ESTCP Cost and Performance Report

(ER-0008)



Biodegradation of Dense Non-Aqueous Phase Liquids (DNAPLs) Through Bioaugmentation of Source Areas - Dover National Test Site, Dover, Delaware

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
ASTM	American Society for Testing and Materials
¹² C	carbon-12
¹³ C	carbon-13
cells/L	cells per liter
cis-1,2-DCE	cis-1,2-dichloroethene
CO ₂	carbon dioxide
CPT	Core Penetrometer Testing
CSIA	compound-specific isotope analysis
DAFB	Dover Air Force Base
DCE	dichloroethene
DHC, <i>Dhc</i>	<i>Dehalococcoides ethenogenes</i>
DHG	dissolved hydrocarbon gases (e.g., methane)
DNA	deoxyribonucleic acid
DNAPL	dense nonaqueous phase liquid
DNTS	Dover National Test Site
DoD	Department of Defense
DO	dissolved oxygen
ECH	electrical conductive heating
EISB	enhanced in situ bioremediation
ERH	electrical resistance heating
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
EW	extraction well
FRTR bgs	Federal Remediation Technologies Roundtable below ground surface
g/day	grams per day
GAC	granular activated carbon
gpm	gallon per minute
GPR	ground penetrating radar
GRFL	groundwater remediation field laboratory
H&S	health and safety
IDW	investigation-derived waste
ISCO	in situ chemical oxidation
ITRC	Interstate Technology Regulatory Council
KAFB	Kelly Air Force Base

ACRONYMS AND ABBREVIATIONS (continued)

LS	lump sum
MCL	maximum contaminant level
μg/L	micrograms per liter
mg/L	milligrams per liter
mmol	millimoles
MNA	monitored natural attenuation
MPE	multiphase extraction
MTBE	methyl tert-butyl ether
NAPL	nonaqueous phase liquid
NETTS	National Environmental Technology Test Sites
NFESC	Naval Facilities Engineering Service Center
NPV	net present value
NTS	National Test Site
O&M	operations and maintenance
OM&M	operation, maintenance, and monitoring
OSU	Oregon State University
ORP	č
ORP	oxidation reduction potential
P/A	per annum
P&T	pump and treat
PAH	polycyclic aromatic hydrocarbon
PCE	perchloroethene (also termed tetrachloroethene)
PCR	polymerase chain reaction
ppb	parts per billion
PRB	permeable reactive barrier
qPCR	quantitative polymerase chain reaction
RNA	ribonucleic acid
ROI	return on investment
rRNA	ribosomal ribonucleic acid
RTDF	Remediation Technologies Development Forum
SCADA	supervisory control and data acquisition
SCIA	stable carbon isotope analysis
SEE	steam-enhanced extraction
SVE	soil vapor extraction
111 ТСА	1,1,1-trichloroethane
1,1,1-TCA TCE	trichloroethene
ICE	
USEPA	U.S. Environmental Protection Agency

ACRONYMS AND ABBREVIATIONS (continued)

VCvinyl chlorideVFAvolatile fatty acidVOCvolatile organic compound

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Since 1976, both perchloroethene (PCE) and trichloroethene (TCE) have been designated by the U.S. Environmental Protection Agency (USEPA) as priority pollutants. The Safe Drinking Water Act Amendments of 1986 strictly regulate these compounds; each has a maximum contaminant level (MCL) in drinking water of 5 parts per billion (ppb) (USEPA, 1996). Additionally, the U.S. Department of Defense (DoD) lists the following directives as high priority requirements:

- 1.I.01.g Improved Remediation of Groundwater Contaminated with Halogenated Hydrocarbons and Other Organics, and 1.I.01.j Improve Remediation of Sites using Natural Attenuation
- Army ER-1-02-02 Management and Remediation of Contaminated Groundwater
- Air Force: 2008, Methods and remedial techniques are needed to more effectively treat groundwater contaminated with chlorinated solvents such as TCE, trichloroethane (TCA), and PCE.

Due to the high costs remediating dense nonaqueous phase liquid (DNAPL) sources, technologies that can effectively treat the saturated zone resulting in destruction and containment, reduced treatment times, and lower costs are critically in demand. A significant number of DoD facilities have used chlorinated solvents as degreasing agents in the past. The estimated capital and operation and maintenance (O&M) cost of cleanup at each site is \$3.6 and \$3.5 Million (M), respectively (present worth).

Bioaugmentation is an in situ remediation approach where complete dechlorination of chlorinated ethenes is stimulated by supplying microorganisms that have demonstrated the ability to completely dechlorinate chlorinated ethenes in the presence of the appropriate electron donors and nutrients. Using either naturally occurring microorganisms or those added through bioaugmentation, enhanced rates of biodegradation at the DNAPL:water interface will increase the concentration gradient driving DNAPL dissolution. Increasing the concentration gradient will result in more rapid DNAPL dissolution and a reduction in the time required for cleanup. In the event that the increase in degradation rates is insufficient to significantly enhance DNAPL removal, rapid biodegradation of the high volatile organic compound (VOC) concentrations typically encountered in DNAPL source zones (e.g., tens to hundreds of milligrams per liter [mg/L]) will provide biological containment of the groundwater plume, thereby reducing cleanup times and/or reducing the O&M cost of conventional containment approach of pump-and-treat (P&T) systems.

1.2 OBJECTIVES OF THE DEMONSTRATION

The objective of the demonstration described herein was to evaluate the performance of bioaugmentation at field scale to enhance rates of biodegradation at the DNAPL:water interface, thereby increasing the concentration gradient driving DNAPL dissolution. This demonstration used PCE as the primary DNAPL in a porous media groundwater system and consisted of field

and laboratory investigations. The combination of these investigations was to determine if bioaugmentation can stimulate complete dechlorination to nontoxic end products, as well as increase the mass flux from a source zone when biological dehalorespiration activity is enhanced through nutrient addition and or bioaugmentation.

1.3 DEMONSTRATION RESULTS

The demonstration was able to prove that biological systems can be applied and promote enhanced dissolution of a PCE DNAPL source zone. To assess enhancement of mass discharge, two types of analysis were evaluated—the production of chloride and the production of daughter products converted to PCE equivalents. These two approaches produced a range in mass discharge increases ranging from 2.2 to 18.6. The most conservative value of 2.2 is calculated based on the increase in chloride ion observed at the extraction wells between the baseline and bioaugmentation phases of the experiment. When using the predicted PCE and the actual PCE equivalents (the sum of PCE and all of the degradation products produced from the PCE), the increase in mass discharge ranged from 4.4 to 18.6. Conservatively, we suggest that this study demonstrated an average increase in mass discharge ranging from 2.2 to 4.5 during the bioaugmentation phase relative to baseline (groundwater extraction only) conditions.

1.4 IMPLEMENTATION ISSUES

Through operation of this bioaugmentation system, we developed (a) an appreciation for the level of monitoring, parameters to monitor, sampling frequency, distribution or mixing of nutrients/microorganisms, and loading of nutrients that are necessary to apply bioaugmentation technology at other sites; (b) an estimation of the enhancement in the mass flux and the corresponding decrease in treatment time that ultimately justifies the selection of this technology as a source remediation alternative; and (c) rigorous operational and performance data that will encourage regulatory acceptance of the technology.

2.0 TECHNOLOGY DESCRIPTION

Bioaugmentation can be applied in a variety of configurations, depending on the site characteristics and constraints. An overview of how this technology was applied at the demonstration site is provided in the following sections.

2.1 TECHNOLOGY DEVELOPMENT AND APPLICATION

Conventional remediation technologies have emphasized treatment of the dissolved phase plume. While a number of plume management technologies, including P&T, air sparging, and permeable reactive barriers (PRB), have proven effective in containing plume migration, the low solute flux from many DNAPL source zones implies that operation and maintenance of the technology will be required for an indefinite duration ranging from decades to centuries (Johnson and Pankow, 1992). The presence of DNAPL at contaminated sites has been identified as one of the principal limitations to the effectiveness of P&T remediation (National Research Council, 1994) since the rate of mass removal is limited by the low aqueous solubility and the weak mixing effects of dispersion. Accordingly, much of the research in the last decade has emphasized the development of treatment technologies that aggressively remove or degrade the DNAPL in the source zone. Of particular interest are biological remediation approaches for chlorinated solvent contamination that use either aerobic or anaerobic degradation processes.

