4). The starting dissolved concentration of PCE was 98 mg/L (186 days before injection), providing indirect support that this location was contaminated with DNAPL. No confirmatory soil concentration was provided. Approximately 3.5 years of monitoring data indicate that groundwater concentrations for PCE and TCE have dropped significantly and remained relatively low (<200 µg/L). The metabolic byproducts *cis*-DCE, *trans*-DCE, VC, and ethane shown significant increases following treatment and remain high after 3.5 years. The total concentration of organic acids also remained elevated at the end of the monitoring period. These results strongly support the efficacy of HRC-X treatment for >3 years. The continued high concentrations of most metabolites suggests that DNAPL probably remains. However, soil samples that would yield important information about the actual residual concentrations of contaminants are not available.

[*Response from Case Study Sponsor:* I agree with your statements.]

Cost

As a pilot-scale activity, this project is not comparable to full-scale remediation at other sites. More extensive monitoring (i.e., more locations) would likely be required for a site of this size. Depending on site conditions, use of multicompletion wells may be required. It seems reasonable that soil samples would be required to supplement groundwater results, especially in the source

area where residual DNAPL may remain for an extended period of time. That would likely be the best way to ensure that rebound will not occur. The analytical parameters measured appear to be appropriate, and it does not seem that more exotic analytes are necessary.

[*Response from Case Study Sponsor:* I agree with your statements.]

Summary

The goals of this case study were to evaluate whether HRC and HRC-X treatment can accelerate PCE degradation, result in complete dechlorination of PCE, and maintain sustainably low VOC concentrations after treatment (and how long the effects of HRC application persist) rather than attaining a specific concentration end point. These objectives were met, at least within the 3.5-year time frame of the project. Although remediation goals for most of the contaminants are not specified for this site, it is probable that they were still exceeded after 3.5 years. Regenesis notes that it is recommending a second injection of HRC and HRC-X. From data made available for this review, it is not possible to determine how close the requirements for a final state of remediation (i.e., destruction of DNAPL) were approached. Clearly, there was significant impact on dissolved-phase concentrations of contaminants, based on the wells that were sampled. Soil samples may be necessary to make a better projection of treatment completion time when a DNAPL source is involved.

[*Response from Case Study Sponsor:* I agree.]

6.8.4 Nancy Kinner Comments

Project Scale and Purpose

Many dry cleaning facilities have problems with chlorinated solvent contamination of the subsurface below the facility. The information/approach in this pilot study could be of interest at many of these sites because there is often limited access when the business is still operating and there are paved areas.

Site Conceptual Model

The SCM, as presented, is not detailed enough to serve as the basis for the pilot-scale study. The only figure presented is a plan view of the site. There should at least be one longitudinal section to make the picture complete in the vertical dimension. The figure shown is also not to scale, which makes visualization of the relationships between wells, etc. for the SCM difficult. In addition, showing contaminant concentration profiles on the figures would be helpful. There are contours shown in Figure 6-1, but these are not labeled. It is not clear from the description at what depths the plume is bounded. If the authors wish to avoid showing contaminant contours along with the groundwater flow direction, they could use a "spider" plot approach.

[*Response from Case Study Sponsor:* Both the cross section and spider plots are good suggestions in data representation.]

Remediation Goals

The goals are articulated well in this section. However, the only concentration-based residual goal is for PCE (5 µg/L). Does ODEQ have goals for potential PCE by-products (i.e., TCE, DCE, and VC)? Is there a specified groundwater management zone within which these remedial goals must be achieved?

[*Response from Case Study Sponsor:* I'm certain that ODEQ would have goals for this site specific to PCE by-products. However, the objectives for this pilot test were as stated, to determine the following:

- the effectiveness of HRC injection, as measured by the degree to which PCE degradation could be accelerated
- whether complete dechlorination (through ethene) of high concentrations of PCE is possible
- how long the effects of HRC application persist
- whether VOC concentrations would remain low after treatment]

Bioremediation Performance Monitoring

The monitoring program is not described in the study, so one must infer this from the results presented in this section. There is no mention of the analytical methods for chlorinated compounds. The team monitored the standard CVOCs (PCE, TCE, DCE, VC) and ethene as well as several of the standard acids. Inorganic analyses included SO_4^{-2}, S^{-2}, dissolved iron and manganese (no speciation), Cl^-, and redox potential. No analytical methods are presented for these. There is no quality control plan provided to support the quality of the data or to determine the detectable differences in concentrations. The rationale for the sampling schedule is not presented. There were no innovative monitoring approaches used. The method for collecting samples from the wells was not provided. There did not appear to be a conservative tracer used to help understand water movement from the injection wells to the monitoring wells.

[*Response from Case Study Sponsor:* Yes, you are correct.]

Effect on the Source Area

Table 6-1 and Figures 6-2 (MW-2) and 6-3 (JEMW-4) are the only data presentations. There is no attempt to visually track the plume impacts in time and space with distance from the source. Without a tracer, it is also difficult to understand groundwater movement in relation to the injection times and locations and the downgradient wells. The team suggested they could use the organic acid data in some way to do this, but these are not conservative and that exacerbates the problem. The data for the chlorinated compounds are all shown in µg/L. While this is important to the regulatory agency, it is not useful in tracking microbial transformations of PCE and its progeny. The team should provide data and graphs with µM concentrations. The profiles with depth in the plume or wells are not shown. Depending on the hydrogeology of the site and how the wells were sampled (large vs. small discrete screened intervals), the results could indicate different conditions in the subsurface. The lack of monitoring information (see Section 6.4) makes assessment difficult. This is a site where use of stable isotopes/ratios could have been very helpful in a few before and after intervals to support the case for biodegradation being stimulated by the HRC/HRC-X.

The lack of preinjection data (only one point provided 186 days before injection) also confounds one's ability to draw conclusions from this pilot study regarding the efficacy of HRC/HRX-X. It seems quite likely that a historical record with respect to VOCs and groundwater velocity/ direction exists for the site. The "before" picture must be more clearly established to strengthen this case study, if at all possible.

The team could also benefit from some support for their arguments for successful PCE bioremediation without stalling. One of the goals of this study was to measure "the degree to which PCE degradation could be accelerated." There is no comparison of background (non-HRC/HRC-X) rates of PCE degradation to those post-injection.

Regarding enhanced dissolution/increased solubility effects, there is little evidence of these in the case study as written. The authors note that the concentrations of c-DCE were greater than those of the parent compound. Again, this discussion would benefit from a comparison of the data in μM concentrations (the team alludes to this in the sentence referencing molecular weight, but direct discussion would be better).

The use of JEMW-5 as a control well is good and helps the study. However, even this well appears to be impacted by the HRC-X at the end of the study. Groundwater elevation data must be available during the study to show contours within the site and support the team's assumptions that JEMW-5 is a control. These groundwater contours could also be helpful in determining how injection of the HRC/HRC-X affected the groundwater movement.

The team discusses the organic acid trends in the text. Time series plots would be more useful to illustrate their points. A discussion of the relationship between the acids would also be useful in deciphering what could be occurring in situ. These also appear to be the main way that the team can make its case regarding the long-term impacts of HRC/HRC-X. Comparative data relative to groundwater conditions (velocity, distance/time downgradient) between the HRC and HRC-X impacted well could help support their assessments.

The team discusses the dissolved iron data and its increasing concentration in support of its case. What is the source of iron in this aquifer? Without Fe^{+3}/Fe^{+2} speciation data, the arguments made are somewhat subjective. The preinjection conceptual model could inform the discussion of what is happening in situ with respect to microbial biogeochemistry. If the aquifer is organic carbon limited, it is important to understand whether the system is poised at sulfate- or iron-reducing conditions and whether the addition of HRC/HRC-X drove the system to more reducing conditions.

The team suggests that Cl^- is an indicator of complete PCE degradation using the concentrations of PCE and Cl^-. This discussion should be reinforced using a mass balance approach.

[*Response from Case Study Sponsor:* These are all good points. I have attempted to address these in my comments above.]

Cost Information

The cost analysis is not easily transferable to other sites because of the lack of detail provided about what was done at this site. For example, it is not clear how deep the wells were for the HRC/HRC-X or how they were installed. The cost per unit volume of the material is not provided. As mentioned above, the lack of sampling and analysis information makes that cost evaluation difficult to transfer.

[*Response from Case Study Sponsor:* As mentioned, the HRC, HRC-X was not placed in wells. Rather the material was injected within borings employing a direct-push rig.]

Overall Summary

Most of my concerns with the study are noted above. The information provided is suggestive of biodegradation, but the lack of tracers, hydrogeologic data, and background information as well as the incomplete pre- and post-conceptual models of the plume provide room for doubt. It is quite possible that this information exists but was just not included. This is a study where a few analyses for stable isotopes could have been very useful.

- Can the team use an approach similar to Newell et al. 2002 to provide more information? *[Sponsor responses in italics:] Yes*
- Can more background data be used to understand the preinjection conditions with respect to iron/sulfate reduction and organic carbon limitation of PCE degradation? *Yes.*
- What do the data suggest about the time and amount of HRC/HRC-X needed to meet the remedial goals for PCE and its progeny? *It is unclear what is meant here. As a practical matter, the goals may be met as we speak, if one were to consider a downgradient monitoring well the compliance point. This project focused solely on its objectives and within a very limited budget.*
- How easy was it to inject the HRC/HRC-X? *The HRC/HRC-X was easily injected.*
- Are the hydrogeologic conditions throughout the site conducive to injecting enough HRC/HRC-X to create an effective treatment "wall"? *Yes, as evidenced by the data.*
- What do methane data suggest about in situ conditions? *Methane data were not collected and analyzed throughout the study.*

7. ENHANCED ANAEROBIC BIOREMEDIATION OF A TCE SOURCE AT THE TARHEEL ARMY MISSILE PLANT USING EOS CASE STUDY SUMMARY

The presentation associated with this case study, given by Robert Borden, Christie Zawtocki, and Walt Beckwith at the forum on March 29, 2006, is included on the CD accompanying this document. The reviewers for this case study were Alex Naugle, Mary Jo Ondrechen, Tom Early, and Nancy Kinner.

7.1 Introduction

Emulsified Oil Substrate is being used to remediate a TCE source area at the Tarheel Army Missile Plant in Burlington, N.C. TAMP is a government-owned, formerly contractor-operated 33-acre facility with a 50-year history of use for production of defense-related and private-sector

electronics. Releases from manufacturing operations and USTs have impacted soils and groundwater at TAMP with petroleum hydrocarbons and CVOCs. Ten years of active remediation, including pump and treat and in situ SVE/AS, have been effective in reducing the BTEX. However, these efforts have had little effect on the dissolved-phase TCE groundwater plume.

In preparation for transfer of ownership of the property, the Army elected to evaluate bioremediation alternatives for the TCE in groundwater. Solutions-IES, Inc. conducted a pilot-scale study to test the ability of EOS to reduce the CVOCs in groundwater. The pilot test was designed to treat a 100 × 100 foot zone believed to be the primary source area for the TCE plume.

EOS is an effective, low-cost substrate for enhancing anaerobic bioremediation of a variety of contaminants, including chlorinated solvents, PCE, nitrate, chromate, acid mine drainage, and explosives. EOS consists of food-grade soybean oil, surfactants, macro- and micronutrients, and vitamins blended to form a stable microemulsion with small, uniformly sized oil droplets. Once injected into the subsurface, the oil droplets stick to the sediment surfaces, providing a residual oil phase. The oil provides a slow-release carbon source for cell growth and electron donor for energy generation, supporting long-term anaerobic biodegradation of the target contaminants. This approach provides good contact between the slowly biodegradable organic substrate (oil) and the contaminants.

EOS is prepared to be stable for extended time periods (e.g., noncoalescing); have small, uniform droplets to allow transport in most aquifers; and have a negative surface charge to reduce droplet capture by the solid surfaces. Laboratory permeameter studies demonstrated that emulsions can be effectively distributed with a low residual saturation in sands and clayey sands with only modest reductions in aquifer permeability (Coulibaly and Borden 2004). Field pilot studies have demonstrated that emulsified oils can be effectively distributed more than 20 feet away from the injection point and provide a long-lasting carbon source to support reductive dechlorination (Borden et al. 2001; Lee et al. 2001, 2003).

The Air Force Center for Environmental Excellence (AFCEE), which has supported emulsified oil projects at several Air Force bases across the country, is developing a detailed technical protocol to aid users in the design, field implementation, and monitoring of edible oil bioremediation projects. In addition, ESTCP is supporting two field demonstrations being conducted by Solutions-IES to evaluate the use of emulsified oils for enhanced bioremediation of perchlorate and chlorinated solvents. A design protocol for the use of emulsified oils will also be developed under this ESTCP project (Number CU-0221).

7.2 Site Conceptual Model

7.2.1 Contaminant Distribution

Soil and groundwater contamination were first detected at TAMP in 1993 after the removal of several USTs in the vicinity of Buildings 2 and 29 on the facility. Soil and groundwater samples collected after closure showed the presence of BTEX and CVOCs. The CVOCs were believed to be from a chlorinated solvent cleaning machine at Building 9 and an associated disposal sump at

the waste accumulation pad located north of Building 2. Subsequent investigations led to the conclusion that there were plumes of both CVOCs and petroleum hydrocarbons in groundwater at the facility.

Since 1995, when active remediation was initiated, soil and groundwater samples have been collected at the site periodically to monitor the effectiveness of the SVE/AS systems. Figure 7-1 shows the TCE plume in April 2002. The TCE plume extends approximately 900 feet west-northwest of the presumed source area in the vicinity of monitor well MW-108. The highest TCE concentrations were in MW-108 at 1900 µg/L and MW-110 at 2600 µg/L. Soil samples collected in the vicinity of Buildings 2 and 29 in April 2002 showed soil contaminant concentrations had declined significantly from 1994 levels (Weston Solutions, Inc. 2003). All CVOC concentrations in soil were less than the remedial target end point concentrations specified in the Corrective Action Plan.

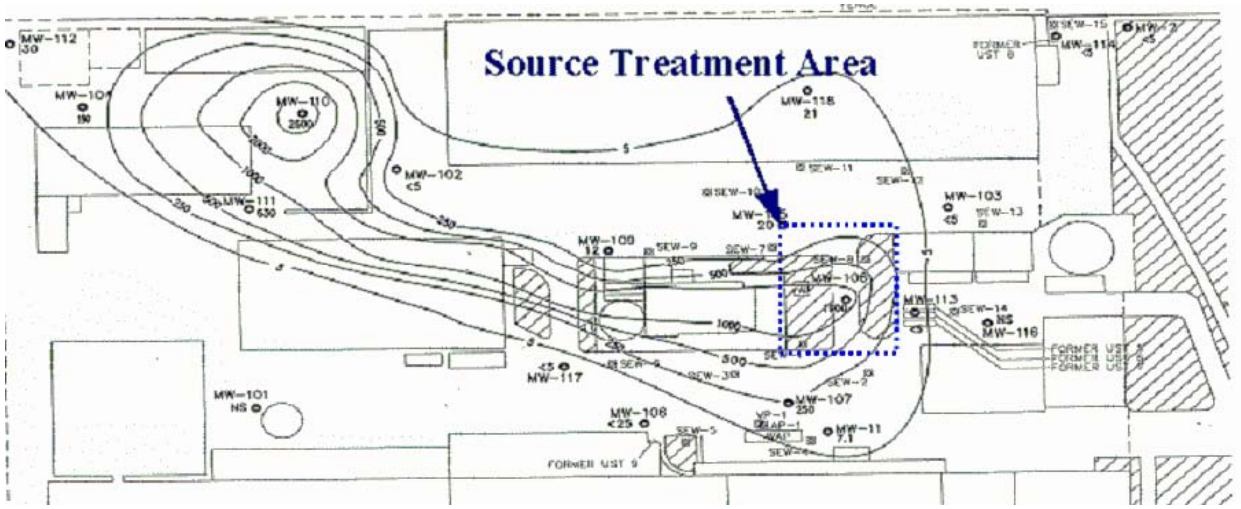


Figure 7-1. Site layout and extent of TCE in groundwater in April 2002.

7.2.2 Geology/Hydrogeology

The TAMP site is located within the Piedmont physiographic province of North Carolina. The Piedmont is characterized by rolling topography and generally well-drained residual clayey soils weathered from igneous and metamorphic bedrock. The area is drained by a dendritic tributary system of the Cape Fear River. The site area has been mapped (North Carolina Geological Survey 1985) as being underlain by metamorphosed granite of late Proterozoic to late Cambrian Age. The rock assemblage is described as megacrystic, well-foliated (granite), locally containing hornblende. Soils are described on many of the site boring logs as tan to yellow brown and green silt, sandy silt, and plastic clay (Unified Soil Classifications of CL, ML, and CH). Soil consistency increases with depth, and deeper soils take on the appearance of highly weathered or degraded rock, locally referred to as saprolite. Bedrock is often shallow.

The conceptual hydrogeologic model for the Piedmont developed by LeGrand (1989) is based on a slope aquifer system where precipitation infiltrates through the unsaturated zone to recharge the water table. Groundwater then moves down slope in response to gravity and discharges as springs in the topographic lows and base flow to perennial streams and rivers, usually within a

distance of 3000 feet or less. In most cases, the water table surface mimics the overlying land surface and surface topography can be used to estimate groundwater flow direction.