Aerobic processes require the addition of co-substrates and are often limited in the concentrations of VOCs that can be treated because of the solubility constraints of oxygen in groundwater and possible toxicity effects of intermediate compounds on the microorganisms. Anaerobic reductive dechlorination does not share these limitations and is more commonly used to degrade chlorinated solvents. Under anaerobic conditions, reductive dechlorination is a well understood degradation mechanism for PCE and the lesser chlorinated alkenes that may result in complete dechlorination to ethene and ethane. Reductive dechlorination involves the step-wise replacement of individual chlorine atoms with hydrogen atoms (Figure 1) where the chlorinated ethene acts as an electron acceptor while an electron donor is required to provide energy for this process (McCarty, 1994). Hydrogen is generally considered the direct electron donor for reductive dechlorination and is typically produced from the anaerobic oxidation of other carbon substrates, such as organic acids or alcohols (Maymo-Gatell et al., 1997).



Figure 1. Reductive Dechlorination Reaction Sequence for Chlorinated Ethenes.

2.2 PROCESS DESCRIPTION

For the purpose of this demonstration, the configuration in Figure 2 was selected. The main reasons for the approach were: (a) the demonstration was conducted within a test cell (Test Cell #1, Dover Air Force Base [AFB]); (b) the configuration provided controlled groundwater flow and well-defined contaminant distribution to allow for better data interpretation; and (c) recirculation of the groundwater provided better contact between the treatment agents (electron donor and dechlorinating bacteria) and the DNAPL. Other advantages included: (a) enclosing the source zone (emplaced 100L PCE) within an impermeable barrier wall contained groundwater flow within the treatment zone, and (b) the impermeable barrier wall ensured complete capture of the injected components (e.g., tracer, electron donor) and simplified the calculation of mass balances. The extraction wells serve to control and induce groundwater flow through the DNAPL zone, which allowed for better mixing and contact. Extracted groundwater was treated using a small on-site treatment system (liquid phase granular activated carbon [GAC]) to remove VOCs from the groundwater. Following liquid phase GAC treatment, the groundwater was amended with electron donors (e.g., lactate and ethanol) to stimulate the activity of the indigenous and/or bioaugmented microorganisms and re-injected, via the injection wells, into the test cell. Bioaugmentation was initiated once the appropriate reducing conditions were present in the aquifer.



Figure 2. Plan and Cross-Section View of Test Cell #1 Dover AFB, Dover, Delaware.

The approach used to meet the project objectives was to compare the mass discharge of VOCs from the PCE DNAPL under Phase 2/baseline conditions (extraction under enhanced pumping conditions/no amendments), to Phase 3/enhanced bioremediation (addition of electron donor), to Phase 4/bioaugmented conditions (addition of a *Dehalococcordes ethenogenes* [DHC] consortium) and Phase 5/bioaugmented conditions without the addition of electron donor. It was anticipated that the removal rate of PCE would be significantly higher during operational Phase 4 (bioaugmented conditions) than during the other operational phases. Further, the VOC mass discharge in groundwater was expected to be lower during Phase 5 (post-bioaugmentation—no electron donor addition) since the dehalorespiring microorganisms will degrade the chlorinated solvents at a lower rate due to electron donor limitations.

Prior to initializing operational Phase 2 (baseline), a tracer test was performed within the test cell to determine the hydraulic characteristics of the aquifer materials. Prior to initializing operational Phase 5 (post-bioaugmentation), a second tracer test was performed for the purpose of identifying possible changes in flow paths within the test cell. This comparison would help with data interpretation collected over the course of the demonstration.

Many operating parameters were maintained at constant set points in order to meet the demonstration objectives. The groundwater circulation rate was maintained at approximately 1 gallon per minute (gpm) during all the operational phases. The groundwater elevation within the test cell ranged from 15 to 17 ft bgs. Phase 2 of operations was initiated with the addition of a daily dose of electron donor (sodium lactate and ethanol) into the injection water stream. The time-weighted average of ethanol and lactate added to the test cell on a daily basis for Phases 2 and 3 was 60 mg/L and 24 mg/L, respectively. In Phase 4, the ethanol and sodium lactate addition schedule was decreased to one dose every two days in order to decrease the concentration of electron donor reaching the extraction wells and the rate of bacterial growth that was fouling the groundwater circulation system. Monitoring the performance of the demonstration consisted of scheduled groundwater monitoring and sampling (Section 3.5), as well as daily system inspections.

2.3 PREVIOUS TESTING OF THE TECHNOLOGY

Field evidence exists to suggest that microbial populations can exist close to DNAPLs and enhance dissolution rates (e.g., Major et al., 1995). Additionally, a growing body of laboratory evidence suggests microbial populations can degrade high concentrations of PCE and TCE (e.g. Yang and McCarty, 2000, and Duhamel et al., 2002). These studies involve column and batch tests where dechlorinating cultures were exposed to saturated or supersaturated concentration of chlorinated solvents. Yang and McCarty (2000) showed that PCE degrading microorganisms could completely dechlorinate PCE at concentrations up to the PCE solubility limit. The dissolution rate of the PCE DNAPL under these conditions was enhanced by ten to 14 times over baseline conditions. Recently completed field tests specifically designed to monitor biologically mediated enhanced dissolution of a DNAPL include Battelle (2004). These field tests demonstrated that the combination of biostimulation and bioaugmentation treatment can significantly decrease the total TCE and DNAPL mass in the target treatment zone. Through linear interpolation and kriging estimation of field-obtained data, the decline in TCE mass due to these treatments was estimated at an average of 99%.

2.4 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The main advantages of the technology are:

- It offers lower expected capital and operation and maintenance (O&M) costs than alternative technologies (McDade et al., 2005).
- Enhancing the dissolution rate of a DNAPL will decrease cleanup times.
- A source zone with a faster dissolution rate will cost less to contain from a long-term O&M perspective.
- Mass will be destroyed and not simply transferred to another medium.
- Expansion of a treatment area to include uncertainties related to the location of a source zone is unlikely to be difficult or significantly increase total cost.
- It can be applied at increased depths (below ground surface) and at lower costs than some comparable technologies.

The main limitations of the technology are:

- Like any source remediation technology there is a need to understand and identify the extent of the source zone and estimate the mass present in order to minimize the zone to be treated. Such an effort would require capital cost expenditures.
- A limitation of all source remediation technologies involves contacting the treatment with the DNAPL/source material. Specifically, for biological processes attempting to enhance the dissolution of the source, this could include limitations related to delivering nutrients and/or microorganisms to the source.
- Certain geochemical conditions (e.g., high sulfate/sulfide) may be inhibitory to biodegradation.
- Some co-contaminants may inhibit dechlorination (e.g., chloroform and hydrogen sulfide).
- Some common biodegradation daughter products can have higher solubilities than the parent products. With very high concentrations of chlorinated solvents, it is feasible that intermediate products formed may be toxic. This impact would be localized and likely transient due to the flux of groundwater through the source zone acting to dilute concentrations.

3.0 DEMONSTRATION DESIGN

3.1 PERFORMANCE OBJECTIVES

Performance objectives were used to meet the project objectives described in Section 1 and to evaluate the performance and cost of bioaugmentation. These performance objectives are provided in Table 1.

Type of Performance Objective	Primary Performance Criteria	Expected Performance	Actual Performance (Objective Met?)
Qualitative	Increase PCE degradation rate	Increase in degradation rate following bioaugmentation	Significant increase in PCE degradation over the baseline and post-bioaugmentation
	Increase extent of dehalogenation	Complete dehalogenation to ethane	Significant increase in ethane generation following a decrease in aqueous PCE concentration
Quantitative	Increased mass flux from DNAPL during treatment > after amendment with electron donor > after bioaugmentation	Increase in mass flux above the base case treatment ¹	No change in DNAPL flux during biostimulation. Large increase in mass flux from DNAPL post bioaugmentation
	Change in PCE mass flux	Decrease in mass flux following bioaugmentation	Large decrease in PCE mass flux post-bioaugmentation
	Reduce DNAPL mass	Reduction in DNAPL mass greater than base case treatment ¹	Uncertain. The young "age" of the PCE emplaced source and residual PCE in the unsaturated zone serving as ongoing source made for significant mass removal in base case. Bioaugmentation resulted in increased DNAPL mass removal compared to biostimulation.
	Decrease mobility of groundwater plume	Decrease in the steady-state length of the groundwater plume	Probably. Given configuration of test cell, this was not simply an extrapolation.

Table 1. Performance Objectives	Table 1.	Performance	Objectives.
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¹Base case treatment—operation of pilot system without addition of electron donor/nutrients or bioaugmentation

These performance objectives provide a basis for evaluating the performance and costs of the technology. Based on the laboratory and field studies conducted for this technology demonstration, the addition of electron donor alone was not able to stimulate the activity of the native microbial population. Bioaugmentation caused an increase in the PCE degradation rate and a corresponding increase in the extent of VOC dechlorination. A summary of the approach taken to assess the mass reduction/discharge from the laboratory experiments is provided in Appendix E and from the field demonstration in Appendix H of the Final Report for Environmental Security Technology Certification Program (ESTCP) Project Number ER-0008 (Naval Facilities Engineering Command-Engineering Service Center [NFESC]/Geosyntec, 2007).

3.2 SELECTING TEST SITE

The site selection screening process identified Test Cell #1 at Dover National Test Site (DNTS) at Dover Air Force Base (DAFB) as the most appropriate site for the demonstration. The test cell consists of a section of aquifer isolated by sheet piling (approximate dimensions of 28 ft x 18 ft), which is intended to contain controlled demonstrations of groundwater monitoring and remediation technologies. DNTS has an on-site analytical laboratory and water treatment infrastructure and held a regulatory permit allowing controlled releases into the test cells.

In addition to the degree of experimental control and the availability of infrastructure at DNTS, the project team was able to link this project with two additional research initiatives conducted by the University of Wyoming (Dr. J. Bradford) and Oregon State University (OSU) (Dr. L. Semprini). These projects focused on evaluating the DNAPL distribution using noninvasive techniques. At the initiation of these projects, the University of Wyoming research team released a known quantity of PCE DNAPL (100 L) into the test cell and used ground penetrating radar (GPR) to delineate the distribution of DNAPL. The OSU research team evaluated the use of radon as a partitioning groundwater tracer. The DNAPL release fulfilled one of the primary criteria in our selection process (i.e., a well-defined source location and mass estimate).

Test cell #1 at the DNTS provided a number of advantages, including:

- A controlled PCE DNAPL release inside a double-walled sheet pile test cell served as the DNAPL source.
- Site infrastructure for the demonstration was available.
- The water table and contamination are located at shallow subsurface depths below ground surface (approximately 12 ft bgs), which minimized drilling costs and provided better control of groundwater flow in the test cell.
- Both the regulators and the personnel at DAFB were receptive to the injection of microbial cultures and had previously approved the injection of electron-donors/nutrients into the subsurface.
- A known mass (100 L) of pure phase PCE was released into injection wells installed in the vadose zone (screened from 4 to 5 ft bgs) and the saturated zone (screened from 12 to 13 ft bgs). This DNAPL release was to enhance performance assessment (i.e., better mass accounting in the system in comparison to a site where the mass of DNAPL was not well defined).
- DNTS has a CPT rig for on-site investigative activities and provided access to data collection and on-site analysis, thereby reducing costs or allowing for additional sampling.

3.3 TEST SITE/FACILITY HISTORY/CHARACTERISTICS

The field demonstration was conducted in test cell # 1 located at DNTS (formerly known as the Groundwater Remediation Field Laboratory [GRFL] National Test Site [NTS]). DAFB is located three miles southeast of Dover, Delaware (population 50,000). DNTS is located within DAFB and covers approximately 3.5 acres in an unused, maintained open area in the northwest

corner of the base. The locations of DAFB, DNTS and the proposed test cell for this demonstration are shown on Figure 3.



Figure 3. Locations of Dover AFB and The Test Cell at DNTS, Dover, Delaware.

DAFB began operation in December 1941, at the site of the partially constructed Dover Municipal Airfield. At this time, the airfield was leased to the U.S. Army Air Corps for use by the Eastern Defense Command as a coastal patrol base. In early 1942, the facility expanded to make the airfield more suitable for heavy aircraft. In August 1943, the mission of the field changed to an operational training base for combat training of fighter pilots. It also became the site for the development of air-launched rockets. The base was deactivated in September 1946 and periodically used by the Air National Guard for training exercises between 1946 and 1950. In July 1950, the base was reactivated and designated DAFB.

DAFB is underlain by sediments of Cretaceous to Recent age, forming a wedge of sediments, which thickens to the southeast. The Pleistocene Columbia (1 million years ago) and Lynch Heights (500,000 years ago) Formations form a water table aquifer in the area. 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, and 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 from 20 to 28 ft beneath the base of the Columbia Formation. The Frederica aquifer is a 22-ft thick fine sand unit within the Calvert Formation that lies approximately 66 to 88 ft bgs. Beneath the upper sand unit is a middle silt and clay unit with a thickness of greater than (>) 80 ft. It is unlikely that sediments deeper than the middle silt and clay unit of the Calvert Formation were of concern at the demonstration site.

Beneath DAFB, the aquitard thickness ranges between 18 and 28 ft (average of 22 ft). The estimated range of the vertical hydraulic conductivity of this unit is 2.7×10^{-8} to 1×10^{-7} centimeters per second (cm/sec) (Leahy, 1982). Regional water supply aquifers in the DAFB area include the Piney Point, Cheswold, Frederica, and Columbia aquifers.

3.4 PHYSICAL SETUP AND OPERATION

Prior to initiating the demonstration, a number of pre-demonstration tasks were completed to collect essential data required to effectively implement this technology demonstration. Complete details of these tasks, which included predesign laboratory studies including microcosm and model aquifer testing, Phase 1 test cell investigation and controlled DNAPL release are presented in the Final Report for ESTCP Project Number ER-0008 (NAVFAC-ESC/Geosyntec, 2007).

As shown in Figure 2, this technology demonstration involved the installation of three fully screened groundwater extraction and three groundwater injection wells, a groundwater circulation and VOC treatment system with automated control system, a network of 13 multilevel monitoring well locations, and four fully screened bioaugmentation wells. There was a total of five operational phases of the technology demonstration. The description and lengths of time for the different phases of operation are presented in Table 2:

Phase of Operation	Description	
Phase 1 – Design, Installation,	- Installation of equipment	
and Tracer Testing	 Perform tracer test to determine the hydraulic characteristics of the aquifer materials 	
Phase 2 - Baseline	- Extracting the contaminated groundwater	
	- Removing VOCs (GAC system)	
	 Re-injecting the groundwater into the test cell 	
Phase 3 - Biostimulation	 Similar to Phase 2 with the amendment of electron donor (ethanol and sodium lactate) prior to re-injection 	
Phase 4 - Bioaugmentation	- Similar to Phase 3 with the test cell bioaugmented with KB-1	
Phase 5 – Post-Bioaugmentation	- The source zone was flushed with groundwater	

	Period of Operation		Total Number of
Phase of Operation	Start	End	Days
Phase 1 - Design Installation and Tracer Testing	1-Apr-01	24-May-02	418
Phase 2 - Baseline	25-May-02	25-Feb-03	276
Phase 3 - Biostimulation	5-Mar-03	16-Jul-03	133
Phase 4 - Bioaugmentation	18-Jul-03	4-Mar-05	595
Phase 5 – Post-Bioaugmentation	11-Mar-05	26-May-05	76

3.5 SAMPLING/MONITORING PROCEDURES

The sampling procedures carried out for this technology demonstration were in accordance to that outlined in the demonstration plan. Table 3 presents a summary of the sampling activities completed for the demonstration. During each phase, groundwater samples were collected from the test cell in tracking the concentrations of the VOCs, dissolved hydrocarbon gases (DHG), volatile fatty acids (VFA), anions, and DHC. Weekly samples were collected from the three extraction wells and from the treated groundwater in order to assess the mass discharge from the test cell and to ensure that VOCs were effectively removed from the injection water by the GAC treatment system. Snapshot sampling events were scheduled at varying intervals within each operational phase of the demonstration to gain detailed information regarding the effectiveness of the technology across three transects within the test cell. The timing of each snapshot sampling round was scheduled based on the VOC concentration in samples collected from the extraction wells in previous months and on the availability of the on-site laboratory. In January 2004, a sampling plan was developed to include quarterly sampling events from all sample locations for analyses, weekly samples for VOC analysis and bimonthly samples for VFA and DHG analyses from the extraction wells. This was adjusted on June 4, 2004, to weekly collection of groundwater samples from the extraction wells for analysis of VOCs, DHGs and VFAs.