The typical Piedmont aquifer system is divided into three zones (Heath 1980). These zones include the unconsolidated saturated soil zone, consisting of residual soil; the underlying saprolite and highly weathered rock (lower unconsolidated aquifer); and bedrock, where openings (joints and faults) within the bedrock comprise the bedrock aquifer system. Joints and fractures tend to be more closely spaced with larger openings near the bedrock surface and decrease in aperture and number with increasing depth. All three zones are interconnected and act as a single aquifer system, although each zone varies in its ability to transmit water. The base of the Piedmont bedrock aquifer is indistinct and occurs where the fracture system is no longer effective in transmitting flow (Daniel 1989). Fractures are commonly non-water-bearing below a depth of 300 feet (Heath 1980). The highest permeability zone in a typical Piedmont aquifer system occurs in the lower unconsolidated zone between the saprolite and the bedrock (the zone targeted by the pilot test).

TAMP has been extensively developed. More than 95% of the land area is covered with buildings and pavements (impervious surfaces). The surface topography has been influenced by past construction (fills and cuts). The net effect results in variable subsurface conditions and minimal potential for groundwater recharge from precipitation.

The EOS pilot test is located in the northeast quadrant of the TAMP site between Buildings 19 and 29, in the immediate vicinity of existing monitor well MW-108 (Figure 7-1). Most of the test area is paved in concrete; the east and west fringes of the test area are landscaped in grass. Several underground utilities exist in the area including a storm water sewer with several drop inlets, gas lines, electric lines, and a water line used for the fire suppression system. An underground pipe chase/pedestrian tunnel is located along the east edge of the test area. The tunnel extends underground from Building 1 to Building 16, passing along the western extent of Building 19.

Existing monitor well MW-108 is located in the center of the pilot test area. According to report data, MW-108 was terminated at 16 feet bgs after penetrating approximately 13 feet of silty clay, which was underlain by 3 feet of clayey silty sand. The subsurface data suggest that there are variable amounts of reddish-brown, silty clay or clayey silt placed as fill in areas of the site during construction. In some areas, the fill contains some sand and/or gravel. Near-surface native soils tend to transition quickly to saprolite. Both tend to be fine-grained clay and/or silt containing variable amounts of sand and rock fragments. Some borings encountered sandy saprolite grading into rock.

In general, compacted sandy silty clay and clayey fine sand were encountered throughout the site in the first 6–10 feet. Gravels and organic material were locally present in association with fill materials at various locations across the site, at depths of approximately 5 feet or less below ground surface. Below 10 feet, the sand content generally increased as the effects of weathering decreased. Bedrock was encountered in many borings between 10 and 16 feet; however, the top of bedrock is irregular. Site soils tend to be very clayey near the ground surface (Unified Soil Classifications of CL, ML, and CH). Soils tend to become more silty and sandy (ML and sandy

silt [SM]) with increasing depth, transitioning to saprolite (decomposed rock) and sheared granite bedrock.

The water table occurs within the soil overburden at depths of 7–13 feet bgs depending on topographic position. At TAMP, groundwater within the unconsolidated overburden flows to the northwest toward an unnamed stream west of the property roughly paralleling the original ground surface slope. Within the test area, groundwater flow is also influenced by the underground pedestrian tunnel. The bottom of the tunnel intercepts the water table and is dewatered with two sump pumps.

Two slug tests have been performed on wells (MW-106 and MW-107) located within TAMP but south of the pilot test site. Based on these limited tests, the horizontal hydraulic conductivity was estimated to be approximately 7.6 feet/day (2.7×10^{-3} cm/second) (Roy F. Weston Inc. 1994). The water table gradient in the central portion of the site is approximately 0.02 foot/foot, based on groundwater elevation data from several groundwater measuring periods. Assuming an effective porosity of 30%, Weston calculated an average groundwater velocity of approximately 0.5 foot/day (1.8×10^{-4} cm/second), or approximately 185 feet/year.

Weston completed additional investigation in the northwest quadrant of the site in 1998 in preparation of an amendment to the Corrective Action Plan. Bedrock cores collected during drilling of the wells indicated the top of bedrock to be highly fractured. Pump tests were performed in April 1998 in the four bedrock-monitoring wells (MW-104, MW-110, MW-111, MW-112) to estimate horizontal hydraulic conductivity (K) and storativity (S) of the fractured bedrock. The tests included constant drawdown, step drawdown, and recovery. Multiple estimates of K and S were derived from each phase of the test. Based on the test data, Weston estimated the hydraulic conductivity of the well field to be 4.7×10^{-4} cm/second and the storativity for the well field to be 4.1×10^{-3}. Actual well pumping yields were lower than expected, suggesting that actual aquifer conditions are more restrictive and that the relatively thin clayey and silty soil overlying granitic saprolite and bedrock yield fluids with some difficulty.

7.3 Remediation Goals

Because of the interest in returning the property to productive use, the Army and the North Carolina Department of Environment and Natural Resources, Waste Management Division, Superfund Section, signed a consent agreement on February 25, 2004, requiring an expedited cleanup of soil and groundwater contamination at the site. This consent agreement established an interim remedial goal of 536 µg/L for TCE in groundwater, which was based on achieving a 50% reduction in the average concentration of TCE in five monitoring wells (MW-104, MW-110, MW-111, MW-107, and MW-108) from the 2001 preremediation average concentration of 1072 µg/L. The interim remedial goal must be met within three years of the implementation of full-scale groundwater remediation. The ultimate remedial goal is to meet the levels specified in 15A NCAC 2L.0202 (North Carolina Groundwater Standards). For the primary CVOCs of concern, the North Carolina Groundwater Standards are 0.7 µg/L for PCE, 2.8 µg/L for TCE, 70 µg/L for *cis*-DCE, and 0.15 µg/L for VC.

7.4 Bioremediation System Construction and Operation

The pilot study was designed to reduce CVOCs in an area approximately 100 × 100 feet, specifically targeting a roughly 10-foot-thick zone extending from the top of hard bedrock upward through the transition zone and extending a short distance into the saprolite. Implementation of an in situ anaerobic bioremediation design in this area presented several significant challenges, including an underground pedestrian tunnel located along the east side of the test area, the presence of subsurface infrastructure, and a relatively low-yielding aquifer. To overcome these challenges, the design consisted of injection followed by temporary recirculation to distribute the substrate throughout the targeted treatment zone.

To implement the design, eight 6-inch-diameter injection wells were installed approximately 30–35 feet apart. Figure 7-2 shows the layout of the pilot test. The wells were extended to the top of competent bedrock using air rotary drilling methods and were constructed using 10 feet of 0.020-inch slotted polyvinyl chloride screen, which intercepted the contaminated zone of the aquifer. The eight wells were completed below grade in vaults and were manifolded together as four well pairs to allow temporary recirculation. To comply with one of the requirements of the underground injection control permit that prohibited reinjection of any extracted contaminated groundwater that was brought aboveground and not treated, all piping between each well pair was run underground in trenches between well pairs.

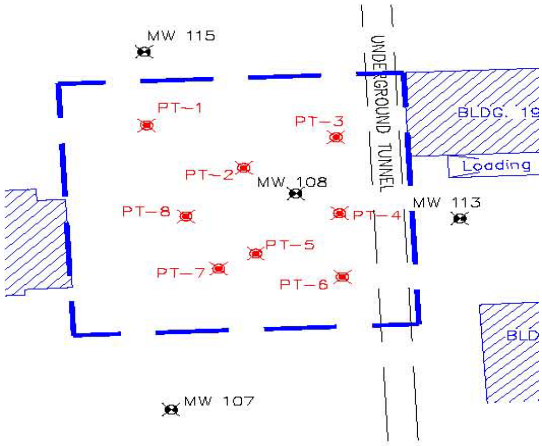


Figure 7-2. EOS treatment area.

The goal of the injection was to successfully move emulsion throughout the treatment zone. This was accomplished using a two-step process. The first step involved diluting emulsion concentrate with potable water and injecting the diluted emulsion into the subsurface. The second step consisted of temporary recirculation of groundwater to distribute the emulsion throughout the targeted treatment zone. Since the SVE/AS system had created highly oxidative conditions in the test area, there was concern that bioaugmentation might be needed. Therefore, the injection activities were implemented in two phases. During the first phase, the emulsion was injected into half (four) of the wells, followed by recirculation to push the emulsion out into the formation. The injection was then terminated to allow the emulsion to sorb to the aquifer materials. Monitoring was conducted to confirm anaerobic conditions had been established and to assess the need for bioaugmentation. After deciding that bioaugmentation was not needed, the injection/groundwater recirculation process was reversed in a second phase to treat the remaining four wells. The recirculation was continued until approximately one pore volume had been recirculated.

The first-phase injection began on June 29, 2004 with dilute EOS concentrate being injected into wells PT-1, PT-4, PT-6, and PT-7. From July 1 through July 6, 2004 (the July 4th weekend), EOS injection was temporarily suspended and temporary recirculation was conducted by extracting groundwater from PT-2, PT-3, PT-5, and PT-8 and injecting into the four wells to test the process. EOS injection resumed on July 6, 2004, and continued until July 13, 2004, when

evidence of dilute EOS was observed in the adjacent tunnel sump. Injection was discontinued, and the water chase was resumed and continued until August 16, 2004, when the first phase of injection/groundwater recirculation activities was terminated. Approximately 12,180 pounds of EOS concentrate and 83,000 gallons of groundwater were recirculated during the first treatment phase.

The second injection phase was initiated on September 10, 2004. Because of the presence of EOS in the tunnel sump during the first injection, the injection plan was revised such that wells located in the west half of the test area (PT-1, PT-2, PT-5, and PT-8) would be injected with dilute EOS. Dilute EOS injection continued until September 17, 2004. Emulsion was again identified in the tunnel sump on September 16, and the remaining dilute emulsion was injected into PT-1. The second phase water chase involved extracting groundwater from wells PT-3, PT-4, PT-6, and PT-7 and injecting into PT-1, PT-2, PT-5, and PT-8. The temporary recirculation was initiated on September 17 and terminated on October 12, 2004, when all injection/groundwater recirculation was discontinued. An additional 6,300 pounds of EOS and 80,000 gallons of groundwater were recirculated during the second phase.

7.5 Bioremediation Performance Monitoring

Eighteen monitor wells had been installed by previous consultants to monitor groundwater conditions at TAMP, and while the wells provided good coverage of the TCE groundwater plume, only one well (MW-108) was located within the pilot test area. The performance of the pilot test was evaluated by monitoring three of the injection/recovery wells (PT-3, PT-6, and PT-8) and monitor well MW-108. As part of some of the performance monitoring events, groundwater samples were also collected from some of the other pilot test injection/recovery wells and from other existing monitor wells at the facility.

The monitoring program consisted of measuring the depth to water, EOS accumulation (if any), DO, ORP, pH, and specific conductance during each event. In addition, to evaluate the effectiveness of the source area treatment in reducing contaminant concentrations, MW-108, PT-3, PT-6, and PT-8 were sampled for CVOCs, light hydrocarbon gases (ethene, ethane, methane), electron acceptors (nitrate, sulfate), electron donors (TOC and VFA), indicator parameters (pH, ORP) and inorganics (dissolved iron, dissolved manganese, and chloride).

Preinjection groundwater samples were collected on June 22, 2004. Samples were again collected after first injection/recirculation phase (August 18, 2004) and after the second injection/recirculation phase (October 14, 2004). Additional performance monitoring events were conducted on approximately two-month intervals on the following dates: December 1, 2004 (Day 154), February 2, 2005 (Day 217), April 14, 2005 (Day 288), and June 23, 2005 (Day 358). The day numbers indicated in parentheses are the number of days since initiation of the first injection phase. A final monitoring event will be conducted in August 2005.

7.6 Effect on Source Area

7.6.1 Performance Monitoring Results

The EOS injection was effective in creating anaerobic, reducing conditions and promoting biodegradation of CVOCs in the source area. The analytical results for the biogeochemical parameters are summarized in Table 7-1 for the one monitor well (MW-108) and three injection/recirculation wells (PT-3, PT-6, PT8) within the treatment zone. Prior to injection, nitrate and sulfate were generally low, ranging 0.5–1.9 mg/L for nitrate and 26–61 mg/L for sulfate. Preinjection groundwater conditions were generally oxidative as a result of the extended operation of the AS system prior to implementing the pilot test. DO ranged approximately 5–8 mg/L, and ORP was positive, ranging from +97 to +495 mV in the test area. Post-injection, DO concentrations quickly decreased and generally remained <0.5 mg/L with the exception of a couple of outlier data points for PT-6. ORP levels also decreased with negative values detected during most of the monitoring events. In general, sulfate and nitrate decreased in the treatment area, confirming that reducing conditions had been established. Methanogenesis was also observed in all of the wells. By one year post-injection, methane concentrations ranged 4.4–14.5 mg/L.

TOC and VFAs were monitored to assess the distribution of EOS® in the subsurface. The TOC and VFA results are presented in Tables 7-1 and 7-2, respectively. Preinjection TOC concentrations were low, ranging from less than 1 mg/L to 11 mg/L. TOC concentrations increased sharply after injection and then decreased as the oil sorbed to the aquifer sediment. Acetic, propionic, and butyric acids were detected in PT-8 and MW-108 after EOS injection, suggesting that the soybean oil is being fermented to organic acids in the vicinity of these wells. Approximately 10 months post-injection, acetic acid is still being detected in these wells.

The CVOC results for each of the monitored treatment area wells are presented graphically in Figures 7-3 through 7-6. Overall, these figures show a decrease in total CVOCs in the source area. PT-3 and MW-108 showed an immediate decrease in total CVOCs after EOS injection. In contrast, PT-6 and PT-8 showed an increase in total CVOCs immediately after injection. These changes are most likely due to the recirculation activities that were conducted to spread the emulsion throughout the treatment zone. Subsequent monitoring events showed decreases in total CVOCs in all of the monitored treatment area wells with complete degradation of PCE and TCE and intermittent production of *cis*-DCE and VC.

Figure 7-7 shows the average molar concentrations of CVOCs detected in the pilot test area during each monitoring event. As shown, on a molar basis, the total CVOC concentration remained essentially unchanged immediately after injection. However, preinjection TCE was the predominant constituent, while immediately post-injection *cis*-DCE predominated. Subsequent monitoring events showed further degradation of *cis*-DCE to VC.