3.6 ANALYTICAL PROCEDURES

The analytical procedures chosen were standard U.S. Environmental Protection Agency (USEPA) or American Society for Testing and Materials (ASTM) methods. Several analytical methods were used in assessing the performance of the technology: gas chromatography with mass spectrometer or flame ionization detector for VOCs and DHGs, respectively; ion chromatography for anions and VFAs; inductively coupled plasma for iron and manganese and 16s ribonucleic acid (RNA) for molecular characterization. Complete details of the analytical methods, including the applicable method number and analysis information, used during the demonstration are presented in Appendix B of the Final Report for ESTCP Project Number ER-0008 (NAVFAC-ESC/Geosyntec, 2007).

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

Table 3. Summary of Sampling Schedule

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

4.0 PERFORMANCE ASSESSMENT

4.1 PERFORMANCE DATA

As presented in Table 3, the extraction well data was collected on a frequent (weekly) basis while the multilevel piezometer data was typically collected on a quarterly basis. Supporting information for the data analysis and interpretation is provided in the Final Report for ESTCP Project Number ER-0008 (NAVFAC-ESC/Geosyntec, 2007). These include: Appendix H (Measurement of Solute Mass Discharge) and Appendix K (Laboratory Analytical Results and VOC Trend Plots).

Figure 4 presents the ratio of each chlorinated ethene to the total ethenes in the groundwater collected from the extraction wells over the demonstration. As described in Section 2.2, a GAC system was used to remove VOCs from the extracted groundwater prior to re-injection. This process did not treat the ethene present in the extracted groundwater. The influent samples (after GAC treatment) were used to correct for ethene in the groundwater. The correction of ethenes was explained in Appendix H (NAVFAC-ESC/Geosyntec, 2007). Figure 5 presents the mass discharge for each phase using data collected during the major sampling events. Figure 6 presents the cumulative mass extracted over time, as PCE in kg. Close examination of the mass removal (Figure 6) indicates that the removal rate increased following the establishment of effective biodegradation (i.e., during Phase 4, or approximately after Day 440 of operation). However, it is difficult to quantitatively estimate the total enhancement using just the mass extracted. This is due to several reasons, including changes in the flow system and the mass of PCE within the test cell. Additional evaluations using both VOC trends at the extraction wells and chloride ion production were completed to evaluate performance (see Section 4.4).



Figure 4. Proportion of Total Ethenes in Extracted Groundwater. Note: Proportion of Total Ethenes corrected for ethenes present in injected groundwater



Figure 5. Mass Discharge by Phase Calculated from Data Collected During Major Sampling Events.

Notes:

(1) Not corrected for ethenes present in circulated groundwater

(2) Mass removal based on data collected from multilevel piezometers and extraction wells during major sampling rounds completed in each phase

(3) Mass removal calculated as the geometric mean of PCE and PCE degradation products as PCE equivalents in grams (see Appendix H for more details)



Notes: As calculated from VOC measurements at the extraction wells, corrected for ethene recirculated, as applicable

Molecular analysis was used to provide semiquantitative estimates of *Dehalococcoides* species (using the DHC-polymerase chain reaction [PCR] assay) and population densities in the source area. The results (Figure 7) show that a dechlorinating culture could be established in a source area. After bioaugmentation, samples were collected to quantify the numbers of dechlorinating organisms present within the test cell. These results clearly show that the nondetectable to low population of *Dehalococcoides* species determined during baseline operations increased to 10⁵ cells per liter (cells/L) one month after bioaugmentation and increased to a maximum population of 10⁹ cells/L five months later. The distribution of *Dehalococcoides* was also relatively uniform throughout the test cell and demonstrated that dechlorinating organisms were not impacted by the presence of PCE DNAPL. The development and eventual commercialization of the quantitative polymerase chain reaction (qPCR) method was of benefit to this project.



Figure 7. DHC Quantitative PCR Results over Time at Select Sampling Locations.

Overall, bioaugmentation was required to promote dechlorination of the PCE to cis-1,2 dichloroethene (cis 1,2 DCE), vinyl chloride (VC), and ethene. The rate of mass discharge increased during bioaugmentation but was limited by biofouling and/or bioclogging; the

biofouling occurred as a result of electron donor addition and eventually caused the flow paths within the test cell to change, and the electron donor was no longer being delivered to those zones with significant amounts of residual PCE (i.e., the uppermost saturated portions of the test cell). The post-bioaugmentation period, where no additional electron donor was amended but groundwater circulation continued, could be characterized as being a time when PCE concentrations at the extraction wells steadily increased (suggesting that the biodegradation rate decreased such that PCE was again reaching the extraction wells).

Although data interpretation was complicated by a loss in permeability in the test cell, this technology demonstration provided evidence of increased PCE degradation following bioaugmentation, as well as complete dechlorination to ethene during both bioaugmentation and post-bioaugmentation. Table 4 compares performance during the demonstration to the expected performance originally anticipated.

4.2 **PERFORMANCE CRITERIA**

The performance of the field demonstration was evaluated using the general performance criteria provided in Table 1. Qualitative and quantitative criteria are classified as either primary or secondary performance assessment criteria, respectively.

The primary criteria constitute the performance objectives (previously presented in Table 1) of the technology demonstration. As stated in Section 1, the general objectives of the demonstration were to enhance the dissolution of the DNAPL source and to contain down-gradient migration of contaminated groundwater by increasing the rate of biodegradation within the source zone. In general, the performance criteria were used to evaluate these objectives by:

- Quantifying the effect of the technology on the mass discharge from the source zone
- Quantifying the effect of the technology on VOC degradation rates
- Assessing the potential benefits of bioaugmentation
- Determining the ability of the added microbial consortia to colonize the source zone
- Evaluating the difficulty in implementing this technology at field scale.

	Performance Expected Performance Confirmation				
	Criteria	Performance Metric	Method ²	Actual	
	Qualitative				
	PCE degradation rate	Increase in degradation rate following bioaugmentation	Interpretation of trend and distribution of VOCs, ethene, and Cl ⁻ in groundwater	Evidence of increased degradation following bioaugmentation; however, data interpretation is complicated by a loss in permeability (biofouling) in the test cell as described in Section 4.1. Between Phases 2 and 4 there was an increase in daughter production from 2 to 278 millimoles (mmol)/day. There was no difference in production of daughter products between Phases 2 and 3.	
	Extent of dehalogenation	Complete dehalogenation to ethene	Analysis of groundwater samples for PCE and PCE daughter products, and stable carbon isotope analysis (SCIA) signature	Complete dechlorination to ethene observed during both bioaugmentation and post-bioaugmentation phases. SCIA analyses at late time indicate PCE dissolution had occurred in some locations within the test cell.	
V	Duration of remediation	Remediation endpoint (e.g., 5 µg/L achieved faster	Interpretation of trends and distribution of VOCs, ethene, and Cl ⁻ in groundwater	Evidence of increased degradation rate following bioaugmentation however data interpretation is complicated by a loss in permeability in the test cell. Data from the chloride mass balance suggest a two-fold increase in degradation; other data (from transects) suggest possibly as high as 4.5 times increase in daughter products from the addition of electron donor.	
ERI	Quantitative				
ITI	Mass Flux from DNA	i			
PRIMARY CRITERIA	1. After amendment with electron donor	Increase in mass flux above the base case ¹ treatment	Measurement of the concentrations of VOCs, ethene, and Cl ⁻	The base case mass flux was elevated over expected amount due to how recently the DNAPL had been released; if the early time data, while DNAPL was still mobile, is not included in the analysis, then there was an increase in mass	
	2. After bioaugmentation	Decrease in mass flux of chlorinated VOCs relative to base case ¹ treatment		discharge (30 grams per day [g/day]) above the biostimulation phase (67 g/day) during the bioaugmentation phase (97 g/day). Chloride results (NAVFAC-ESC/Geosyntec, 2007) indicate that mass discharge increase as a result of biodegradation processes was measured by an increase of chloride (12 kg) between the biostimulation and bioaugmentation phase. During bioaugmentation phase, 4.5 times more daughter products were extracted compared to PCE (22 vs. 4.5 g/day)	
	DNAPL mass	Reduction in DNAPL mass greater than base case ¹ treatment	Mass balance based on the estimated PCE mass flux	There was a significant decrease in PCE DNAPL mass at the extraction wells between the base case (biostimulation—56 g/day as PCE and more than 98% of the mass extracted was as PCE) and the bioaugmentation phase (5 g/day as PCE with this being less than 20 % of the total mass extracted; the remaining 80% was TCE, cis-1,2-DCE, VC, and ethene).	
	Mobility of groundwater plume	Decrease in the steady- state plume length	Calculated based on simulated steady-state plumes using degradation rates estimated with from VOC, geochemical, and SCIA results	Results suggest that steady state plume had not been reached, even during biostimulation and bioaugmentation phases. This suggests that predicting a decrease in steady state plume may not yield meaningful results. The SCIA results (measured by a stable PCE parent isotope signature) indicate that PCE indicative of a source zone persisted in most of the monitor locations for the duration of the test.	