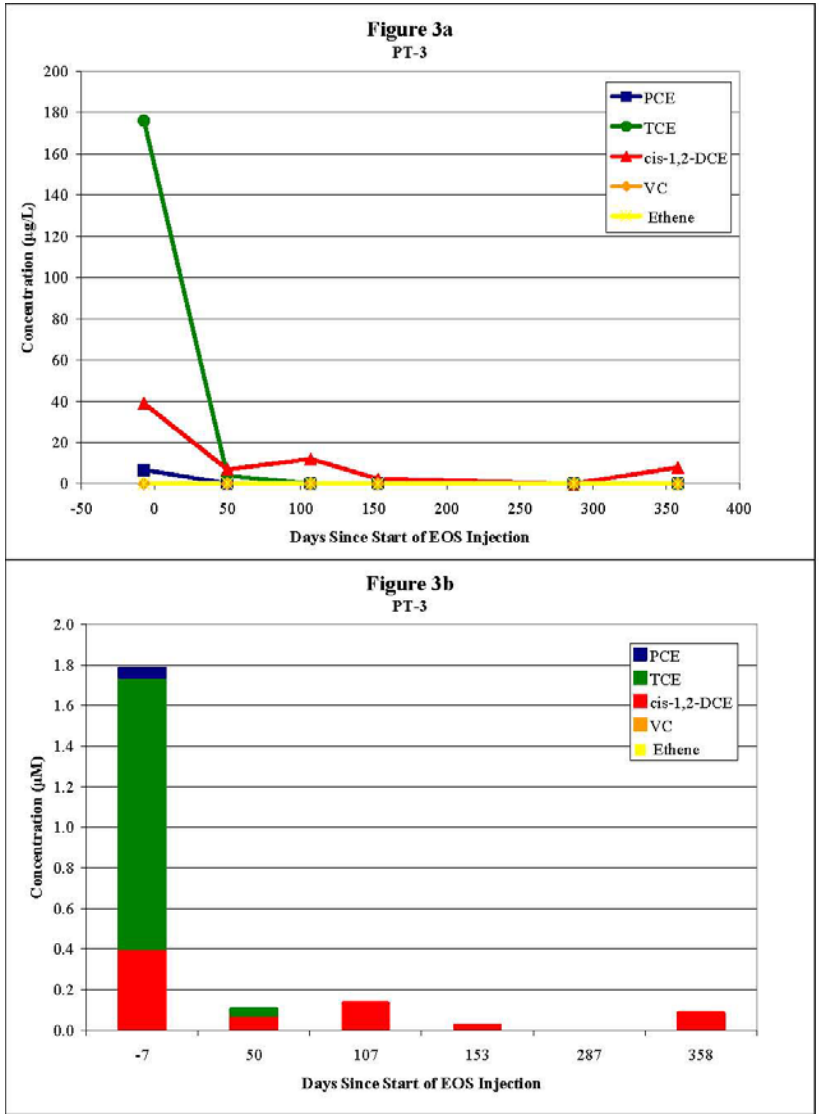
Table 7-1. Biogeochemical results

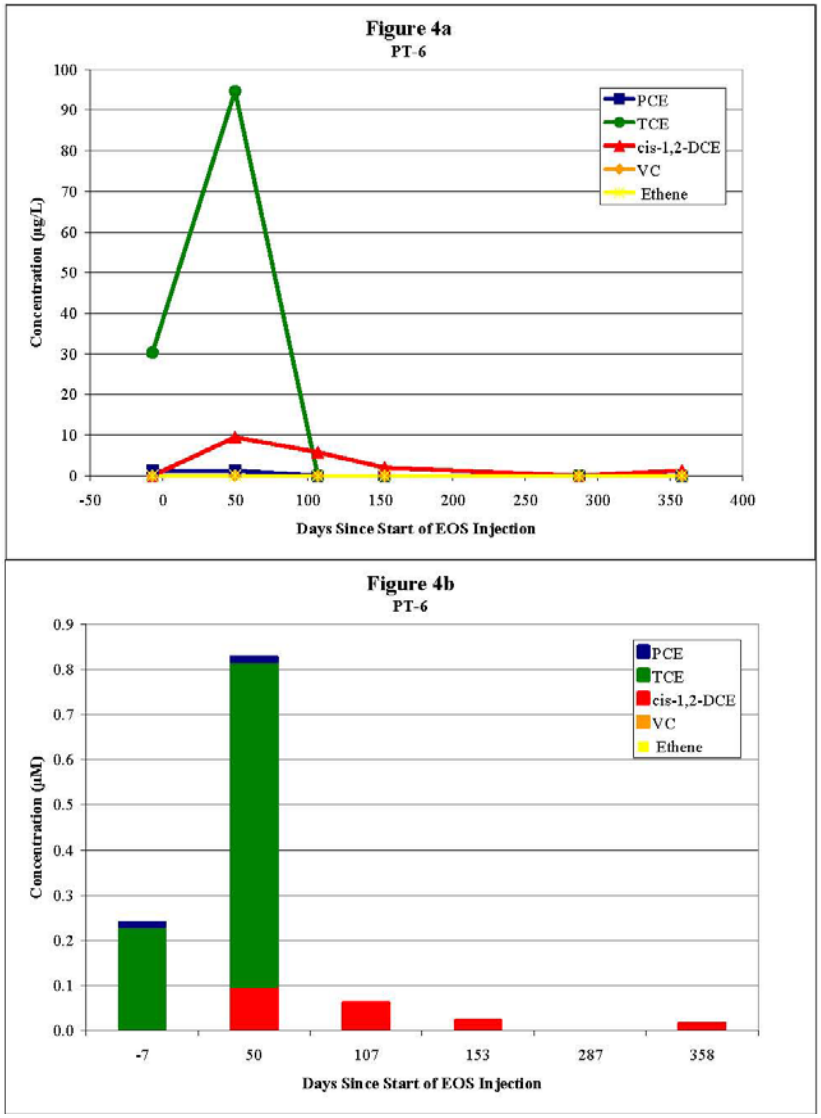
Well ID	Sample date	Days Since start of injection	Total organic carbon (mg/L)	Total inorganic carbon (mg/L)	Methane (µg/L)	Nitrate (mg/L)	Sulfate (mg/L)	Chloride (mg/L)	Dissolved iron (mg/L)	Dissolved manganese (mg/L)	Dissolved oxygen (mg/L)	ORP (mV)	pH (SU)	Temperature (°C)	Conductivity (µS/cm)
PT-3	6/22/04	-7	1.7	18	2.0	0.52	46.0	14.4	NA	NA	6.78	139	6.78	19.3	732
	8/5/04	37	377.0	NA	NA	NA	NA	NA	NA	NA	1.48	-46.3	5.53	22.1	1261
	8/18/04	50	NA	NA	103.7	<0.11	9.23	1.95	NA	NA	0.14	-209	7.09	26.2	140.0
	10/14/04	107	16	NA	3,180.4	<0.10	19	3.1	0.11	NA	0.39	-65	7.02	23.5	510
	12/1/04	155	4.3	19	3,214.6	<0.5	7.3	0.9	0.060	<0.010	0.09	-2.0	6.84	20.8	341
	2/2/05	218	2.6	25	NA	<0.5	NA	NA	NA	NA	0.49	-45.2	6.30	17.2	154.4
	4/14/05	289	2.3	29	1,200.9	<0.5	12.3	0.9	<0.10	0.066	0.41	21.9	7.65	16.8	179
	6/23/05	359	4.9	39	4,442.4	<0.5	9.6	0.8	NA	NA	0.37	-123.1	6.46	19.4	149.9
PT-6	6/22/04	-7	2.2	14	<0.2	1.06	44.0	12.8	NA	NA	6.05	151	5.0	22.2	495
	8/5/04	37	14.8	NA	NA	NA	NA	NA	NA	NA	0.37	-180	5.99	21.2	528
	8/18/04	50	NA	NA	4.1	0.23	24.1	8.86	NA	NA	0.43	-181.5	7.06	26.5	167.0
	10/14/04	107	2.6	NA	122.0	0.87	16	2.0	<0.050	N/A	5.61	56.3	7.66	22.0	368
	12/1/04	155	1.6	10	493.1	<0.5	5.1	1.0	0.097	<0.010	0.08	26.5	6.20	19.7	272
	2/2/05	218	1.3	16	NA	NA	NA	NA	NA	NA	5.02	-112.2	7.23	16.1	128.8
	4/14/05	289	<1.0	15	490.6	1.6	10.1	1.2	2.6	0.11	1.09	11.4	7.92	17.8	134
	6/23/05	359	3.1	21	9,385.1	<0.5	9.6	1.2	NA	NA	1.32	-294.9	6.54	19.2	154.3
PT-8	6/22/04	-7	11	9.2	59.2	0.7	26.5	19.3	NA	NA	0.16	135	1.82	18.1	705
	8/18/04	50	NA	NA	5.1	<0.11	8.13	25.9	NA	NA	0.14	-213	6.61	24.9	525
	10/14/04	107	140	NA	1,874.6	<0.10	<5.0	17	8.4	NA	0.51	-111.3	6.20	21.7	923
	12/1/04	155	120	96	7,268.9	NA	NA	NA	11	5.8	0.02	-106.5	6.03	18.6	1085
	2/2/05	218	31	200	5,150.2	NA	NA	NA	25	16	0.08	-109.0	6.29	15.7	983
	4/14/05	289	40	250	9,621.9	<0.5	<0.5	9.7	25	23	0.10	28.1	7.12	15.7	1344
	6/23/05	359	2.4	390	14,540.2	<0.5	<0.5	10.9	NA	NA	0.08	-200.5	6.67	18.0	1142
MW-108	4/14/04	-76	2.06	NA	NA	1.94	NA	16.8	NA	NA	5.71	96.9	6.77	13.5	355
	6/22/04	-7	2.2	17	0.5	4.43	61.2	16.4	NA	NA	2.67	171	6.1	19.3	689
	8/5/04	37	177	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	8/18/04	50	NA	NA	121.0	<0.11	4.75	9.99	NA	NA	0.13	-178.5	6.31	26.0	539
	10/14/04	107	170	NA	4,583.0	<0.10	8.2	9.7	32	NA	0.46	-80.4	5.61	23.4	1,324
	11/30/04	154	91	110	3,751.6	NA	NA	NA	52	1.9	0.01	-91.4	6.10	18.0	602
	2/2/05	218	65	210	1,259.5	NA	NA	NA	54	6.6	0.11	-88.0	6.21	16.5	900
	4/13/05	288	37	190	6,998.0	<0.5	11.9	9.3	30	5.0	0.30	90.2	6.18	14.8	903
	6/23/05	359	84	220	6,104.6	<0.5	1.7	7.1	NA	NA	0.22	-246.7	6.56	19.4	974

NA = not analyzed.

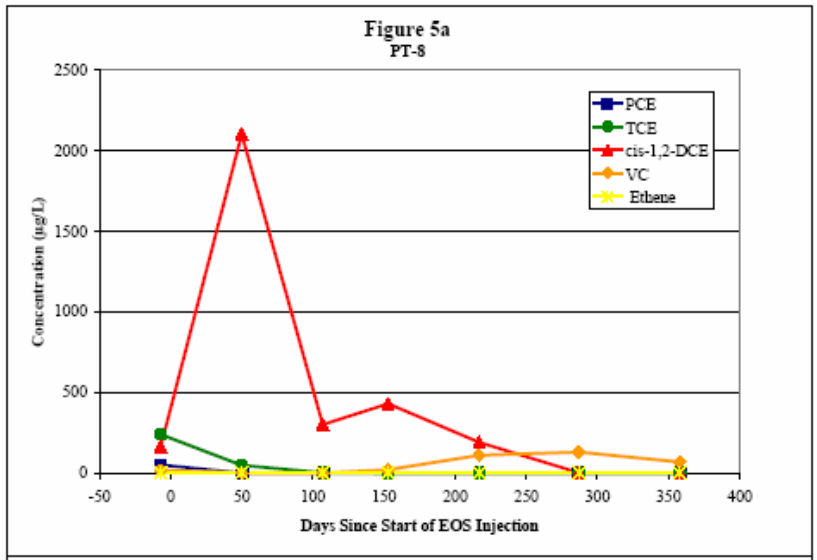
Table 7-2. Volatile fatty acids in groundwater

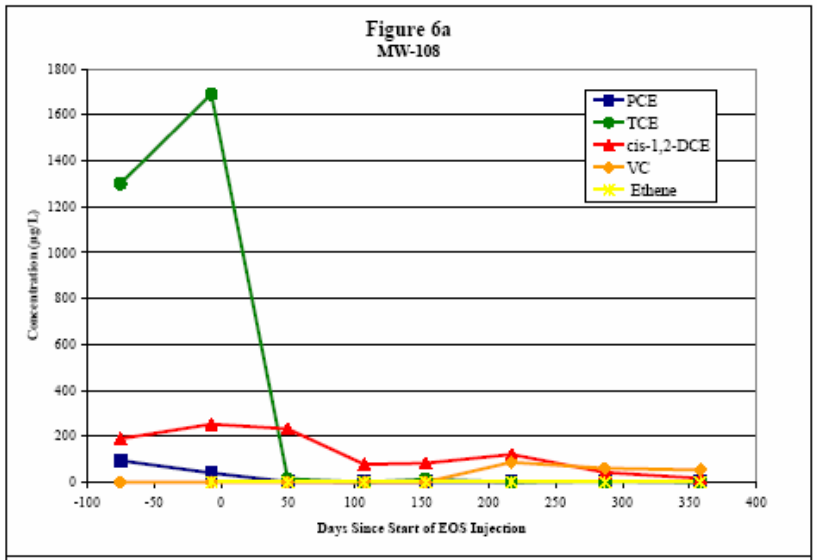
Well ID	Sample date	Days since start of injection	Pyruvic acid (mg/L)	Lactic acid (mg/L)	Formic acid (mg/L)	Acetic acid (mg/L)	Propionic acid (mg/L)	Butyric acid (mg/L)
PT-3	6/22/04	-7	<4	<1	<1	<1	<1	<1
	8/18/04	50	<4	<1	<1	<1	<1	<1
	4/14/05	289	<4	<1	<1	<1	<1	<1
PT-6	6/22/04	-7	<4	<1	<1	<1	<1	<1
	8/18/04	50	<4	<1	<1	<1	<1	<1
	4/14/05	289	<4	<1	<1	<1	<1	<1
PT-8	6/22/04	-7	<4	<1	<1	<1	<1	<1
	8/18/04	50	<4	<1	<1	40.8	13.8	<1
	2/2/05	218	<4	<1	<1	17.9	<1	<1
	4/14/05	289	<4	<1	<1	15.7	<1	<1
MW-108	6/22/04	-7	<4	<1	<1	<1	<1	<1
	8/18/04	50	<4	<1	<1	33.8	8.4	9.4
	2/2/05	218	<4	<1	<1	138.0	11.7	2.2
	4/13/05	288	<4	<1	<1	94.3	<1	<1

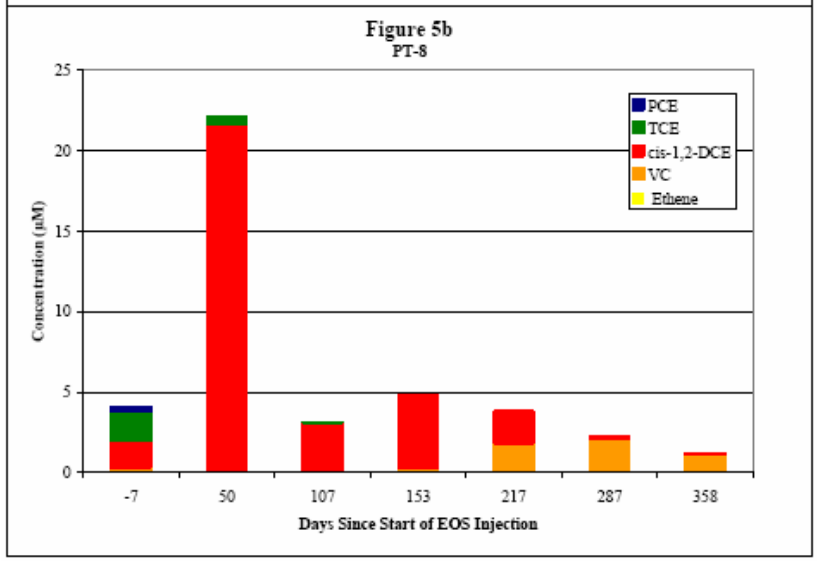


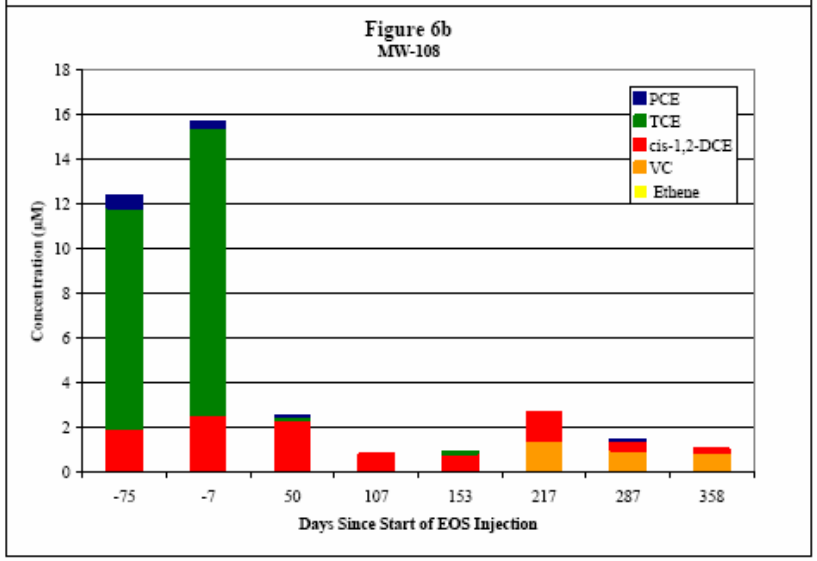


Figures 7-3 and 7-4. Monitoring well CVOC concentrations.









Figures 7-5 and 7-6. Monitoring well CVOC concentrations.

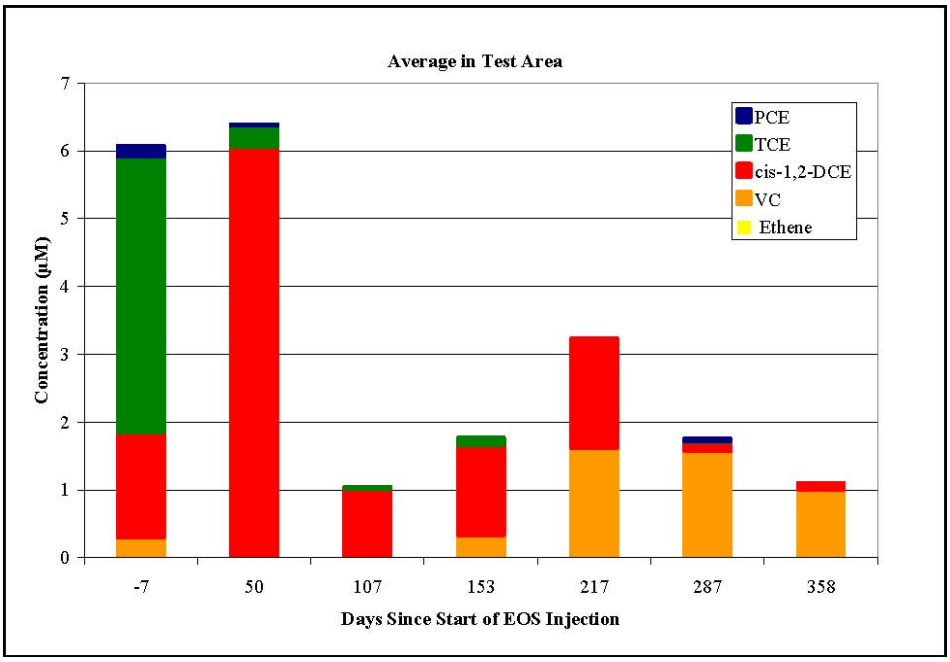


Figure 7-7. Average molar concentrations of CVOCs detected in the pilot test area during each monitoring event.