Table 4. Expected Performance and Performance Confirmation Methods.

Table 4. Expected Performance and Performance Confirmation Methods. (continued)

	Performance	Expected	Performance Confirmation			
	Criteria	Performance Metric	Method ²	Actual		
	Oualitative					
	Microbial activity in source zone	Increase in the concentration of biomass and the extent of colonization of source by bioaugmented consortia	DGGE and DHE analyses and molecular probes to identify bioaugmented consortia	There was a large increase in biomass throughout the test plot as evidenced by the PCR Gene Trac analysis in Table K4 of Appendix K of the Final Report for ESTCP Project Number ER-0008 (NAVFAC-ESC/Geosyntec, 2007)		
	Factors Affecting Performance					
SECONDARY CRITERIA	1. Location and amount of biomass injected into test cell	Mobility of biomass may be limited in porous media; accumulation of biomass in the source zone preferred	Experience from operation of demonstration; collection of samples for microbial characterization. This demonstration found increased biomass at extraction wells (reductions in well yield).	Groundwater results (VOC and PCR Gene-Trac) suggest that biomass developed throughout the test cell. The proximity to DNAPL was not investigated through soil sampling.		
	2. Location and concentration of electron donor injected into test cell	Electron donor may be preferentially consumed by biomass without stimulating dehalogenation of chlorinated ethenes	Experience from operation of demonstration; collection of groundwater samples and analysis of electron donor concentration. Results from the demonstration showed the electron donors were detected in most (>80 %) of the sample points. PCE degradation products were also observed in a majority of sample locations.	The injection technique was able to distribute electron donor throughout the test cell. Biofouling within the test plot and injection wells interfered with the distribution of the electron donor and negatively impacted performance.		
	3. Geologic heterogeneity	Low permeability may limit the delivery of electron donor and biomass to the source	Experience, i.e., visual confirmation during daily operation of the demonstration and tracer testing.	Tracer test indicated that there was some variability within the groundwater flow paths within the test cell that were attributed to geologic heterogeneity and would have affected electron donor distribution during the early part of the demonstration.		
	Ease of Implementation	Operator training required	Experience from demonstration operations	Acceptable—operator training was successful with minor expense.		
	Safety 1. Personal protective equipment	PPE Level D required	Experience from operation of demonstration	No health and safety incidents occurred.		
	2. Chemical hazards	None expected	N/A	Ethanol (electron donor) is a flammable substance. Review of storage and volumes stored should be completed prior to electron donor selection.		
	Maintenance requirements	Replacement of tubing in peristaltic pumps; frost protection; adjustment of injection level control system; replenishment of amendments	Experience from demonstration; evaluation of maintenance records	See Appendix I of the Final Report for ESTCP Project Number ER-0008 (NAVFAC-ESC/Geosyntec, 2007) for Summary of Operations, which details O&M activities. In general, for this demonstration the maintenance requirements were more than expected, but this was due to the nature of the test cell. Specifically keeping the water table within a 1-ft interval took effort. This would not be required at other sites. Equipment wear/tear/replacement was as expected.		

1				
	Performance	Expected	Performance Confirmation	
	Criteria	Performance Metric	Method ²	Actual
	Quantitative			
CRITERIA	Achieve appropriate redox conditions	Anaerobic and reducing groundwater in test cell	Field measurements of dissolved oxygen (DO) and oxidation/reduction potential	Appropriate redox conditions achieved. During bioaugmentation phase, conditions ranged from sulfate reducing to methanogenic (-50 to -250 mV).
	Process waste	GAC vessels disposed of by DNTS	Experience from operation of demonstration	Minimal
	Reliability	Fraction of time system is shut down (zero flow)	Evaluation of system operational records	Moderate—some system shut down time due to biofouling and operations, see Appendix I (NAVFAC-ESC/Geosyntec, 2007).
1	Hazardous materials generated	None	Analysis of groundwater samples for PCE daughter products	No hazardous materials generated other than the production of temporary degradation intermediate daughter products (cis-1,2-DCE and VC) as PCE is

converted to ethene.

Table 4. Expected Performance and Performance Confirmation Methods. (continued)

Notes

SECONDARY

The base case condition consists of flushing the source zone with unamended groundwater; the rate of DNAPL removal is analogous to remediation using pump and treat.

² All chemicals and microbial analyses were performed using the sampling and laboratory methods and QA/QC protocols described in Appendix A and B (NFESC/Geosyntec, 2007)

DGGE – Denaturing Gradient Gel Electrophoresis

DHE – Dehalococcoides

4.3 DATA ASSESSMENT

The total mass of PCE removed from the test cell, via groundwater treatment means, was estimated to be 77 kg. Of this 15 kg as PCE was estimated to be degradation products, which is supported by the chloride mass balance. Overall, bioaugmentation was required to promote dechlorination of the PCE to cis 1,2 DCE, VC and ethene. The rate of mass discharge increased during bioaugmentation but was limited by biofouling and/or bioclogging; the biofouling occurred as a result of electron donor addition and eventually caused the flow paths within the test cell to change, and the electron donor was no longer being delivered to those zones with significant amounts of residual PCE (i.e., the uppermost saturated portions of the test cell). The post-bioaugmentation period, where no additional electron donor was amended but groundwater circulation continued, could be characterized as being a time when PCE concentrations at the extraction wells steadily increased (suggesting that the biodegradation rate decreased such that PCE was again reaching the extraction wells).

4.4 TECHNOLOGY PERFORMANCE

It is extremely difficult to estimate cost and performance of alternative innovative approaches within a test cell where a "controlled release" of 100 L of PCE has taken place. Furthermore, cost for test cell demonstrations, even if estimated would lack much meaning as extensive sampling and monitoring go into the effort. However, for comparison purposes, five USEPA demonstrations were completed within the test cells at Dover. These technologies and their percent removal efficiencies (shown in parenthesis) for PCE included cosolvent solubilization (64%), cosolvent mobilization (80%), surfactant solubilization (65%), macromolecular solubilization (43%), and air sparging/soil vapor extraction (SVE) (88%). No cost data was developed for these technologies applied at the Dover test cells. For this bioaugmentation demonstration (ER-0008), PCE removal efficiency was estimated to be 52%, when the experiment was terminated; however, degradation was still occurring at that point.

Section 5 compares costs between bioaugmentation and other innovative approaches. Yet, performance of any of these alternative approaches is difficult to assess. Since the design of the recirculation system is similar in operation to a P&T design, comparisons to the additional benefits of bioaugmentation over just P&T can be easily extrapolated from the site data.

Two approaches to evaluate the enhanced in situ bioremediation (EISB) technology to P&T were conducted. The first involved comparing the trends observed at extraction wells during Phase 2 and 3 (baseline and biostimulation) and Phase 4 (bioaugmentation) using PCE and its degradation products. The second involved using the chloride ion concentration changes observed between Phase 2 and Phase 4 at points within the test cell and at the extraction wells. The following subsections summarize these evaluations.

Trend Analysis to Estimate Enhanced Mass Discharge

Figure 8 shows the PCE equivalents (i.e., PCE and all daughter degradation products are converted to an equivalent PCE mass) as mmol for each extraction well. Extraction well samples were collected weekly over the operational period. The measured concentration of PCE in groundwater at the extraction wells (baseline and biostimulation [blue diamond] and bioaugmentation [dark pink diamond]) is presented. Estimates of the removal of PCE using fitting equations are shown in Figure 8. This analysis indicates that without bioremediation (or bioaugmentation) the concentration of PCE would continue to decline but remain above MCLs, for an extended period of time. This predicted low concentration of PCE would represent the continued mass discharge of PCE from sorbed, residual DNAPL and DNAPL architecture with respect to the flow regime. However, the application of bioremediation showed an increase in mass discharge over the projected concentrations, thus indicating that the biological activity close to the source area generated more PCE equivalent mass over time. The exponential decay from the fitted line (predicted PCE, orange line in each graph) was used to then predict the PCE concentration without bioaugmentation (predicted PCE). The total ethenes as PCE equivalents (total ethene; light pink line) is also plotted to show the difference between the predicted and actual. Enhanced mass discharge due to biodegradation occurs when the total ethenes mass exceeds the predicted PCE mass (Yang and McCarty, 2000).



Figure 8A. Mass Reduction Predicted Versus Actual—Extraction Well 1.



Figure 8B. Mass Reduction Predicted Versus Actual—Extraction Well 2.



Figure 8C. Mass Reduction Predicted Versus Actual—Extraction Well 3.

The chart below summarizes the calculated mass enhancement. The predicted PCE values are the average PCE concentration predicted to be captured at the extraction wells based on the fitted equation (shown in each figure). The predicted value (mmol/L) shown in the table below is the average PCE mass over Phase 4 (bioaugmentation). The actual PCE values is the reported PCE concentrations at the specified extraction well over this same period (i.e., Phase 4), calculated as PCE equivalents. The enhancement is the actual divided by the predicted of each of these values. The enhancement factor at extraction well (EW)3 is likely overestimated due to changes in the flow patterns within the cell (i.e., more groundwater was collected at EW3 in the latter stages so more mass was captured at this well). But these results clearly show that mass enhancement occurred and that this type of application would be useful for a biocontainment approach. Biocontainment could accelerate the treatment times and reduce source longevity.

Extraction Well	Predicted PCE (Mmol/L)	Actual PCE (Mmol/L)	Enhancement
EW1	0.0198	0.0867	4.4
EW2	0.0094	0.0594	6.3
EW3	0.0014	0.0261	18.6

Chloride Production to Estimate Enhanced Mass Discharge

During Phase 4, 2.9 kg of PCE and 12.9 kg of PCE daughter products (TCE, cis-1,2-DCE, VC and ethene) were captured at the extraction wells (NAVFAC-ESC/Geosyntec, 2007). In this same interval more than 12 kg of chloride was produced (see Appendix H of Final Technical Report, NAVFAC-ESC/Geosyntec, 2007). Chloride concentrations at some monitoring points were up to 4 times greater in bioaugmentation (Phase 4) than baseline (Phase 2). The carbon compound-specific isotope analyses (CSIA) results (Figure 12 of Final Technical Report) indicate that DNAPL was present, as measured by a stable PCE isotope signature, for more at least half of the bioaugmentation phase (Phase 4). Using chloride production, the enhanced mass discharge at the extraction wells in the Phase 4 is about two times that observed during Phase 2. This is the most conservative approach to evaluating the enhanced mass discharge.

Overall, the demonstration achieved the objectives (See Section 4.2 above). These results suggest that the enhanced mass discharge may have ranged from at least two (conservatively, based on the average increase in chloride mass at the extraction well) to 19 (based on the daughter products observed during Phase 4 compared to the amount of PCE in this same period). Finally, it should be noted that the intent of the demonstration was not to attain MCL during operation.

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5.0 COST ASSESSMENT

5.1 COST REPORTING

Project costs were tracked, by milestones, as shown in Figure 9, to determine the cost effectiveness of bioaugmentation as a remedial approach for source zones. The highest-cost milestone was operation of the demonstration system (including monitoring), which comprised 34 % of the total project cost.



Figure 9. Distribution of Project Expenditures by Major Milestone.

The total cost of the demonstration was \$850,000, resulting in the treatment of approximately 77 kg of PCE. The corresponding unit costs of the demonstration are \$11,000 per kg of PCE. The unit costs incurred during the demonstration are much higher than those likely to be experienced during full-scale implementation due to 1) the small scale of the demonstration, 2) the extensive monitoring effort, and 3) the implementation of a groundwater recirculation system.

5.2 COST ANALYSIS

Two types of cost analyses were completed to determine bioaugmentation costs. The first involved comparing the mass extracted during bioaugmentation (Phase 4 of the demonstration) to the mass extracted without biostimulation and bioaugmentation (Phase 2). The second approach develops a hypothetical site containing a source and similar geochemical and physical aquifer properties to the DNTS test cell, and compares conventional source remediation

approaches (e.g., in situ thermal and in situ chemical reduction to EISB). The following sections present these evaluations.

5.2.1 Comparison of Actual Costs from the Pilot Test

During Phase 2 of this demonstration (baseline operation, which consisted of extracting unamended groundwater), the system operated in a manner very similar to P&T, with extraction wells and GAC treatment as a component of the test cell design. The additional cost due to EISB can be obtained by comparing to P&T (by using the results of mass captured and treated in Phase 4). The assumption is that if no biodegradation occurred within the test cell, then the mass of PCE extracted would be that which was captured from a P&T system. This was the basis for this comparison.

The costs to operate the system were estimated on an annual basis and the mass extracted as PCE (equivalent to P&T) and that with bioaugmentation and electron donor (EISB) were compared. These tables were developed using the format outlined in Federal Remediation Technologies Roundtable (FRTR, 1998). Tables 5A and 5B present the cost comparisons between EISB and P&T, respectively. In this scenario, the quantity of PCE extracted and treated by P&T was taken from the PCE concentrations observed at the extraction wells of the demonstration during Phase 4 for EISB and Phase 3 (biostimulation) for P&T, respectively. Using this value (0.067 kg PCE per day), the annual mass of PCE extracted using a P&T configuration was estimated. For EISB, the PCE and the total daughter products, as PCE equivalents, are used. Using this value the annual mass of PCE extracted using EISB is determined. These are then used to estimate the costs of removal per kg. In this scenario the costs per kg of PCE removed for P&T and EISB are estimated to be \$5,726 and \$4,796, respectively. This is a function of the design (i.e., low flow and using recirculation for EISB).

	Cost (\$/Year Basis)	Cost for Calculating Unit Cost
1. Capital Costs		
Mobilization, set up	\$25,000	
(\$5K labor, \$10K site preparation (electrical), \$10K mobilization for subs)		
Planning and Preparation	\$15,000	
(4 days @ \$1,500/day, remainder for drawings and specifications)		
Site work (well installation)	\$48,900	
Equipment (pumps, controller, supervisory control and data acquisition [SCADA],	\$125,000	
dose pump)	\$40,399	
Start-up and testing (baseline sampling, bioaugmentation)		\$254,299
Total Capital Costs		
2. Operation, Maintenance, and Monitoring (OM&M) (per year)		
Labor (weekly visit, monthly biofoul mice, snapshot sampling 6 times a year)	\$55,200	
(4 hours for weekly and monthly @\$75/hr, semi-annual, 2 staff 120 hours @		
\$75/hr)		
Materials (electron donor, supplies, pump replacement, sampling equipment)	\$6,500	
Utilities and fuel (overwinter protection)	\$2,100	
Equipment ownership, rental or lease	\$2,500	
Performance testing and analysis - (weekly cost of \$600—\$300 labor and \$300	\$57,480	
laboratory costs)		
Total OM&M Costs		\$123,780

Table 5A. Cost Summary Table—Enhanced In Situ Bioremediation.

Table 5A. Cost Summary Table—Enhanced In Situ Bioremediation (continued).

	Cost (\$/Year Basis)	Cost for Calculating Unit Cost
3. Other Technology Specific Costs		
Compliance testing and analysis	\$0	
Soil excavation collection and control	\$0	
Disposal of residues	\$0	
4. Other Project Costs		
None	\$0	
Total technology cost (Year basis for cost)	\$378,079	
Total cost for calculating unit cost		\$378,079
Quantity treated (kg of PCE and daughter products produced during bioaugmented	79	
phase, per year)*		
Calculated Unit Cost (/kg of PCE)		\$4,796

Notes: Anticipated system configuration: recirculation, up to 3 gpm, using 3 extraction wells and 3 injection wells *Amount listed is based on 3 gpm total flow

Table 5B. Cost Summary Table Pump-and-Treat Alternative.