7.6.2 Effect of EOS on CVOC Sorption/Dissolution

During reductive dechlorination of chloroethenes, the more hydrophobic compounds (PCE, TCE) are sequentially reduced to *cis*-DCE, VC, and ethene. These reduced degradation products have a higher aqueous solubility and reduced tendency to sorb to aquifer material. As a consequence, the total chloroethene concentration (sum of PCE, TCE, *cis*-DCE, and VC) in the aqueous phase may temporarily increase as PCE and TCE desorb from the aquifer material and are converted to *cis*-DCE and VC.

When EOS is injected into an aquifer, the small soybean oil droplets rapidly attach to the aquifer surfaces. Partitioning of CVOCs between soybean oil and water is very similar to partitioning between octanol and water (Pfeiffer 2003). As a consequence, the increased amount of oil (organic carbon) attached to the aquifer material can increase the apparent sorption of CVOCs and reduce aqueous-phase concentrations. The impact of chlorinated solvent partitioning to the soybean oil can be evaluated using a retardation factor (R) approach where

$$R = \frac{\text{sum of aqueous phase and sorbed mass}}{\text{mass of pollutant in the aqueous phase}}$$

The retardation factor can be calculated as

$$R = 1 + \rho_B \times foc \times Kp/n$$

where

ρ_B = aquifer bulk density (g/cm^3)
foc = organic carbon fraction of the sediment (g/g)
Kp = octanol-water partition coefficient (mL/g)
n = porosity (mL/cm^3).

This approach assumes that oil-water partitioning is rapid relative to groundwater flow and that partitioning between the oil and water is approximately linear. Long and Borden (2006) found that the retardation factor approach provided a reasonably good approximation of chlorinated ethene transport in laboratory columns treated with emulsified soybean oil.

Table 7-3 presents estimated retardation factors for PCE, TCE, *cis*-DCE, and VC in the TAMP aquifer before and after EOS injection. Kp values were assumed to be the maximum values reported by Pfeiffer (2003). No data were available on the organic carbon fraction (foc) of the TAMP aquifer prior to injection, so a typical value of 0.001 g/g was assumed. The post-injection foc was calculated assuming the 21,120 pounds of injected EOS (9,504 pounds carbon in soybean oil) was uniformly distributed throughout the 100 × 100 × 10 foot treatment zone, increasing the organic carbon content of the sediment by 0.0008 g/g to 0.0018 g/g.

Table 7-3. Estimated retardation factors for different chlorinated ethenes

Comment	Preinjection	Post-Injection
Sediment bulk density, ρB (g/cm^3)	1.86	1.86
Porosity, n	0.3	0.3
Oil fraction (g/g)	0.0010	0.0018
PCE retardation factor (Kp = 1240)	8.7	14.8
TCE retardation factor (Kp = 338)	3.1	4.8
cis-DCE retardation factor (Kp = 61)	1.4	1.7
VC retardation factor (Kp = 26)	1.2	1.3

The analysis presented in Table 7-3 indicates that EOS injection will initially cause a small increase in partitioning of PCE and TCE to the solid phase. However, given the natural variations in contaminant concentrations, the expected reduction in aqueous-phase PCE and TCE may not be detectable. Over time, EOS addition is expected to reduce sorption by enhancing conversion of PCE and TCE to *cis*-DCE and VC.

Monitoring data collected over the past year were generally consistent with the analysis presented in Table 7-3. While TCE concentrations in some wells did decline following EOS injection, TCE concentrations in other wells increased, so there was little or no change in the average TCE concentration (Figure 7-7). It is not clear whether the declines observed were due to enhanced sorption or simply to redistribution of the dissolved TCE during groundwater recirculation.

Within a short time after EOS injection, average TCE concentrations declined with concurrent increases in *cis*-DCE, VC, and then eventually ethene. However, conversion of TCE to more reduced degradation products did not significantly enhance dissolution of sorbed TCE. This is consistent with previous monitoring results indicating the pilot test area did not contain substantial quantities of nonaqueous-phase liquid or sorbed contaminants. However, this area did

act as the primary source area for a 900-foot-long dissolved-TCE plume. Previous operation of an air sparging system in this area for over 10 years had been unsuccessful in reducing TCE concentrations.

Over time, the concentration of total ethenes (sum of PCE, TCE, DCE, VC, and ethene) in the injection and monitor wells has declined (Figure 7.7). The reason for this decline is not clear but could be due to oxidation and/or volatilization of *cis*-DCE, VC, and ethene or to migration of dissolved contaminants out of the pilot test area. In previous studies we have observed this same effect, where total ethene concentrations remain relatively constant or increase somewhat (due to enhanced dissolution) following EOS injection, then gradually decline as *cis*-DCE is converted to more reduced products (Lee et al. 2003, Zawtocki et al. 2004).

7.7 Summary

EOS was effectively distributed throughout the source area, resulting in successful treatment of CVOCs. The two-step process of dilute emulsion injection followed by groundwater recirculation effectively moved the emulsion throughout the targeted treatment area. Visual observation of water samples collected from MW-108 and from the pedestrian tunnel showed that it was possible to move the EOS more than 20 feet from the injection points. The low yield of the injection/extraction wells increased the time required to complete the injection and recirculation activities. However, most of the water recirculation process was performed unattended, and a portion of the EOS was successfully gravity drained into the injection wells, keeping labor and equipment costs low.

EOS injection quickly created anaerobic reducing conditions in the test area, as evidenced by decreases in DO, ORP, nitrate, and sulfate and increases in methane. The pilot test has effectively reduced concentrations of total CVOCs in the source area at TAMP and has stimulated anaerobic biodegradation of PCE and TCE to less-chlorinated daughter products. The interim remedial goal and the final remedial goal (the North Carolina Groundwater Standard of 2.8 µg/L) for TCE have been achieved. The final remedial goals for PCE and *cis*-DCE have also been achieved; however, VC concentrations remain above the North Carolina Groundwater Standard of 0.15 µg/L. VC concentrations appear to be decreasing. A final groundwater monitoring event is scheduled for August 2005, and further degradation of VC will be assessed.

7.8 Future Activities

Elevated concentrations of CVOCs also exist in the northwest quadrant of TAMP in the area where groundwater recovery is being used to prevent off-site migration of the plume. Based on the success of the EOS pilot test, the Army is considering performing an additional injection(s) of EOS within this area of the site. This would have the benefit of allowing the site to meet the 50% reduction of TCE concentrations as measured in the five compliance wells. The second benefit would be to enhance further natural degradation of the remaining (daughter) CVOCs to eventually meet the North Carolina Groundwater Standards. Using 2004 preinjection groundwater quality data for MW-108, the TAMP site scored 1 point on the BioScreen screening form. BioScreen was rerun on MW-108, after collecting groundwater samples in April 2005. Conditions in MW-108 now score 28 points, and there is strong evidence of reductive dechlorination. The additional injection(s) should also have the same effect in NW corner of the site.

7.9 Available Resources and References

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7.10 Reviewer Comments

7.10.1 Alec Naugle Comments

Introduction

There is no mention of the possible or likely presence of DNAPL or of vadose zone contamination until the very end of the summary. This information should be described up front in the introduction and SCM.

Site Conceptual Model

- Although outside the treatment area, there appears to be a second source location centered around MW-110. Discussion of this should be included or at least mentioned since it is prominently displayed in Figure 7-1 of the summary write-up. Also, Figure 7-1 labels the date of monitoring as April 2002, but the July 2003 report has the same figure labeled April 2003.

- What happens to the groundwater that is extracted for the pedestrian tunnel? Presumably, this water is contaminated and must be treated and/or disposed of.

- There is no cross-sectional figure showing the site geology, well depths and screen interval, TCE distribution with respect to bedrock or other transmissive zones, saturated thickness, and the water table. This seems like a major omission and as a result hampers a quick understanding of what's going on.

Bioremediation System Construction and Operation

This section states that monitoring was performed to confirm the need for bioaugmentation. Please discuss how this monitoring was conducted and what analyses were used. Were indigenous microbial populations evaluated? Were the "correct" microbes identified that would degrade *cis*-DCE and VC to ethene? Was there evidence of biodegradation of TCE to DCE, VC, and ethene?

Bioremediation Performance Monitoring

- The use of four wells to monitor the entire 100 × 100 foot test plot seems questionable given the demonstration nature of this project. Furthermore, three of the wells were also used for injection and recirculation, making them an easy target for the claim that the treatment cleaned up monitoring wells but maybe not so much of the rest of the plot. Was this

considered during the design? How was the decision made to use only four wells and to use the same wells used for injection/recirculation?

- A preinjection baseline concentration was not established within the test plot. I recognize that there is limited value to doing this since the recirculation would potentially redistribute the contaminants. On the other hand, this could have provided a good opportunity to better evaluate the average concentrations in the test cell for comparison after the test. Was this considered during design, and if so, why was it not done?

Performance Monitoring Results

The graphs in Figures 7-3 through 7-6 are very helpful. Please consider including the Phase 1 and 2 start and end dates along the x-axis. Three of the four monitoring wells show an increase in TCE/DCE immediately following treatment. I agree that this is likely an artifact of the redistribution of contaminants following injection/recirculation. However, could this also be evidence that an acclimation period was needed after biostimulation before degradation could occur? Figure 7-7 seems to support this idea since TCE was initially converted to DCE but stalled for a short period until concentrations later declined.

Effects of EOS on CVOC Sorption/Dissolution

- The first equation for retardation (R) will always result in a value that is less than or equal to 1. However, the second equation presented will always result in a value that is greater than or equal to 1. Please explain this discrepancy.

- Please discuss whether the increase in sorption due to EOS injection is beneficial to biodegradation or a hindrance. My understanding is that it is a benefit in that it brings the contaminant into contact with the aquifer materials, which is where the microbes are. However, at the same time it can result in lower aqueous concentrations, which makes it more difficult to evaluate.

- It seems to me that any time a recirculation system is used, it will not be clear if concentration changes (declines or increases) are due to enhanced sorption, increased dissolution (via biodegradation), or simply contaminant redistribution. It also seems to me that the only way to separate these effects is to better estimate the average concentration (or mass) in the source zone before and after the treatment. This would require a denser monitoring network.

- If previous findings demonstrated that there was no "substantial quantities of nonaqueous-phase liquid or sorbed contaminants," then that means most was in the aqueous phase. If that is the case, then it seems plausible that this biostimulation project (injection/recirculation of EOS) could have simply cleaned it all up, which is the simple explanation for why there was no apparent increase in TCE dissolution and why total ethenes declined. Since there was no estimate of the total mass or average soil/groundwater concentrations before and after the test, there is no way to know for sure.

- Was a decline in total ethenes expected after the test? If so, by what mechanism? As suggested above, one mechanism could be that the test cleaned it up. However, it seems that

there are also other competing forces, and it is not clear which is expected to be dominant. For example, adding EOS increases TCE sorption, thus reducing aqueous concentrations. At the same time, increased biodegradation can cause increased dissolution of TCE, higher concentrations of breakdown products, and perhaps even higher total ethene concentrations. A discussion and evaluation of these processes would be helpful.

- The semiannual monitoring report dated July 2003 by Weston Solutions shows that there were marked reductions in TCE levels in several wells from 1995 to 1998. It also shows that some wells had significant increases. What were these changes attributed to if not to SVE/AS or other remedial measures? Was this simply due to plume expansion?

Summary

- What effect did the treatment have on the larger plume? It would be helpful to include an evaluation of this larger effect in the discussion along with groundwater concentration maps showing the results.

- The EOS treatment appears to have resulted in meeting the groundwater remedial goals for the site, with the exception of VC. Further, it appears that EOS injection/recirculation was an effective method for biodegrading the residual TCE concentrations. Monitoring should continue to evaluate the long-term results and effect on TCE rebound concentrations and potential for buildup of DCE and VC. Future testing should attempt to evaluate the average concentration and/or mass in soil and groundwater before and after the test to fully evaluate performance.

7.10.2 Mary Jo Ondrechen Comments

Project Scale and Purpose

This is a pilot study where EOS was used to promote bioremediation of TCE DNAPL. This appears to be a fairly common type of DNAPL contamination site.

Site Conceptual Model

The sponsor has provided a detailed description of the site and its features, including the contaminant distribution, the site geology, and hydrology.

Remediation Goals

The sponsor describes precise goals for the reduction of TCE in the groundwater.

Bioremediation Performance Monitoring

The description of the monitoring is fairly good.

Effect on the Source Area

There does appear to be significant reduction of chlorinated ethylenes, although dechlorination is incomplete. VC concentrations do not meet standards.

Cost Information

No information was given.

Summary

Again, results of this study are encouraging. The sponsors have demonstrated reduction in the concentration of polychlorinated ethylenes. Again, I wonder about the cost of repeated EOS injections over the entire site. This appears to require on the order of at least a few years. Is this cost-effective? Can this process be scaled up to clean up the entire site and achieve complete dechlorination? Can VC be eliminated by this method?

7.10.3 Tom Early Comments

It is my understanding that the purpose of the case studies being collected by the ITRC BioDNAPL Team is to evaluate various bioremediation strategies that have been applied to DNAPL sources to accelerate dissolution/destruction and to determine whether this general approach has proven to be effective in terms of both performance and cost. Although the TAMP case study involves an area where groundwater clearly is contaminated with CVOCs, there does not appear to be confirmation that DNAPL was present in the project area at the time of the investigation. The highest dissolved TCE concentration in the study area (MW-108) was 1.9 mg/L prior to treatment, a value that is not clearly indicative of the presence of DNAPL. The summary also notes that prior AS/SVE remediation in the area has resulted in significant reduction in soil CVOC contamination since 1994. Consequently, ITRC may want to determine whether this project meets the basic objective of the case study exercise.

Project Scale and Purpose

The approach used at this site should be applicable to many other sites. However, as the distribution of an oil emulsion is required, it will be most effective in unconsolidated media that is sufficiently permeable. Its application to fractured rock or very heterogeneous unconsolidated media, where matrix effects can be significant, may be problematic.

Site Conceptual Model

There is a good summary of the site geology and hydrogeology. The presence of a significant saprolite zone above bedrock creates an interesting problem. Saprolites are highly structured and retain remnants of structural features such as bedrock fractures. As such, groundwater flow and contaminant migration in saprolite is very heterogeneous with narrow, preferential pathways. This feature also can impact the distribution of the emulsion. Of course, if the saprolite is highly fractured, it may behave more as a porous medium.

The discussion of the study area could benefit from inclusion of one or two cross sections to show lithologies, monitoring well completion, and groundwater levels. I noted that several cross sections are provided in one of the Weston reports.

The summary mentions several water/utility lines (buried?), a storm water sewer line, and a tunnel in the vicinity of the study area. Only the tunnel has been located on a map, and it appears to have some influence on groundwater. What about the other buried utilities?

The list of analytes monitored before and during the project is broad and appropriate.

Remediation Goals

There are two sets of remediation goals: interim and final. The interim goal for TCE (536 µg/L within three years) is achievable. The final goals are much more stringent and even below EPA drinking water standards for some analytes. These goals will be much more challenging, and meeting them probably will depend on favorable subsurface saprolite/soil conditions.

Bioremediation Performance Monitoring

The monitoring program for this project appears to be appropriate and includes primary contaminants, indicators of soybean oil breakdown, and parameters to assess the redox state of the aquifer system. It is not clear how long the emulsion is expected to persist in this environment (are there estimates based on other studies?). Therefore, the approximately one-year duration of monitoring may be insufficient to assess any potential rebound that will occur.

Apparently, the monitoring wells all are completed with 10-foot screens so that depth discrete samples across the saturated zone could not be obtained. Depth discrete groundwater samples can be very helpful when targeting zones for treatment and for assessing treatment effectiveness.

Effect on the Source Area

As noted under the general comments, it is not clear to me that a DNAPL is present in the treated area. Consequently, this project may not be a good example to include in the ITRC case study report.

Cost

No cost information was provided.

Summary

The first issue to resolve is whether this is an example of bioremediation of a DNAPL source. If not, or if the presence of DNAPL is questionable, then it might not be a good candidate for inclusion in the case study document. Nonetheless, the application of an oil emulsion to stimulate biodegradation is interesting and could be a very good alternative for remediation at many sites. Important information regarding the longevity of the emulsion in the aquifer and its adhesion to aquifer materials that helps the microdroplets resist being flushed out by groundwater flow can result from these types of investigations.

7.10.4 Nancy Kinner Comments

Introduction: Project Scale and Purpose

The TAMP site remediation with EOS is potentially applicable to other TCE-contaminated sites in the United States. The key question surrounding the use of EOS is the ability to move this substrate in the aquifer from the point of injection throughout the contaminated subsurface. Hydraulic control therefore becomes of paramount importance. While the issues of EOS movement, capture, and distribution and aquifer permeability are acknowledged in the

introduction, the case study would be well served by clearly stating the importance of aquifer hydraulics and its control in the effectiveness of this remedy. For example, the field pilot studies by Borden and Lee (2001, 2001, and 2003), cited as successful with respect to distribution, are not discussed in any detail with regard to hydraulics/aquifer characteristics, but success was very much a function of these aquifers' conductivities.

Site Conceptual Model

Figures 7-1 and 7-2 are very difficult to read. Figure 7-1 would benefit by being larger. The source treatment area is clearly shown, but there is no arrow showing the general direction of groundwater flow. The team provides a good description of the site geology and hydrology in the text, but the overall conceptual model would benefit greatly by including a section view of the aquifer showing the stratigraphy, well distribution and screening, and contaminant distribution. The team mentions that the petroleum hydrocarbons were remediated by previous treatment (SVE/AS). It would be helpful to know those levels prior to the start of EOS injection. The case study needs to include a preinjection conceptual model with respect to biogeochemistry. It appears that prior to injection TCE predominated (from Figures 7-3, -4, -5, -6 and -7) with some PCE (source?) and DCE. What does the team hypothesize was controlling (limiting) the biodegradation of TCE prior to injection of EOS (organic carbon/electron donor limitation)? Was the 1-11 mg/L TOC recalcitrant? Was the system oxic enough to prevent anaerobic bioremediation of TCE? The answer to all of these questions most likely is yes. It would be good to see a discussion of this as part of the preinjection conceptual model. The database provided for preinjection is one point (seven days before injection except for MW-108). Are more preinjection data available to make the case for whether TCE was mobilized in PT-6 and PT-8 (at Day 50) or just responding to the same history as the seven-day samples in the other wells?

Remediation Goals

These are clearly stated for the short and longer term (three years and ultimate goals). They appear measurable, but this is not totally known because the detection limits for the species are not stated, the time to ultimate treatment is not specified, and the extent of the groundwater management zone over which these criteria apply is not designated. The levels for PCE and VC are particularly low. It would be good to know the off-site aquifer concentrations of these species.

Bioremediation Performance Monitoring

The pilot scale site shown in Figure 7-2 as a plan view is hard to read. A section view should also be provided to show the stratigraphy, borehole screening, and relationship of the site to the tunnel. Injection of a conservative tracer along with the EOS could have been useful in understanding the site hydraulics. Unfortunately, this was not done. Could some substance naturally present in the groundwater be used in lieu of a specific conservative tracer? What was the dilution of the EOS, and why was this dilution selected? What was the desired mass loading of EOS per mass of CVOCs in situ? Were any sediment cores taken before/after injection to gauge the distribution of EOS in the sediments?

There is virtually no information given on the sampling methods used or the well construction. The analytical methods are not detailed either. (Several reports were provided with the case study as background, but it is not clear whether similar analytical methods were used or the well

characteristics were similar to those of the PT wells.) There did not appear to be any information collected on molecular biology or stable isotope ratios. The quality control criteria and detection limits are not presented, so one must assume the issues of detectable difference were not considered. Again, some acknowledgement of this would be helpful. Also, analysis of TOC can be done with ultraviolet persulfate or combustion, and each gives different types of information. How were DO and redox measured/calibrated? These are important facts to know to assess the value of the data presented. Finally, there did not seem to be any controls to show that the EOS was the sole source of the reduction in CVOCs and that no significant role was played by recirculation.

Effect on Source Area

The team starts by describing the transformation in the biogeochemistry of the pilot site (e.g., the change in DO, ORP, decrease in nitrate and sulfate, methanogenesis). The preinjection/post-injection conceptual model change is therefore very important. This argues for inclusion of some of the information discussed above in the conceptual model section. It also suggests that pre- and post-injection (section view) conceptual models (possibly with spider plots of the well data) would be helpful. What are the trends with Fe and Mn? Another way of examining the data would be to calculate degradation rates/half-lives that could be compared to the literature or other EOS-remediated sites. It would also be useful to know how well the redox data predicted the change in the biogeochemical regime, as a means for deciding the usefulness of this analysis.

The conclusions regarding the effect on the source area, as mentioned previously, would be strengthened by having more preinjection data to establish baseline conditions. What does the lack of VFAs in PT-3 and PT-6 suggest vs. PT-8 and MW-108? On a mass balance basis, was the amount of VFAs expected or are the values at this level because they are not conservative?

The decrease in TCE at wells MW-108 and PT-3 vs. the increase at PT-6 and PT-8 is discussed as a recirculation or enhanced sorption issue. This argument would benefit from use of a conservative (hydraulic) tracer or a discussion of the pilot site hydraulics (perhaps with an accompanying figure (the post-injection conceptual model) including the borehole screened intervals. If the boreholes were screened over wide intervals, how representative were the samples collected?

Figure 7-7 is the μM average concentration at the pilot site. Can any mass CVOC/volume aquifer be calculated with the data (with uncertainty bounds included). Did the μM data support the contention that TCE is mineralized to CO_2 as a result of the EOS injection?

Table 7-3 shows estimated retardation factors for the CVOCs. The uncertainty associated with these numbers should be included in the table.

Why did the team select 0.001g/g for the foc?

The study could have benefited greatly from including a few pre- and post-injection stable isotope ratios and from the use of a conservative (hydraulic) tracer.

Cost Information

No cost data were presented.

Summary

The EOS pilot project was interesting, but its application to other aquifers is not necessarily advanced by this study, where basic questions about hydraulics and cost and the effect of the EOS on enhanced sorption or redistribution did not appear to be addressed/ answered.

Questions for the team were incorporated in sections above.

8. SUMMARY

8.1 Credible Evidence for ISB of Sources

The primary question posed to the expert panel was, "Do we have credible evidence that bioremediation of chlorinated ethene source zones is a viable remediation option?" The conclusion of the panel was a unanimous, "Yes." Panel members indicated that the weight of evidence was "impressive" and the potential for this technology "exciting," particularly the potential for effective use in difficult environments such as fractured media. However, the panel did express some caveats.

First, they recognized that it is still early in the development of this technology, and the niche for this technology is not fully understood. Given the small number of case studies with appropriate data available to make this assessment, more experience is needed regarding the characteristics of sites where ISB is applicable. The panel's initial thoughts on where this technology might be appropriate are discussed further in Section 8.4.

Second, the panel noted some concerns about the potential for mobilizing nonaqueous-phase liquid during electron donor injections. From a regulatory perspective, they were also concerned about the potential for increasing overall risks due to partial degradation to more volatile, more mobile, and/or more carcinogenic intermediates. These concerns reinforced the panel's recommendation of having a buffer zone downgradient of the source area treatment zone.

Another primary comment from the panel was that much of the "credible evidence" is based on measurements of aqueous-phase concentrations. These measurements have inherent technical limitations, particularly for this technology, which has several interacting physical, chemical, and biological processes that can affect dissolved-phase concentrations. Similar issues for all DNAPL remediation technologies are discussed in a recent ITRC document *Strategies for Monitoring the Performance of DNAPL Source Zone Remedies* (DNAPLs-5, available for downloading in the ITRC Web site. The view of the panel was that monitoring for ISB of DNAPL source zones should progress to using other performance metrics in addition to groundwater concentrations where appropriate (e.g., soil concentrations, mass flux, etc).

A fourth caveat presented by the panel was that the overall impact of ISB of source zones on the restoration time frame is not clear. The primary reason for this uncertainty is that monitoring has

been done over relatively short time periods; therefore, the impacts on source and plume longevity are not well understood. Even for the case study with the longest data history (the INEEL TAN project at seven years), the impact of ISB on remediation time frame is uncertain.

Finally, the panel noted that a distinction could be made regarding the types of data collected and presented for ISB of source zone projects: data for presentation to regulatory agencies and the public and data for internal analysis and interpretation for managing the process. Some of the case studies reviewed for this forum were more research oriented, and as such had a wealth of data, including several innovative monitoring techniques. Some panel members commented that these data, while interesting, may actually hinder a regulator's or the public's understanding of the overall progress of remediation. They noted that, in these venues, more basic presentations may be more appropriate.

8.2 Major Issues

An important result of the Case Study Forum is a compilation of issues regarding the effectiveness, understanding, and acceptance of the ISB of chlorinated DNAPL contaminants. The major technical and regulatory issues raised are common to most in situ remediation technologies and result in part from the heterogeneity of the system and our inability to directly observe what is occurring in subsurface environments. Further complications and issues arise when the target of the remediation is a chlorinated DNAPL source zone rather than a dissolved contaminant plume. These issues need to be addressed in the process of gaining acceptance for this technology. Overall, the panel identified the following needs, which are discussed further below:

- developing an understanding of all processes affecting subsurface contaminant fate and distribution (physical, chemical, biological), including the effects of electron donor addition
- addressing uncertainty regarding the level of DNAPL source zone characterization required to apply ISB remedies effectively
- guidance on monitoring the technology
- consideration of remediation time frame when deciding between ISB and other source area remediation technologies

First, the panel expressed the need to develop an understanding of all physical, chemical, and biological processes that affect subsurface contaminant fate and distribution. In addition to biodegradation, there are a number of physical and chemical processes that can lead to changes in contaminant concentration in the aqueous phase. It is necessary to demonstrate the effectiveness of ISB in actually biodegrading chlorinated solvents to innocuous products, rather than physically diluting and/or displacing the contamination downgradient during electron donor amendment, transferring the contaminants to another physical state (e.g., volatilization), or partially degrading the contaminants to more mobile and/or toxic compounds (i.e., VC). Technically rigorous estimations of the rate and extent of biodegradation, which is correlated to the observed decreases in contaminant concentrations, is an important factor in demonstrating the efficacy of this approach. The inherent uncertainty and heterogeneity in biological systems can make this a difficult task, but the uncertainty involved needs to be estimated and considered when selecting a remedial technology.

The addition of electron donor is another confounding factor that can lead to changes in concentration for several reasons:

- Contaminants can partition into certain donors, causing decreases in concentrations.
- Surfactant/cosolvent effects of the donor can enhance dissolution and mobilize contaminants, causing temporary increases in concentrations
- Bioclogging of transport pathways by biomass growth and/or the production of gases can also change contaminant concentrations.
- Partial degradation can produce more mobile and soluble compounds.

The second major issue identified by the panel was the level of biological, geochemical, and DNAPL source characterization required for this technology. For chlorinated solvents, there is evidence that populations responsible for complete degradation to innocuous end products are not ubiquitous in aquifer environments. Therefore, guidance is needed on how to determine the potential for indigenous communities to biodegrade contaminants, which would affect decision making regarding the choice between a biostimulation vs. a bioaugmentation approach. In addition, current practitioners of ISB have differing opinions regarding the amount of biogeochemical characterization that needs to be done to select and design this remedy for a specific site. Some biostimulation methods are designed to overwhelm the existing aquifer biogeochemistry by adding many (50–100 or more) times the aqueous stoichiometric electron donor demand to create the appropriate conditions for anaerobic dechlorination. Other implementation strategies for ISB that add a much smaller amount of donor (5–10 times the aqueous donor demand) require a better understanding of the existing biogeochemistry before selecting and designing the remedy.

The nature and extent of residual and/or DNAPL contaminants in source zones also affects decision making for implementation of ISB. Adequate characterization of sources prior to implementing ISB requires more information than for more robust technologies not dependent on amendment distribution, such as thermal remediation. It is difficult to define how much characterization is in fact "adequate." An "observational approach" of ongoing characterization and treatment is therefore recommended. There was consensus among the panel that guidance regarding the types of site characterization necessary for technology selection is needed.

Third, in addition to guidance on site characterization needed for selection and design of an ISB remedy, the panel identified the need for guidance on monitoring during and following remedy implementation for process control, for confirmation of mass balance of contaminants and degradation products, and for confirmation of long-term performance. One specific concern was that due to a number of factors cited above, monitoring well data in and near source areas can provide misleading information on the progress of the remedy if they are not interpreted properly. It is very important that the limitations of relying on monitoring well data be recognized and the data interpreted accordingly. These issues are discussed in ITRC's *Strategies for Monitoring the Performance of DNAPL Source Zone Remedies.* In addition to the amount and types of data gathered, the length of time that monitoring will be required once active operations have ceased is not known. Monitoring may be required for long periods of time to ensure that conditions have equilibrated and that unacceptable rebound does not occur.

The final major issue identified by the panel was the fact that the overall remediation time frame for this technology is uncertain. The panel noted that time can be a critical factor in deciding whether to select this technology. The overall opinion of the panel was that ISB may take longer than more aggressive technologies but that it likely will be significantly faster than pump and treat. In addition, while ISB may take more time than more aggressive technologies, this may well be offset by the fact that capital and operating costs for ISB can be much lower than for other technologies. In this case, the end result is a lower life-cycle cost.

8.3 Lessons Learned

The panel was asked to summarize the lessons learned from the case studies presented during the forum and comment on their interpretation of the collective data set. The following key themes emerged in identifying areas of improvement:

- defining uncertainty associated with incomplete characterization of the environmental conditions that dictate biological performance
- defining the effects of biological treatments on DNAPL sources
- predicting treatment outcomes
- predicting and verifying the impact of ISB source zone treatment on achieving MCLs
- assessing the potential for adverse effects as a result of treatment
- selecting the appropriate electron donor(s) to use for site specific conditions and remedial objectives
- defining an appropriate level of monitoring to assess ISB performance

Addressing these topics will be important in the development, application, and acceptance of ISB for DNAPL source zone treatment and are discussed further below.

Application of ISB is dependent on the development and/or optimization of suitable environmental conditions that favor efficient biodegradation of contaminants. The heterogeneity inherent in most subsurface environments, however, makes difficult a detailed understanding of critical environmental design parameters, such as hydraulic properties, microbial diversity and activity, and contaminant distribution and architecture. In addition, given the general use of aqueous-phase groundwater data to monitor performance, the mass balances required to assess the fate of contaminants are generally poor, leading to some concern regarding the ability to fully understand the process involved and verify that remedial objectives are being met. While application of ISB can result in decreases in aqueous concentrations to near MCLs within the treatment area, none of the case studies were of sufficient length to present data showing maintenance of MCLs over the long-term following treatment or significant impacts to the site care requirements over the short term. The potential for source depletion is also not well defined, resulting in a general lack of understanding about remediation time frame. Therefore, decisions about the application of ISB are often made with an incomplete understanding of site conditions and/or uncertainties in the design and performance parameters, which in turn affects the ability to predict treatment outcomes.

The panel identified several other aspects of ISB that were not well understood. The panel was particularly concerned about understanding the potential for negative “side effects” of ISB. In particular, the accumulation of more toxic intermediates and the potential to enhance NAPL

dissolution, as was observed with some of the injection strategies presented, without subsequent degradation were discussed. In addition, the rationale behind the application of specific electron donors was not well defined in many of the case studies, resulting in confusion regarding how to select the most cost-effective electron donor for specific site conditions and objectives.

Among the case studies presented there were vast differences in the quantity, quality, and types of data that were collected. There were types of data that were consistent between the studies, but there was an apparent lack of consensus regarding the necessary analytes and data needs for selection, design, and application of the technology. In addition, many of the case studies had major data gaps that made interpretation of the data difficult. Therefore, defining an appropriate level of monitoring for a given site and remedial objective will be important in the future application of the technology.

8.4 Application Guidance

The ISB case studies illustrated relatively successful application of this technology to a variety of DNAPL-contaminated sites. However, the panel identified several issues that require guidance, regarding the applicability, implementation, and research needs specific to ISB in a DNAPL source zone. The panel identified areas where guidance would greatly advance the ability to apply this technology to contaminated sites, including the niche conditions where ISB would be best suited as a viable remedial technology; the development of an SCM that includes the hydrologic, geochemical, and microbiological parameters and the extent and fate of contaminants that determine success of ISB; the application of bioaugmentation; and the research needs that would greatly improve the state of the art.

Although EISB may be applied successfully at some sites contaminated with chlorinated solvent DNAPLs, the panel recognized the technology's limitations and identified key characteristics that might represent the niche for ISB treatment as a viable remedial alternative:

- relatively low-strength residual sources characterized by nonaqueous-phase contaminants present primarily at residual saturation levels with no massive DNAPL pools
- relatively homogenous and permeable subsurface environment that would facilitate amendment injection and distribution throughout the contaminant zone (it was noted that this could include some fractured rock sites)
- sites with relatively long remedial time frames amenable to the achievable rate of contaminant mass destruction
- sites with sufficient access to facilitate the required amendment injections
- sites with sufficient hydraulic capture and/or downgradient buffer zone to ensure that the treatment effects, such as production of dissolvent metals and/or partial degradation products, such as VC, do not impact potential receptors
- sites where cost is a major driver in the technology selection process

Collectively, these characteristics represent niche conditions where ISB may be applicable.

The panel also identified the need for guidance regarding the characterizing and monitoring environmental conditions that control the success of ISB. Groundwater hydraulics were identified as a key issue that affected all aspects of ISB from design of an amendment injection

system to monitoring and performance assessment. The ability to distribute injected amendments throughout the treatment area and control the environmental conditions required to facilitate biological degradation are dependent on the hydraulic conditions of the aquifer system. In addition, guidance on source zone characterization requirements prior to implementing ISB is needed. As noted above, adequate characterization of sources prior to implementing ISB requires more information than for more robust technologies such as thermal treatment. It is difficult, however, to define how much characterization is in fact "adequate." Based on information provided in the case studies, an "observational approach" of ongoing characterization and treatment was therefore recommended. In addition, guidance is needed on the quantity, quality, and types of monitoring data to collect to assess potential and performance of the technology. Specifically, innovative diagnostic monitoring techniques that are specific to performance of ISB, including compound-specific isotope analysis and molecular characterization, should be addressed. The applicability of non-technology-specific techniques such as flux monitoring and soil sampling to assess performance should also be considered. In all cases, the panel felt that molar mass balance data should be presented to assess the rate and extent of biodegradation performance.