	Cost (\$/Year Basis)	Cost for Calculating Unit Cost
1. Capital Costs		
Mobilization, set up	\$25,000	
(\$5K labor, 10K site preparation [electrical], \$10K mobilization for subs)		
Planning and Preparation	\$15,000	
(4 days @ \$1,500/day, remainder for drawings and specifications)		
Site work (well installation)	\$48,900	
(drilling and oversight to install wells)		
Equipment (design, air stripper, vapor phase GAC, piping)	\$125,000	
(estimate from vendor for skid mounted system to treat VOCs listed)		
Start-up and testing (baseline sampling)	\$40,400	
hydraulic testing, flowfield verification and sampling: (2 months of labor @		
\$600/day plus \$16,400 equipment and lab)		
Total Capital Costs		\$254,300
2. Operation, Maintenance, and Monitoring (per year)		
Labor (weekly visit)	\$15,600	
(4 hours per week @\$75/hr)		
Materials (carbon, pump replacement, sampling equipment)	\$15,000	
(8 drums GAC/yr [8K], \$5K pump, \$2K sampling equipment)		
Utilities and fuel (overwinter protection)	\$2,100	
(estimate based on site use at Dover)		
Equipment ownership, rental or lease	\$2,500	
(water tape, pH, oxidation reduction potential [ORP], DO meters)		
Performance testing and analysis (3 locations weekly)	\$24,000	
(weekly cost of \$600—\$300 labor and \$300 laboratory costs)		
Other		
Total OM&M Costs		\$59,200
3. Other Technology Specific Costs		
Compliance testing and analysis	\$0	
Soil excavation collection and control	\$0	
Disposal of residues	\$0	
4. Other Project Costs		
None	\$0	
Total technology cost (year basis for cost)	\$313,500	
Total cost for calculating unit cost		\$313,500
Quantity treated (kg of PCE removed during biostimulation phase per year)*	55	
Calculated unit cost (/kg of PCE)		\$5,726

Notes: Anticipated system configuration: recirculation, up to 3 gpm, using 3 extraction wells and 3 injection wells

*Amount listed is based on 3 gpm total flow
5.2.2 Comparison of Costs for Hypothetical Site

The second approach to cost analysis involved developing a full scale system to treat a hypothetical plume, using commercially available source treatment options. Using this hypothetical plume, costs for the following technologies were compared:

- In situ thermal remediation (electrical resistance heating [ERH])
- In situ chemical oxidation ([ISCO]; modified Fenton's reagent)
- P&T
- EISB (biostimulation with emulsified vegetable oil [EVO] and bioaugmentation).

The P&T scenario was used as a benchmark. The assumptions for this source area and plume are provided in Table 6. The site would consist of a treatment area, roughly 300-ft wide, 600-ft long, and have PCE contamination over a 30-ft thickness. The aquifer system presented in Table 6 is for a system similar (geochemically) to the one at the Dover test cell but with larger extraction rates and treatment areas. Tables 7A, 7B, 7C, and 7D summarize the costs associated with each alternative.

Start-up costs consist of all activities through installation, planning, sample collection, regulatory negotiations, and permitting. Capital costs include costs related to supply/equipment acquisition and any necessary modification made to existing infrastructures. Operation and maintenance costs include calibration of instruments, sampling, analytical work (field and laboratory based, but excluding site characterization), maintenance, replacement of consumables (e.g., electron donor), but not waste handling and disposal as these costs tend to be region-specific. The following sections provide a review of the specific configuration of the treatment technology for this evaluation and, for in situ thermal and ISCO, a summary of the treatment technology and the application selected for this evaluation.

5.2.2.1 <u>Alternative 1: Pump and Treat</u>

P&T systems can be designed for different remediation objectives. Possible objectives of P&T systems include removal of dissolved contaminants from the subsurface, containment of contaminated groundwater to prevent migration, and DNAPL removal/source area remediation. If removal of dissolved contaminants is the chosen objective of the P&T system, the level of cleanup must be determined. If containment is the chosen objective, groundwater pumping is used as a hydraulic barrier to prevent off-site migration of contaminant plumes. P&T is used for control and treatment of groundwater plumes and is not generally used in source areas. If P&T is used in source areas, it is generally applied as a multiphase extraction (MPE) system. P&T is often used as a plume containment remedy in conjunction with other DNAPL source area remedies (e.g., in situ bioremediation, surfactant flushing, or chemical oxidation).

This scenario assumes installation of three groundwater extraction wells screened over a nominal thickness of 30 ft and equipped with electrically operated submersible pumps. The total groundwater extraction rate is assumed to be 10 gpm. Extracted groundwater will be treated using an air stripping tower and then recharged back to the aquifer via an infiltration gallery. The vapor stream from the air stripping tower will be treated using two GAC vessels connected

in series. The system would operate for 30 years. Cost drivers for this technology include the ongoing O&M costs (see Table 7A).

5.2.2.2 <u>Alternative 2: Enhanced In Situ Bioremediation</u>

With EISB applications, nutrients (e.g., electron donors, cometabolites, electron acceptors) are added to enhance biodegradation. Several delivery approaches are in common use for EISB applications. These include:

- Active and/or semi-active (i.e., short duration pulsed injections) in situ biobarrier systems that capture impacted groundwater through groundwater extraction wells, amend it with an optimized concentration of nutrients, and recharge the amended groundwater to the aquifer through injection wells to encourage bioactivity in situ
- Passive and/or semi-passive in situ biobarriers established through injection of slow-release nutrients. Groundwater is allowed to flow through these passive biobarriers under natural gradients, and the target chemical is then treated in situ within and/or downgradient of the biobarrier. Examples of slow release electron donors include emulsified edible oils (e.g., soybean or canola oil), lactate polymers, wood chips, etc.

For this case a passive biobarrier approach was selected. The treatment area was configured to contain six rows of injection wells, set on 20 ft centers with 15 injection wells per row. It was assumed the wells would be installed using direct push technology to minimize investigation derived waste disposal costs. The selected electron donor was EVO, a long term electron donor that would be applied at years 1, 5 and 10. After 15 years it was assumed that remediation was complete based on mass reduction observed in this and other demonstrations. For this analysis the enhanced mass discharge for EISB was set to be 2 (the most conservative number obtained – see Section 4.4 above). The principal cost drivers for the technology infrastructure are injection well installation and electron donor, labor required for the injection events, performance monitoring, and reporting.

5.2.2.3 <u>Alternative 3: Thermal Treatment Using Electrical Resistance Heating</u>

Thermal treatment technologies are a group of technologies that use heat to facilitate contaminant mobilization, solubilization, removal, and/or degradation. Thermal treatments that are most commonly applied for in situ remediation of chlorinated solvents include steam enhanced extraction (SEE) also referred to as steam flushing; ERH, both three-phase and six-phase heating; and electrical conductive heating (ECH) also referred to as in situ thermal desorption and thermal conductive heating. In most cases, in situ thermal treatments are used in nonaqueous phase liquid (NAPL) source areas, and the technology is used in conjunction with SVE to contain and recover contaminant vapors.

ERH involves the application of electrical current into and through the subsurface via electrodes that generate heat. ERH uses the naturally occurring electrical resistance of the subsurface that allows electrical energy to be focused into a specific source zone. Steam is generated when the in situ resistance heating heats the subsurface to the boiling point of the pore water. The steam

strips the contaminants from the soils and enables them to be extracted from the subsurface. In addition, the heat causes the contaminants to be directly volatilized from unsaturated soils and can catalyze abiotic degradation of certain solvents (e.g., 1,1,1-trichloroethane [1,1,1-TCA] hydrolysis to acetic acid). The extracted liquids and vapors are treated using conventional aboveground treatment technologies. ERH may be used for several remedial purposes, including steam stripping VOCs, enhancing SVE and MPE efforts, increasing biological degradation rates, and increasing chemical dechlorination reaction rates.