The panel also expressed confusion about the decision-making process to guide the application of bioaugmentation. Therefore, guidance should be developed that details the sequence of steps required to make the bioaugmentation decision, including requirements for site assessment and details of cost/benefit analysis. This issue is discussed in a recent white paper prepared for ESTCP entitled *Bioaugmentation for Remediation of Chlorinated Solvents: Technology Development Status and Research Needs*. This white paper can be downloaded at http://docs.serdp-estcp.org/viewfile.cfm?Doc=BioaugmentationWhitePaper.pdf.

The panel provided some guidance that highlighted several research and development needs in the field of ISB for source areas as this technology is still considered an innovative and evolving technology:

- Efficacy for aged sources—Most source zones are decades old, and these aged sources are different from the fresh spills used in some of the research cases to date. In aged sources, much of the source material may be found in low-permeability zones, dissolved into matrix materials, and within the plume itself as a result of aging processes. Understanding the ability of ISB to treat contaminants in the less accessible areas that are more common in aged source zones should be an important research goal.

- Applicability for difficult sites—Some of the cases suggested ISB could be used for difficult sites, particularly fractured media. Treatment may be at the interfaces of the fractures, or some could be occurring within the matrix itself. Given the difficulty in evaluating performance within such difficult sites and the lack of effective remedial options, it is important to understand how well this promising technology can work in these environments.

- Impact of various electron donors—Varying donor amendments can have a wide range of biological, physical, and chemical impacts, and the properties of varying amendments can be quite different. To date, there is no guidance on which donors to use for specific site conditions or remedial objectives.

- Rigorous demonstrations—There is currently not sufficient information available on costs, performance, optimum operating conditions, efficacy in difficult environments, and the contributions of different processes (especially biodegradation). Careful field-scale demonstrations will be helpful in defending and improving this technology. In particular, long-term monitoring of performance is needed to understand the impacts over time.

9. SIMULATION AND OPTIMIZATION OF SUBSURFACE ENVIRONMENTAL IMPACTS: INVESTIGATIONS, REMEDIAL DESIGN, AND LONG-TERM MONITORING OF BIONAPL REMEDIATION SYSTEMS

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Abstract

The current state of practice described in the preceding chapters represents some of the most advanced deployments of bioremediation for DNAPL impacts in the United States. The examples consist primarily of a set of data models; that is, they basically represent a set of sites on which varying degrees of data and some qualitative or quantitative physics-based understanding is offered. During the course of the ITRC work on this report, questions of how to optimally design and operate a bioremediation system were repeatedly asked:

- How long will the bioremediation take remediate the site?
- What will it cost?
- Will remediation be complete (i.e., meet MCLs) everywhere?
- If only partial DNAPL mass removal is achieved, what will be the benefits?
- What will the DNAPL and dissolved plumes look like over time?
- What are the best design and operations parameters (materials to add, microbes to add if any, rates, concentrations, frequency of injections, etc.)?
- How can the impact and remediation best be monitored?

An integrated methodology for optimizing the responses to these issues is discussed here. This chapter addresses development of single source or integrated sitewide optimal design for environmental issues with focus on DNAPL contaminants and their natural or enhanced bioremediation.

It is important to note that "optimization" refers not just to cost minimization but also to the effective and efficient balance of cost, performance, risk, management, and societal priorities along with uncertainty analysis. This approach integrates all of these elements into a single decision framework, if desired. It provides a consistent approach to designing optimal solutions that are tractable, traceable, and defensible.

The approach is modular and scalable. It can be applied either as individual components or in total. By developing the approach in a complex systems framework, a solution methodology represents a significant improvement over the nonoptimal "trial and error" approach to environmental response(s).

How to Read this Chapter

The purpose of this chapter is to provide the reader with anywhere from a overview of modeling and simulation of bioremediation systems to a quite detailed discussion of the models, physics, numerical methods, and examples of codes that can be downloaded from developer sites. This chapter consists of several components:

- This text, which describes the overall simulation and optimization of modeling and optimizing bioremediation systems
- Modeling support appendix (see companion CD):
  - A presentation which illustrates all the methods discussed in this chapter
  - A report for the DOE-Pantex site discussing how to evaluate and select a numerical model for a complex site analysis such as bioremediation design, and an example of achieving unanimous stakeholder sign-off on modeling approaches
  - Additional helpful references

  In all, the CD provides more than 300 pages of information links to additional resources.

9.1 Bioremediation Physics Models

The subsurface environmental processes (physics) involved in subsurface bioremediation of DNAPL source zones described in the case histories are represented primarily by mathematical equations, primarily linear and nonlinear elliptic and parabolic equations (Charbeneau 1999, Ewing 1996). Charbeneau (1999) is especially helpful in providing numerous worked examples, spreadsheet calculators, and working models. These works, along with specific model documentation, illustrate the equations that describe—and the techniques that solve—the physics of the subsurface system, the partial differential equations.

"Subsurface models" are the computer codes that solve these equations by incorporating the aspects of the SCM to the extent practicable or desired. They use numerical methods including those for multiphase flow (water, soil-gas, nonaqueous-phase liquid [NAPL]) and multicomponent transport (e.g., volatile organic chemicals, geochemistry of bioremediation and MNA).

When the physics of the subsurface processes are only partially known or the model selected for the analysis does not have all the physics represented to solve the bioremediation design, equation writing tools such as genetic programming (Deschaine and Francone 2004) can be used to generate these functions, which can then be incorporated into the numerical models.

9.2 Subsurface Modeling and Design Optimization

There is a breadth of subsurface modeling and design optimization capabilities and experience available to investigators and practitioners of nonaqueous-phase liquid bioremediation projects. One can use case studies like those presented elsewhere in this document and infer what may happen at a site being considered for this technology, one can develop a site-specific model to quantify the potential site-specific effectiveness, or one can do both, which is the preferred method for complete and comprehensive understanding.

To manage expectations on what design modeling for bioremediation of NAPL (bioNAPL) can provide, it is important to realize that some sites are easier to model accurately than others. For example, simple first-order decay modeling, or even alcohol-assisted bioNAPL modeling, in a mildly heterogeneous porous media is relatively straightforward. An example is provided in the appendix. BioNAPL modeling in a highly heterogeneous aquifer including fractured media with matrix effects is not straightforward. An example of this is also provided in the appendix. In either case, collecting the data to determine the parameters of the model may seem overwhelming. National working groups are currently dealing with the issue of parameter estimation and uncertainty (http://www.iscmem.org). Most importantly, by understanding all the parameters needed to properly define the biophysics and their relative importance and comparing this knowledge to available site field data, one can quantify what is known and not known about the site and bioreaction process and rates, limitations, and sustainability. Upscaling issues of the biophysics and multiphase flow in highly heterogeneous materials is discussed in Ewing (2002). Extensive documentation of all the work is recommended since it can be such a multidisciplinary and complex undertaking. This quantification and information allow informed decisions to be made, even on projects with high degrees of uncertainty.

An effective approach to systematically assess the effectiveness of a bioNAPL design is to develop a "reference" model, an approach commonly used in earth sciences. The reference model may at first be a crude approximation of the real system. At this level of analysis, it acts as a guide to understand the systems and processes, as well as a communication tool. The effectiveness of the remediation can then be compared to the reference model and the value of various remedial approaches tested by relative comparison. This is done with the understanding that the model is representative but is expected to deviate from the actual field performance. These relative comparisons can provide a great deal of insight and help guide additional data collection and pilot studies to fill the key data/information gaps. As the model is developed, it transitions from guide to design tool(s) for predictions and use in optimal design calculations.

To implement a bioremediation design, we first present some modeling and optimization tools. Then we follow this with a proven approach for applying these tools to complex sites.

9.3 Modeling Tools

The industry standard tools as well as examples of some of the more complex codes that have relevance to the bioNAPL challenge are described below. Many models are available: what follows is a sampling of some of the more common or powerful ones. Space does not permit a thorough review of all the codes available for this type of project, and mention or omission of a code constitutes neither endorsement nor otherwise.

The companion CD includes a report (BWXT and SAIC 2002) that demonstrates proven comprehensive model selection for a complex site. This approach received unanimous sign-off from the stakeholder group. It is important that before selection or starting with any code, the objectives of the model calculations, limitations, and uncertainties be clear to the modelers and decision makers. This understanding helps to clearly manage expectations of the work, as well as retain knowledge of decisions as individuals transition in and out of stakeholder teams, which can be the case on the longer-term projects.

9.3.1 Groundwater

Here, the translation of the SCM is converted to the numerical model. This is an important step as it is where the solutions begin to be developed. They can consist of analyses using either analytical or numerical tools. Two excellent entry-level and useful books include Pinder (2002) and Charbeneau (1999).

For numerical modeling, the default industry standard is the U.S. Geological Survey (USGS) MODFLOW model code. This code has been around since the late 1960s, the original technology and code being developed by Dr. George F. Pinder. In the mid-1980s it was modularized and taught in the universities, and now, more than 40 years since inception, it has become the most widely used code for groundwater modeling. Many individuals have contributed to the technical advancement and popularity of the code over the years. It is well tested, verified, and documented, and it has graphical user interfaces developed by USGS and private parties that greatly facilitate its use.

MODFLOW is a groundwater model that solves saturated flow in three dimensions using the finite-difference method. This numerical technique has some restrictions with respect to how it incorporates geological geometry and parameters. It does not solve transport; rather, its flow field is used by many add-on model codes (as listed below) to solve the transport. The Princeton Transport Code (PTC), developed by Dr. Pinder, solves saturated flow and transport in three dimensions using finite elements, so it can handle more complex model geometries. Advanced codes, including BioFT3D and DOE-FEHM, can solve even more complex geometries and biophysics aspects of sites, including unsaturated flow. These are discussed below.

- Modpath: Particle tracker for MODFLOW.

- MT3DMS and MOC3D: Simple transport code for use with MODFLOW.

- BioRedox-MT3DMS and RT3D: Multicomponent transport package with MODFLOW; solves redox zone–specific natural degradation.

- BioFT3D: Saturated or variably saturated (Richards's equation) steady-state or transient coupled flow and transport in three dimensions using finite elements; solves level or undulating complex geologic systems, including transient perched aquifer behavior:
  - BioFT3D-path: Particle-tracking algorithm for BioFT3D, which correctly solves particle movement in complex subsystems.
  - Transport capabilities include single- and multiple-component organic or comprehensive metal/radionuclide systems in single- or dual-porosity systems. Biological reactions include first-order decay or monod kinetics.

- DOE-FEHM(N): Saturated or variably saturated (Richards's equation) steady-state or transient coupled flow and transport in three dimensions using finite elements; solves level or undulating complex geologic systems.
  - Particle-tracking algorithm solves particle movement in minor complex subsystems.

- Transport capabilities include single- and multiple-component organic or simplified metal/radionuclide systems in single- or dual-porosity, double-porosity/double-permeability systems. Biological reactions include first-order decay or monod kinetics.
- The effect of heating (non-iso-thermal) processes is accommodated.

Bioremediation of DNAPLs is described by multiphase processes. The above models treat the DNAPL portion of the problem as either a nonmobile source that depletes, or fluxes in the dissolved phase are computed and the DNAPL is assumed depleted by the modeler when the estimated mass (computed as total mass flux multiplied by time) is reached. These techniques are widely used in much of the reported literature.

9.3.2 Multiphase

The simulation of true three-phase (air, water, NAPL) systems is a complicated undertaking. This includes for example LNAPL or DNAPL in porous or fractured media above and/or below the water table and may include remedial designs such as air sparging or bioassisted alcohol flushing or heating. Code selection here is highly specific and may need either approximations or modifications to solve some of the more complex aspects or simulation/remedial design projects. Moreover, the efficiency of the bioremediation processes may not be well understood for the specific geologic media or mass distribution under consideration. The site project histories discussed in the preceding chapters are beginning to help quantify these aspects. Even these well-conducted studies have complications from the upscaling issues discussed above and in Ewing (2002). In lieu of specific knowledge with respect to the bioremediation process efficiency, look-up tables can be generated to show ranges in performance and costs using different assumptions on efficiency.

Codes typically used for the base analysis of a bioremediation design include the following:

- USEPA MOFAT (extended to SA_MAPS)
- USEPA NAPL (extended to bioNAPL to simulate microbe growth, oxygen depletion, and alcohol-assisted remediation)
- UTCHEM (University of Texas)
- TOUGH-2 family of codes (Lawrence Berkley National Laboratory)

As noted, various researchers have added advanced capabilities to the original models. These aspects and other approaches are the focus of current research efforts at SERDP and ESTCP.

Some of the basic and the more advanced multiphase codes require special training to correctly use and understand. The multiphase, variable saturated physics are much more complex than is saturated groundwater flow, described by MODFLOW or PTC, for example. Similarly, redox zone–dependent multicomponent transport is much more complex than an approach which uses a single component transport with a simplified single biodecay half-life and a Kd for retardation. Also, computer run times are longer as the complexity of the model increases for the same size numerical grid. Hence, the graded approach to solving site challenges is prudent, as discussed in BWXT and SAIC (2002).

To ensure the modeling work meets expectations, it is important that the skills of the modeling analyst and multidisciplinary team be consistent with the computations and analyses performed.

9.3.3 Optimization

During the ITRC meetings, the question was often asked how to design and optimize bioremediation systems. System design is handled by the modeling discussed above. The system optimization is discussed below.

For completeness, there is a current debate whether or not DNAPL source depletion is necessary, or if so, to what extent, vs. plume management (see EPA 2003 and Teutsch et al. 2001). This is not necessarily a binary (either-or) decision but can be a graded approach to DNAPL remediation. This then becomes an optimization problem. One of the issues in using active remediation is it often involves a high initial capital cost. Optimization consists of linking the above physics models with formal optimization algorithms to provide best designs. It is a matter of linking the optimizer with the physics model used on a project.

A well-conducted masters thesis (Smalley 1998) demonstrates the optimization of bioremediation designs. This thesis, "Risk-Based In Situ Bioremediation Design," uses a simplified physics model (Bio2D), geostatistics, a well-defined objective function (minimize the total present value cost of a bioremediation system), and formal linkage with an optimization method, a noisy genetic algorithm.

To wit, the approaches discussed below extend these concepts by including more powerful physics models and more robust optimization methods. They also solve different aspects of the challenge, including plume finding, source finding, and optimal long-term monitoring. Examples of tools used in design optimization include the following:

- plume finding: physics model (PTC) linked with Kalman filter and spatial information processing algorithm
- a source-finding algorithm being developed under the SERDP program
- long-term monitoring optimization: physics model (PTC) linked with Kalman filter and spatial-temporal information processing algorithms and a genetic algorithm
- optimal remedial design: physics model (PTC, FEHM) liked with optimization code (outer approximation algorithm)
- optimal pump-and-treat design: MODMAN, MODOFC, SOMOS

General optimization tools and methods used to solve these or similar types of design challenges include Lipschitz global optimization, DIRECT, the outer approximation and numerous evolutionary computation methods (genetic algorithms are one such method).

The field of design optimization is a large and dynamic growth area (www.informs.org). The above examples illustrate proven applications, some at the research level and some deployed at field sites. More and more, these tools are being developed and deployed. Optimization codes other then the ones listed above exist and can be used based on the project needs. Should optimization tools need to be linked with physics models not yet linked, that can be done as well.

Similar to the modeling skill set, it is important that the skills of the optimization analyst be consistent with the computations performed.

Development of numerical models is an active area of research. Hence, a review and available modeling packages is prudent at the start of any modeling project of significant size or complexity. By storing georeferenced information in a database, the input files for different models can be generated. This approach minimizes the costs of upgrading models as more complex simulations are needed and facilitates model input quality assurance/quality control functions (EPA 2002).

These tools can be used to design optimal bioNAPL responses as discussed in the above case studies, including MNA and incorporate pump-and-treat containment (with or without bioremediation) and/or can be used to develop provable technical impracticability zones within plume areas.

9.4 Modeling Approach

The above is an example of some of the tools in simulation and optimization. However, not each project needs all those capabilities brought to bear. A graded approach to solving challenges is often prudent, starting simply and adding complexity only when it will provide benefit to the project.

A key aspect of the modeling approach is the ability to obtain approval by stakeholder groups. One key example of success is the unanimous sign-off by the DOE-Pantex TAG team on the model approach, discussed above and included in the companion CD.

9.4.1 Simple Approaches

The simple approaches often consist of developing flow models in the widely used USGS MODFLOW modeling code. Particle flow paths and simplified transport analysis can be conducted with tools discussed above, among the simplest to use being MODPATH and MT3DMS. These codes, widely used and understood by many, are helpful in baselining the understanding of the subsurface system and developing the SCM(s). The solution obtained from MODFLOW may differ from the true field conditions when the problem is complex in geology and geometry. In these cases, the finite-element approach is more appropriate (Zyvoloski and Vesselinov 2006), such as implemented in the DOE-FEHMN and BioFT3D codes.

9.4.2 Moderate Approaches

A moderate approach includes cases where the flow is still fairly simple and saturated but the transport is more complex. This would be a multicomponent transport analysis that includes redox zone–dependent MNA processes. It is conducted in tools such as BioRedox-MT3DMS or RT3D, which are compatible with the USGS MODFLOW code. BioRedox, for example, solves for the redox zone (oxygen, nitrogen, iron, sulfur and methane) as a function of space and time and includes first-order decay constants linked to the ever-changing or steady-state redox zones in the system. The complexity arises in calibrating the model. For example, a redox zone dependent solution to the TCE degradation included at least 15 rates constants, five each for the

three major chemicals (TCE, DCE, and VC) in the five different redox zones, as well as the geochemical parameters in the aquifer and soil matrix. Other biogeochemical processes can be added, as needed.

9.4.3 Complex Approaches

These analyses are used when the complexity of the biophysics or hydrogeology overwhelms the simple approach's ability to be used as the final solution. This includes subsurface systems in which the unsaturated and saturated processes are important or where multiphase, multicomponent steady-state or transient solutions are needed.

A prime example of this type of challenge is the DOE-Pantex site. This project comprises a 17-square-mile, 1000-foot-deep volume that consists of an approximately 16BG perched aquifer overlying and separated from the regional Ogallala aquifer by an underlying secondary vadose zone (Stovall et al. 2004, provided on the companion CD). The three-dimensional Richards equation is solved using BioFT3D with completely transient flow. The chemicals are solved with coupled flow and transport such that the system is never, in reality or simulations, at steady-state conditions. It is one of—if not the—largest full-scale three-dimensional projects of its kind that is this far along. Another example of a complex analysis is a fractured/karst system where the diffusion into and out of the aquifer matrix is an issue and DNAPL is present. An example of this type of dual-porosity modeling analysis, which used the DOE-FEHM modeling code, is provided in the presentation on the companion CD.

DNAPL simulation is accomplished using the tools above, such as UTCHEM, USEPA NAPL or (BioNAPL), or others as needed. These comprehensive bioremediation applications which formally solve the DNAPL and multibiophysics are highly complex and project specific. The reader is referred to the model documentation to ensure the model is capable of solving the task at hand.

More formulations/approaches for solving complex sites are available than there is space to describe. If model formulations do not exist as needed for a project, they can be coded as needed. The "bio" portion of the USEPA NAPL code is an example of capabilities that were added to a public domain source code by a student to solve the microbe growth and decay due to alcohol addition in DNAPL zones.

Much research is constantly ongoing, and modeling codes are improved and expanded. It is prudent to review available codes and capabilities at the start of the modeling project and during them as these projects often take years to complete. By storing modeling information in georeferenced databases and or ASCII text files, new or advanced model codes can be implemented while not losing the previous work conducted with other codes.

9.4.4 Sampling and Design Optimization

Optimization is also used in designing the best plume delineation and long-term monitoring network, as well as the optimal design of remedial systems. The optimal monitoring well network tools use a stochastic representation of the groundwater model with the information from soil borings and monitoring wells and extended Kalman filtering. This is done to design

either the best investigative strategy for plume delineation ("plume finding") or the best long-term monitoring strategy.

The long-term monitoring strategy is similar in some concepts to the "plume finding" but formally includes the space-time correlation with the Kalman filtering to allow for the decay of information from a monitoring well as time passes (Deschaine 2003). Whereas the plume finding tools specifies the best location for the monitoring wells, the long-term monitoring tool specifies the sampling location *and* frequency to collect the samples.

Source finding solves the inverse challenge as plume finding in that the source location is identified with the least number of monitoring wells installed (SERDP project ER[CU-1347], in progress).

9.4.5 Summary

Whether the challenge is simple or complex, a graded use of models will develop a graded level of understanding for a site. Starting with simple approaches helps to identify and quantify data or information needs. Complexity and advanced calculations can be added as project needs dictate. Communication of expectations of modeling objectives and results along with the strengths and limitations of the analysis is key for success.

9.5 Limitations and Uncertainties

Model development and simulations will always have to some extent a degree of uncertainty. The uncertainty and sparse nature of information in earth science simulations sometimes necessitate stochastic—as opposed to deterministic—representations. The effectiveness of various bioremediation approaches also have a degree of uncertainty associated with them. Specifically, some of the key aspects of a bioremediation design may have significantly uncertainties:

- The SCM may be uncertain, and the site may have one or more SCMs proffered.
- Within an SCM, there can be uncertainties associated with geologic picks and material properties of the geologic units (such as hydraulic conductivities and unsaturated flow parameters, porosities, retardation), as well as uncertainty in model boundaries, aquifer recharge, gradients, future land-use effects, and the like. These properties can also change over time.
- The DNAPL source zone may not be known with certainty. This is particularly true of fractured systems. The DNAPL properties change over time as well.
- The hydrobiogeochemistry of the site may be known with limited certainty and can change over time. Aspects of key importance here include biological decay rates (first-order or monod kinetics); the geochemistry that enables the bioreactions to occur; the microbes, catalysts, and sustainability of the bioremediation processes, whether naturally occurring or engineered; and the like.

Documentation of model limitations and uncertainties—a tracking of all input parameters, as well as simplifications used in the model formulation—is needed (Helton et al. 2006, EPA 2002). Hence, the following statement from Helton is very beneficial to keep in mind when performing these types of complex analyses:

> Quality documentation essential: Not everyone will agree with what you did, **but** everyone should be able to know what you did.

This is the reality in modeling complex systems such as a bioremediation action in complex geology. (Helton is involved in the DOE Radioactive Waste Disposal project. The quotation is from his keynote presentation to the French Statistical Society, June 2006)

9.6 Examples of Bioremediation/DNAPL Modeling Presentation

A presentation addressing simulation and optimization of bioremediation systems was given at the Case Study Forum in March 2006. The six case studies were reviewed, and examples of how to solve them using numerical models was developed and assembled into the presentation, which is included on the companion CD. A full-size color print-out will facilitate following the discussion below. Since some of the simulation methods overlapped for each case history, they are presented as general approaches. Each case history was not specifically simulated; rather examples are presented demonstrating the methods and codes that are applicable. There is great benefit in knowing something can be done, and that path followed as warranted.

Slides 1–7. Introduction of the presentation, which is described above.

Slide 8. Example of one of the most complex coupled flow and transport projects in the United States. It solves the variable saturation (Richard's equation) for coupled flow and transport in three dimensions. It includes a large perched aquifer overlying a regional aquifer. The model code used is BioFT3D.

Slides 9–20. This work illustrates solving for the biochemical transport of multicomponent transport using a flow solution from the USGS MODFLOW model and BioRedox-MT3DMS. The biological system is modeled as first-order decay (half-lives), and the redox zones are computed—and vary—as a function of space and time. Each zone has its own half-life associated with it.

Slides 21–29. Here, a DNAPL release is simulated in an aquifer with two distinct hydrogeologic units. The upper is more permeable than the lower unit. The groundwater flows from left to right. This shows how the DNAPL can migrate downwards until reaching an aquitard. Note how it spreads out over the aquitard, even to the left, which is upgradient direction for the water flow. Simulator used is UTCHEM.

Slides 30–38. This example is similar to the above with the exception that the aquitard has preferential flow paths interspersed in it. It is clear how the DNAPL starts to migrate in a similar manner as the above (Slides 21–29) and that when the DNAPL reaches the aquitards, it flows downward. Simulator used is UTCHEM.

Slides 39–48. This set of slides shows the effect of various forms and configurations of DNAPL removal and the resulting change in concentrations in the groundwater, along with changes in mass flux from the DNAPL zone. These show how the geometry of the DNAPL removal and the percent DNAPL removed affects the performance of the remediation. Note that in some cases the bioremediation will increase the dissolution rate of the DNAPL. Simulator used is USEPA-NAPL.

Slides 49–53. This demonstrates the effect of microbes growth and decay when considering bioremediation. In the case studies, various amendments were used. In this example, alcohol was used. The results show the concentration of oxygen, microbes, and alcohol in the system. As in slides 39–48, the concentrations of TCE and many other outputs are available. Tools like these help the remedial designer answer the questions of optimal remedial design and performance monitoring. The simulator used is an extension of the USEPA NAPL code (BioNAPL) developed by Drs. Pinder and Mckay at the University of Vermont.

Slides 54–58. Some systems exhibit a dual porosity nature to them. These are sand/clay, fractured clay, or fractured rock systems. In these conditions, there is faster-moving water in the higher-permeability zones, and slower-moving water in the lower-permeability zones. When the bulk movement of the water from the high-permeability zones into the low-permeability zones (e.g., rock and clay matrices) is negligible, the movement of chemicals into the matrix is described by the diffusion process. This is known as the dual-porosity formulation. When there is nonnegligible movement of water in the matrix, then a double-porosity/double-permeability formulation is used. The slides show the results of the matrix effect in a fully three-dimensional double-porosity flow system. The DNAPL is assumed to dissolve itself out of existence in ½, 70, and ~3600 years. The time to reaching MCL in the fractures and matrix is provided. For large matrix blocks and long DNAPL times, the TCE can exist above MCL for thousands of years.

Slide 59. This slide summarizes that simple and complex flow is able to be simulated at the field scale. It also demonstrates that biological decay and bioremediation can be simulated using various approached including redox-independent first-order decay, redox-dependent first-order decay, or as a comprehensive NAPL/monod kinetics formulation. Hence, a graded/focused approach to simulating complexity is recommended.

Slides 61–60. These show examples of using genetic programming to develop the equation that describe the physics of a remediation process from pilot scale data if a numerical model does not exist. The equations can then be added to existing model code or used to develop one. See Deschaine and Francone (2004) for more information on this technique.

Slides 62–64. Optimization tools are useful in developing the best plans and approaches for finding plumes and source zones, as well as long-term monitoring programs and optimal remedial design of the bioremediation system. For the most part, they are model independent and can be made to work with any subsurface model.

Slides 65–73. Plume finding is the optimal estimation of the plume fringe(s) at a specified time. It is optimized by fusing geostochastic flow and transport simulations with the information content of data using a Kalman filter (McGrath and Pinder 1996). The result is an optimal

monitoring sensor network; the decision variable is location(s) of sensor(s) in three dimensions. In this example, the uncertainty (or value) of the existing monitoring well system is quantified, as is the value of a set of proposed new monitoring wells. One quickly sees the value of the existing monitoring well network is high, and adding additional monitoring wells reduces the uncertainty of the plume fringe only marginally.

Slides 74–75. Source finding is the optimal location of finding the DNAPL source. This is a project still under development under SERDP. The goal is to develop the best knowledge of source location, which directly relates to where to apply remedial action.

Slides 76–82. Long-term monitoring extends the plume finding approach and formally integrates the spatial-time correlations to optimize the decision variables of where to sample and when to sample over the project life cycle (Zhang and Pinder 2002). Optimization of location and timing of samples to meet the desired accuracy of temporal plume movement is accomplished using enumeration or genetic algorithms. In the plume finding, the uncertainty surface is driven basically to zero where the sample (monitoring well) is placed. With long-term monitoring, this uncertainty surface can begin to rebound as the information content of the sample gets less and less (decays) over time. When the uncertainty reaches a certain threshold, a sample is triggered, thereby reducing the uncertainty at that location to basically zero, as seen on Slide 80. Since this information propagates through the analysis and is remembered by the algorithm, the number of samples to achieve plume certainty decease significantly with time, as shown on Slide 81.

Slides 83–91. Optimal remedial design solves the multicomponent, multiphase system of equations and incorporates into solution design constraints on life-cycle costs, maximum annual costs, maximum allowable annual discharge (for assessing the MNA solution), and constraints on where remedial system component(s) can be located, including management overrides to force certain solutions to be chosen. It uses a suite of optimization techniques, including the outer approximation method (Karatzas and Pinder 1993, 1996), Lipschitz global optimization (Pinter 1996), and evolutionary algorithms. The automated optimal remedial design algorithm requires a stable simulator be available for the simulated process. This is commonly the case for all above specifications without true three-dimensional multiphase flow. Much work is currently being conducted in the industry to develop stable three-dimensional, three-phase simulators for the bioremediation simulations and predictions of bioDNAPL.

Slides 92–100. These slides discuss a formal approach for the optimization of a sitewide environmental remediation response. This formal, sitewide environmental impact remedial design optimization system forms a bridge between the "trial and error" or segmented approach and site remediation and treats the site response as an integrated system. Information needed to maximize the effective deployment of this tool includes the following:

- A mathematically correct statement of the flow properties of the aquifer. This model can be deterministic or stochastic.

- A mathematically correct statement of the transport properties of the aquifer, including the biogeochemical processes affecting them in space and time. This model can be deterministic or stochastic.

- An annual and project life-cycle cost function that represents both the capital and operational costs of the various remedial options under consideration.

- The constraints on the solution include the maximum desired annual costs, the limits on contaminant discharge or concentrations at point(s) of compliance, and the constraints as to where the remedial action can be physically located and where it cannot. Management overrides—specifying or prohibiting a remedial option at a specific source—are important and are accommodated by the tool.

The integrated optimization algorithm reads the above information and provides feasible and optimal or near-optimal solutions when all things are considered. The main technologies consist of genetic and other evolutionary computation algorithms, Lipschitz global optimization, the Tabu search algorithms, and Monte Carlo and Latin hypercube simulation algorithms.

The sitewide risk-based optimizer integrates the physics of flow and transport with the economics of project management. It uses the subsurface flow and transport models as subroutines, so it is physics model independent. The most suitable model can be chosen for the site/question, expanding the flexibility, adaptability, and solution correctness of the optimizer. Slide 96 shows the graphical user interface for the tool.

The algorithm links the science and economics, offering feasible solutions that allow for business, regulatory, physical, and social constraints. Specifically, these business algorithms provide the functionality to optimize the integrated sitewide remediation decision. Because each algorithm must be customized for a specific site, only a general description of the algorithm is possible. Such a description is provided below.

1. Using a suitable subsurface flow and transport model, develop a mathematically correct statement of the source-specific flow and transport system, as is, and predict future impacts if the contaminant is allowed to migrate unabated. This output can be the result of deterministic simulations (i.e., simulate one "best" aquifer) or of stochastic simulation of equally likely aquifers (i.e., use GSLIB to simulate the realizations of equally likely aquifers). Store these results.

2. Screen remedial options using standard European or EPA guidance, for example, and select the most likely options per source area if multiple sources are present. Perform value engineering on new or existing solutions, as appropriate. Assess whether the treatment effectiveness is known (deterministic) or estimated. If estimated, build an option-specific stochastic function. Store these results.

3. Assemble the cost constraints, which can be per source area, per year, or per life cycle. Assess whether the cost constraints are known or estimated. If estimated, build an option-specific stochastic function. Store these results.

4. Assemble the environmental and physical constraints. These constraints can be the point of compliance, cleanup level, discharge mass per year, or treatment system component location

and can be per source area, per year, or per life cycle. Assess whether the environmental constraints are known or estimated. If estimated, build an option-specific stochastic function. Store these results.

5. Assemble the management override constraints. These constraints are typically to force a certain remediation at one location or prohibit one at another and often relate to land use, for example, force capping on a land parcel for sale or prohibiting pumping and treating using vertical wells on an airport runway.

The current implementation of the sitewide optimizer uses a combination of optimization techniques (discussed below) and Monte Carlo and Latin hypercube simulation to optimize the solution under uncertainty. It designs and answers the following questions:

1. What is the least-cost solution to the site remediation? How does this solution vary if annual funding is constrained or changed?

2. How will the solution change if cleanup levels are relaxed, points of compliance are changed, or time to clean up varies? How will it change if various remedial alternatives are selected or deselected?

3. When multiple projects or opportunities for savings are present, which ones should be implemented first?

4. Given a desire to be 95% confident that a sitewide solution strategy will be protective of the environment and all constraints will be met, which course of action is best? How will this change if desired confidence is 90% or 50%?

A simplified version of this business process optimization algorithm was used to save an estimated $90 million over a five-year period (Deschaine et al. 1998). This optimization work, conducted at the DOE's Savannah River Site, received the National Performance Review "Hammer Award" in 1997. (Slide 95). An extended version of this algorithm was developed for energy systems and technologies research and development program design for DOE's Vision 21 Energy Development Program (Deschaine et al. 2001).

9.7 Value Engineering

Value engineering is used to specifically define the cost function(s) of the various site management options, including scope of investigation, remediation alternatives, and long-term monitoring. This consists of essential meetings with the various stakeholders to develop the goals of the management policy. The stakeholder group(s) heuristically optimize, to the extent practical, the decision components. This step is the precursor to the formal optimization and supplies the accreditation and facilitates acceptance of any optimal solutions developed. The investigation and remedial options are evaluated and using a combination of costs in the project databases or actual operation costs, a detailed cost matrix is developed. The cost function is developed so that changes in one aspect of a solution policy under consideration propagate throughout the integrated sitewide optimization system.

9.8 Life-Cycle Cost Function

The cost of the remediation project can essentially be broken down into two components: the capital cost and the variable or annual cost. There may or may not be a balloon payment at the end of the project, typically associated with final closeout proof and documentation. In the cost function discussed above, there are costs that the polluter pays and costs borne by society. The cost function is developed by an assembly of stakeholders who decide or negotiate which cost components are included in the analysis and optimization of the response policy. This work, which may not be a trivial exercise in many cases, allows for the flexible and comprehensive complete or partial analysis of cost functions.

The capital portion of a remedial design consists of the cost of the infrastructure, such as the treatment building(s), permits, and ancillary components. The variable cost portion (cost of operations and maintenance over the project life cycle) consists of such items as the recovery wells and pump systems; the pipe and trenching; and the cost of the cleanup operation, including system operation, maintenance, and environmental sampling. The total project life-cycle cost, which consists of both components, is the cost function that is optimized within the annual funding and other project constraints discussed above. The "balance" question is to decide which capital improvements to plume management to make when and when, versus costs for operations and maintenance. This is decided while recognizing that either action or inaction may have both economic and social costs when the total cost of plume existence is considered. With bioremediation, the challenge is which source(s) to treat and how aggressively to treat them.

The total cost of ownership is developed in the value engineering phase. In this phase, the stakeholders are assembled, and each aspect of the problem and potential solution is quantified to the best of the group's ability, recognizing and cataloging uncertain aspects. Solving for the optimal solution based on this quantification and acknowledged uncertainties is discussed below.

9.9 Pseudo-Code for the Sitewide Optimizer

The generalized pseudo-code for the optimization tool that incorporates the above is provided here as a guide on developing an optimal solution for this challenge. Each site will present its own unique challenge and hence its own sitewide optimization formulation. The following illustrative formulation provides a solid starting point for formulating and solving these challenges. It is an extension of (Deschaine 1992) as documented in (Deschaine 2003, 2004).

- Minimize total economic and social cost of plume presence
    - Total cost = f (investigation, remediation, monitoring reporting, administration, increase in health services, loss of recreational and other use, loss of natural resources, etc.).
- Subject to:
    - The risks to human health and the environment are within acceptable levels within the specified time frame and locations. This can be computed either as a deterministic or stochastic calculation.
        - ($C_{i,t}$*<$C_{i,max}$), concentrations $C_{i,t}$ for all spatial locations (i) within exposure time (t).

- The mass flux into receptors is less than assimilative capacity (natural attenuation) of the receiving system, such as a receiving surface water body or aquifer for the time frame considered. This can be computed either as a deterministic or stochastic calculation.
  - ($M_{i,t}$*<$M_{i,max}$), mass fluxes $M_{i,t}$ for all spatial locations (i) within exposure time (t).

- The annual costs are below a specific value for all time periods (t), either with 100% certainty or with certainty "D^*_{cost}"—for example with X certainty (such as 95% certainty) that all costs will be below budget in any given year.
  - ($D_{cost,t}$* [or the X^{th} percentile of $D_{cost,t}$*]<$D_{t,max}$), dollar requirements for all annual times (t).

- Experts' consensus expectation of success—either for a single remedial alternative such as bioremediation or a combined suite of alternatives—is greater than some minimum threshold success value "S_{min}," or with probability from subject matter experts P_{sme} that success not less than S_{min}. It is important to capture experts' expectation of a technology's success, either for a single remedial alternative such as bioremediation or a combined suite of alternatives or treatment train, at one or multiple interacting source areas. For example, one expert may rank a remediation approach as having a high probability of success, while another may rank it as more risky. These opinion(s) are retained as a distribution. Either the distribution of opinions is used directly, or the information can be consolidated into a single number via a form of averaging. The information or single number is then used to assess whether a potential remedial action solution's expected success is greater than the fixed minimum threshold remediation program success value "S_{min}." If the distribution of the experts' opinions—as opposed to a single value average—is used in the analysis, a stochastic analysis is performed. Great insight is seen in evaluating the distribution of independent expert opinions as well as collaborative opinions. The distribution of expert opinions is sampled using Monte Carlo or Latin hypercube sampling. Then, either the average or the number at a defined probability of the subject matter experts' estimate of remedial technology success P_{sme} will not be less than the minimum threshold for the remedial program S_{min}. For example, the decision maker may request design of the best remedial alternative program that, in the opinion of the remedial expert panel, will succeed with at least 75% probability and 95% confidence, but with no less than a 5% probability of the success being less than 80%. The risk-reward tolerance is accommodated. Different approaches can be developed for different risk-tolerant areas (see Deschaine 2001 et al. for details). This constraint balances the "risky" but potentially high-reward options with the tried and true methods. For example, a pump-and-treat system's effectiveness may be relativity easy to predict with certainty, but it may take an inordinate amount of time. Bioremediation may be more difficult to predict with certainty, but may be projected if it works to be 2–10 times faster than pump and treat. This is similar to balancing a portfolio of investments for highest safe return while minimizing the downside risk. Safe return is evaluated through the [$S_{min;}$ P_{sme}] arrays. For example, one may wish to set a constraint stating the value of the 25^{th} percentile of the selected portfolio of projects must be above some absolute downside value, below which the remediation program is deemed unsuccessful. Contingency planning to mitigate downside risk is captured at this stage. This captures

the certainty or uncertainty of the experts' ability to know a priori the success of the various site remediation management approaches.

- ($[P_{se}]>P_{sme\_min(i)}$ and 25th percentile $P_{se}>P_{sme\_min(j)}$)

Modifying a well-known and widely used decision support algorithm, the analytical hierarchy process to accept stochastic inputs, captures the experts' uncertainty. This allows constraints on the solution's downside even when great uncertainties exist on technological approaches. The Analytic Hierarchy Process algorithm is presented in Saaty (1996). Other useful methods and viable options to this approach to represent human behavior and include approximate reasoning, fuzzy logic, nonmonotonic reasoning, expert systems, reinforcement learning, and the like. The specific human behavior method is flexible in this tool so long as the results pass the Defense Modeling Simulation Organization requirements for validation of human behavior in simulations.

9.10 Summary and Conclusions

An approach for simulating and optimizing bioNAPL designs is presented, with examples. It provides a consistent approach to designing optimal bioremediation systems that are tractable, traceable, and defensible. The approach is modular and scalable. It is presented in a manner that can be applied either as individual components or in total. Very few sites will need this type of system deployed in total; many will benefit from focused use of the most pertinent approaches for the site under consideration.

As a final note, the modeling of bioremediation systems in subsurface environments is a complex undertaking. This is true whether performed in porous or fractured media. Expectations should be managed as to the accuracy of the predictions, with limitations and uncertainties clearly defined.

The question will certainly be raised with all this complexity, why attempt to model at all? This was well answered in 1980 by Dr. John R. Pierce, Bell Telephone Labs and the California Institute of Technology:

> Further, the programming of computers to solve complicated and unusual problems has given us a new and objective criterion of understanding. Today, if a man says that he understands how a human being behaves in a given situation or how to solve a certain mathematical or logical problem, it is fair to insist that he demonstrate his understanding by programming a computer to imitate the behavior or to accomplish the task in question. If he is unable to do this, his understanding is certainly incomplete, and it may be completely illusionary.

It is therefore critical—to ensure that bioremediation programs are designed, implemented, operated, and monitored correctly—that a foundation of mathematical understanding of their expected performance based on an understanding of the physics be achieved. This is realized through a combination of environmental sampling, bench and field pilot-scale tests, and predictive or comparison modeling. One of the values of simulating a natural attenuation or bioremediation system is quantifying which parts of the system are known and which are uncertain. This knowledge then may drive/focus the needs for additional data collection or testing until confidence in the approach applied to a various site is working is achieved.

9.11 Acknowledgments

A great deal of the insights for the physics modeling and optimization approaches discussed herein and in the references included on the companion CD were inspired by Dr. George F. Pinder and his students, for which the past 20 years of collaboration has been invaluable. The sitewide global optimization under uncertainty aspect of the work is part of my Ph.D. work at Chalmers University in Sweden. Dr. Ashok K. Katyal developed BioFT3D_Geochem family of models, which solves bioremediation designs in highly complex/heterogeneous environments and passed the harsh DOE-Pantex verification test. Dr. Melissa McKay developed the BioNAPL extension to the USEPA NAPL code as her dissertation. Sharad Regmi assisted by performing or checking many of the physics-based simulations shown in the presentation. A comprehensive list of professionals that have contributed to this simulation/optimization tool/approach is included at the end of the corresponding presentation on the companion CD.

9.12 References

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9.12.3 General References

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Appendix A

Example Letter to Reviewers

EXAMPLE LETTER TO REVIEWERS

Dear Reviewer,

On behalf of the Interstate Technology and Regulatory Council (ITRC) Bioremediation of DNAPLs (BioDNAPLs) Team, I would like to invite you to participate in our Bioremediation of DNAPL Case Study Forum on (DATE TBD) in (LOCATION TBD). Based on telephone conversations, you have agreed to be an expert review panel member and to provide us with your technical opinion related to the bioremediation of chlorinated ethene DNAPLs.

Enclosed, please find individual information packages for a total of six case study sites where bioremediation was applied to remediate chlorinated ethene DNAPL source zone contamination. The BioDNAPLs Team has selected three of these case studies for your detailed review and comment. The remaining three case study sites have been assigned to other expert review panel members. The three case studies specifically assigned to you for your detailed review and comment are:

1) Test Area North Site
2) Dover Test Cell Bioaugmentation
3) PCE DNAPL Manufacturing Facility

For each case study site, the enclosed information package includes the case study summary and any available background materials.

To maintain consistency among the expert reviewers, the Bio DNAPL Team has prepared a set of evaluation areas upon which to focus your review (please see attached). We ask you to provide your expert opinion related to these areas for each of your assigned case studies, as well as any follow-up questions you have for the case study site sponsors. We greatly appreciate your providing your written case study comments and questions via an electronic version to the address below no latter than November 7th, 2005.

During the forum, the case study site sponsors will provide overview presentations about each of the project sites (about 45 minutes each). Based on the written comments received from you and the rest of the invited expert review panel, the team will prepare and present an expert review summary for each site, as well as any questions raised by the panel. Following the presentation for each site, there will be open discussion, primarily among the panel members and the site sponsors, as well as additional participation from audience members.

During the first half of 2006, the BioDNAPLs Team will produce a technical case study document, using all of the technical information collected from the expert review panel's written comments and the forum discussions. The Team would welcome your review and comment on the draft of this document prior to publication.

On behalf of the BioDNAPLs Team, I would like to extend our deepest appreciation for your participation in our efforts to provide the environmental and regulatory community with the

latest on the bioremediation of chlorinated ethene DNAPLs. Thank you and we look forward to seeing you at the forum next (MONTH TBD).

Sincerely,

N. Akladiss

Naji Akladiss
ITRC BioDNAPLs Team Leader

Appendix B

Reviewer Case Study Focus Areas

REVIEWER CASE STUDY FOCUS AREAS

ITRC BioDNAPLs Team Case Study Evaluation Focus Areas for Project Summaries and the Expert Review Panel

The following areas of focus serve dual purposes for the Case Studies Forum. First, these areas will be described by each case study sponsor in a 12–15 page summary of his/her project that will serve as the centerpiece for the expert review panel evaluation and eventually as a key component of the BioDNAPL Case Study document. The project summaries will be sent to the expert review panel, along with appropriate supporting documentation.

The second purpose of the areas of focus is to provide topics that the expert review panel is asked to specifically address in its review. Specific questions for the panel could be developed for each topic if the team determines this to be appropriate.

1. Introduction: Project Scale and Purpose
   - The case study sponsor will state whether the project is pilot or full-scale. He/she will describe the purpose of the project, including whether it is being conducted for research/demonstration or if it directly supports restoration of a contaminated site. If applicable, he/she should also describe which information/approaches used in the case study are investigatory/R&D and which are practical tools/approaches that can be applied to other sites across the country.
   - Evaluation: This is mostly for informational purposes for panel members to understand the purpose of the project. Panel members are asked to evaluate the assessment of which information/approaches may be applied to other sites across the country.

2. Site Conceptual Model
   - The case study sponsor will present the site conceptual model, with the goal of communicating the degree of understanding of the subsurface for the area of the site where bioremediation is being conducted.
   - Evaluation: Panel members are asked to evaluate whether the degree of site characterization is sufficient for assessment of bioremediation performance, given the project purpose and remediation goals as stated above (research or pilot-scale projects may require more detailed characterization).

3. Remediation Goals
   - The case study sponsor will discuss the remediation goals that are to be met for the project. This may include a description of project phases and the associated goals for each phase. The sponsor will also state the regulatory program under which the project is being conducted. The role of the regulatory agency and any additional regulatory goals for the site will also be discussed.
   - Evaluation: Panel members are asked to evaluate the goals that have been set for the project and provide input as to whether they are measurable, realistic, and achievable.

4. Bioremediation Performance Monitoring
   - The case study sponsor will describe the monitoring program for the bioremediation project. This includes the number of locations sampled, frequency of samples, and the duration of data collection. It also includes the analytical techniques and parameters included in the monitoring program. The practicability of the monitoring program should be described in terms of which aspects are commercially available or can be easily adapted to other sites in a relatively cost-effective manner, if applicable.
   - Evaluation: Panel members are asked to evaluate the overall performance monitoring program for the project. They are also asked to evaluate the utility and value-added of innovative monitoring approaches that are being used at a site (e.g., carbon isotopes, molecular analyses, flux meters, etc.)

5. Effect on the Source Area
   - The case study sponsor will describe in detail the extent to which bioremediation is impacting the source area at a site, taking advantage of enhanced dissolution from the DNAPL or sorbed phase. Supporting data will be presented. Sponsors should also describe previous or concurrent remedial actions and their impacts to the source, if applicable.
   - Evaluation: Given that enhanced dissolution/increased solubility effects have been put forth as the primary reason to use bioremediation for source areas, panel members are asked to critically evaluate the magnitude of this effect.

6. Cost Information
   - On an optional basis, the case study sponsor may provide project cost information. If so, explanation about the context of the costs, underlying assumptions, or other qualifying information should be given.
   - Evaluation: Panel members are asked to critically evaluate the applicability of the case study project costs to other sites across the country.

7. Overall Summary
   - Case study sponsors will summarize the project, including current status, important achievements, and future directions, as well as approaches used in the case study that can be practically applied to other sites across the country.
   - Panel members are asked to provide an overall assessment of the project, in particular related to the goals and purpose. Panel members are also asked to comment on research and development aspects or new mechanistic knowledge that may be demonstrated by the case study. In addition, any comments that panel members wish to provide that do not fit in any other category should be communicated here. This could include questions that the panel members would like to ask of the case study sponsors in advance of the workshop.

8. Available Resources
   - Case study sponsors will list supporting documents that could be sent to panel members. These documents may include:
     - Sampling plan
     - Work plan

- Project reports that present results (i.e., reports prepared for funding agencies, annual results reports, etc.)
- Data validation reports
- Published articles for the site (if available for distribution)
- Any other information sources that case study sponsors could provide that may be useful for panelists during their evaluation

Appendix C

BioDNAPLs Team Contacts

BIODNAPLS TEAM CONTACTS

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Appendix D

Acronyms

ACRONYMS

AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
AS	air sparging
B.E.T.™	Bioavailability Enhancement Technology
bgs	below ground surface
bioDNAPL	bioremediation of DNAPL
bioNAPL	bioremediation of NAPL
BTEX	benzene, toluene, ethylbenzene, and xylenes
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CH	clay, high plasticity (Unified Soil Classification)
cis-DCE	*cis*-1,2-dichloroethene
CL	clay, low plasticity (Unified Soil Classification)
COC	contaminant of concern
COD	chemical oxygen demand
CVOC	chlorinated volatile organic compound
DCE	dichloroethene
DNAPL	dense, nonaqueous-phase liquid
DNTS	Dover National Test Site
DO	dissolved oxygen
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
ECOS	Environmental Council of the States
EISB	enhanced in situ bioremediation
EOS®	Emulsified Oil Substrate
EPA	U.S. Environmental Protection Agency
ERD	enhanced reductive dechlorination
ERIS	Environmental Research Institute of the States
ESB	Engineering Support Building
ESTCP	Environmental Security Technology Certification Program
FID	flame ionization detector
foc	organic carbon fraction
GAC	granular activated carbon
GC	gas chromatography
GRFL	Groundwater Remediation Field Laboratory
HRC®	Hydrogen-Release Compound
IFT	interfacial tension
INEEL	Idaho National Engineering and Environmental Laboratory
ISB	in situ bioremediation
ITRC	Interstate Technology & Regulatory Council
JP-4	jet propellant (specified by MIL-J-5624E)
K	hydraulic conductivity
LC34	Launch Complex 34
LNAPL	light, nonaqueous-phase liquid

MCL	maximum contaminant level
ML	silt, low plasticity (Unified Soil Classification)
MNA	monitored natural attenuation
MW	monitoring well
NAPL	nonaqueous-phase liquid
NFESC	Naval Facilities Engineering Service Center
ODEQ	Oregon Department of Environmental Quality
ORP	oxidation-reduction potential
OSU	Oregon State University
OU	operating unit
PCE	perchloroethene
PCR	polymerase chain reaction
PE	performance evaluation
PLFA	phospholipid fatty acid analysis
PTC	Princeton Transport Code
RAO	remedial action objective
ROD	record of decision
S	storativity
SCM	site conceptual model
SERDP	Strategic Environmental Research and Development Program
SITE	Superfund Innovative Technology Evaluation
SM	sand, silt (Unified Soil Classification)
SPME	solid-phase microextraction
SVE	soil vapor extraction
TAMP	Tarheel Army Missile Plant
TAN	Test Area North
TCE	trichloroethene
TOC	total organic carbon
trans-DCE	*trans*-1,2-dichloroethene
T-RFLP	terminal restriction fragment length polymorphism
TSF	Technical Support Facility
UST	underground storage tank
UW	University of Wisconsin
VC	vinyl chloride
VER	vacuum enhanced recovery
VFA	volatile fatty acid
VOC	volatile organic compound