For this case, ERH, using three-phase heating, was selected as the thermal application method. A vendor quote was obtained, which recommended that the treatment area contain about 560 heater wells set on 20-ft centers (Table 7C). It was assumed the system would operate for up to 700 days. The vapors would be extracted and treated using GAC. The principal cost drivers for the technology infrastructure were injection heater well installation, electrode costs and electrical costs.

5.2.2.4 <u>Alternative 4: In Situ Chemical Oxidation Using Modified Fenton's</u>

ISCO refers to a group of specific technologies that each use differing combinations of oxidants and delivery techniques. ISCO has been shown to destroy or degrade an extensive variety of hazardous wastes in groundwater and soil, including fuel hydrocarbons, chlorinated solvents (e.g., PCE, TCE), fuel oxygenates (e.g., methyl tert-butyl ether [MTBE]), and polycyclic aromatic hydrocarbons (PAH). Various oxidants have been used in laboratory and field applications to aggressively destroy chlorinated solvents, including permanganate, ozone, and Fenton's reagent. The oxidants react with the contaminants (i.e., breaking molecular bonds of and capturing electrons from the contaminant) and convert them to innocuous compounds commonly found in nature such as carbon dioxide (CO₂), water, and inorganic chloride. Interstate Technology Regulatory Council (ITRC) provides a review of the various oxidants available and the characteristics of each.

Modified Fenton's was selected for this site as its application (commonly by direct push injections) and is similar to the EISB approach selected above. The treatment area was configured to contain 220 injection points set on 25-ft centers. It was assumed the wells would be installed using direct push technology to minimize investigation derived waste disposal costs. A solution containing 12% hydrogen peroxide and catalyst would be amended to each point. The target treatment area was set to 20% of the pore volume. Most vendors prefer to perform a pilot test to confirm site-specific application concerns (natural oxidant demand, geological heterogeneities). These are refined before full-scale application. It was assumed that a second injection to a subset of the treatment area would be required. A 5-year remediation program was selected. The principal cost drivers for the technology are oxidant, labor required for the injection events, performance monitoring, and reporting.

Parameter	Unit	Quantity
Site Characteristics		
Source dimensions (200 m x 90 m x 10 m)	m3	180,000
Porosity	v/v	0.27
Pore volume	m3	48,600
Bulk density	kg/m3	1,800
Mass of soil	kg	87,480,000
Total depth of treatment area	m	20
Depth to water	m	10
Geochemistry		
Average PCE concentration in soil	mg/kg	75
PCE mass in soil to treat	kg	6,560
Sulfate	mg/L	150
Oxygen	mg/L	<1
EISB: Electron Donor Approach		
Select emulsified vegetable oil, amend in barrier configuration		
20 ft return on investment (ROI), amend at 3% EVO	row	6
Number of points per row	points per row	15
Total number of points		90
ISCO: Application of Modified Fenton's		
Modified Fenton's (hydrogen peroxide)	dose %	12
Radius of injection	ft	25
Number of amendment points	points	230
Volume to amend per point	L	42,000
Thermal: Application of ERH		
Number of electrodes	each	559
Distance between electrodes	m	6.1
Off-gas treatment with GAC	kg	63,000
Treatment Parameters		
Duration of pump and treat	years	30
Duration of ISCO	years	5
Duration of EISB (amend three times in 10 years)	years	15
Duration of thermal	years	2
Discount rate	%	4.5

Table 6. Parameters for Cost Basis.

Task CAPITAL COSTS Extraction Wells	Unit LS ²	Unit Cost	Quantity	Cost	20% Contingency
CAPITAL COSTS Extraction Wells			Quantity	Cost	Contingency
Extraction Wells	LS ²				
	LS^2				
	LS			#73 000	¢0,< 100
nstall 4-6-inch SS extraction wells (mob/demob, development, IDW ¹)				\$72,000	\$86,400
Oversight of drilling	Per day	\$900	6	<u>\$5,400</u>	<u>\$6,480</u>
Subtotal				\$77,400	\$92,880
<u>Freatment System Construction and Start-Up</u>					
Frenching	LS			\$50,000	\$60,000
Air stripper tower	LS			\$75,000	\$90,000
Vapor phase carbon activated carbon vessels (2 each)	Each	\$45,000	2	\$90,000	\$108,000
Piping, instrumentation, and process control	LS			\$55,000	\$66,000
nfiltration gallery	LS			\$100,000	\$120,000
Construction oversight	Per day	\$2,300	40	\$92,000	\$110,400
Shakedown and start-up testing	Per day	\$2,500	10	\$25,000	\$30,000
Subtotal				\$487,000	\$584,400
FOTAL CAPITAL COSTS				\$564,400	
FOTAL CAPITAL COSTS (with 20%					\$677,280
contingency)					
ANNUAL OPERATION, MAINTENANCE, AN	ND MONIT	ORING C	OSTS		
Activated carbon changeout	LS			\$125,000	\$150,000
Maintenance	LS			\$25,000	\$30,000
System operation (technician)	Day	\$1,500	52	\$78,000	\$93,600
Equipment replacement (5% of capital annually)	%	5%	\$564,400	\$28,220	\$33,864
Performance monitoring (sampling and analytical)	Sample	\$550	56	\$30,800	\$36,960
Reporting	LS			\$15,000	\$18,000
TOTAL ANNUAL OM&M COSTS				\$302,020	
FOTAL ANNUAL OM&M COSTS (with 20%					\$362,424
contingency)					

Table 7A. Alternative 1—Pump and Treat.

¹IDW – investigation-derived waste ²LS – lump sum

					Cost Plus
		Unit			20%
Task	Unit	Cost	Quantity	Cost	Contingency
CAPITAL COSTS	r				
Amendment Wells					
Install 90 temporary 2-inch PVC wells to 20 m	per well	\$1,750	90	\$157,500	\$189,000
(mob/demob, direct push, IDW)					
Install 12 monitoring wells (2 inch PVC,	per well	\$2,700	12	\$32,400	\$38,880
conventional drilling)					
Oversight of drilling	per day	\$900	60	<u>\$54,000</u>	<u>\$64,800</u>
Subtotal				\$243,900	\$292,680
Amend Electron Donor					
Electron donor (amend as 2% EVO)	kg	\$2.2	181,600	\$399,520	\$479,424
Injection labor (assume 5 gpm injection rate, total	day	\$2,400	60	\$144,000	\$172,800
injection per point of 14,000 gal, two staff					
required to complete work)					
Equipment for Injection (tanks, containment,	LS	\$75,000	1	\$75,000	\$90,000
injection manifolds)					
Bioaugmentation	per well	\$1,500	90	\$135,000	\$162,000
Oversight (design, reporting, H&S ¹ , supervise				<u>\$250,000</u>	<u>\$300,000</u>
injection)					
Subtotal				\$1,003,520	\$1,204,224
Amend donor again in Years 3 and 6				\$2,007,040	\$2,408,448
TOTAL CAPITAL COSTS				\$3,010,560	
TOTAL CAPITAL COSTS (with 20%					\$3,612,672
contingency)					
ANNUAL OPERATION, MAINTENANCE, AN			OSTS		
Performance monitoring (sampling and	Sample	\$600	96	\$57,600	\$69,120
analytical)					
Reporting	LS			<u>\$25,000</u>	<u>\$30,000</u>
TOTAL ANNUAL OM&M COSTS				\$82,600	
TOTAL ANNUAL OM&M COSTS (with 20%					\$99,120
contingency)					

Table 7B. Alternative 2—Passive EISB.

¹ H&S – health and safety

					Cost Plus
					20%
Task	Unit	Unit Cost	Quantity	Cost	Contingency
CAPITAL COSTS				-	
Design, work plans, permits	LS	\$114,000	1	\$114,000	\$136,800
Electrode materials mobilization	LS	\$2,442,000	1	\$2,442,000	\$2,930,400
Subsurface installation	LS	\$597,000	1	\$597,000	\$716,400
Surface installation and start-up	LS	\$930,000	1	\$930,000	\$1,116,000
Drilling and soil sampling	LS	\$1,806,000	1	\$1,806,000	\$2,167,200
Drill cuttings and waste disposal	LS	\$439,000	1	\$439,000	\$526,800
Remediation system operation (about 700 days)	LS	\$3,570,000	1	\$3,570,000	\$4,284,000
Demobilization	LS	\$178,000	1	<u>\$178,000</u>	<u>\$213,600</u>
TOTAL CAPITAL COSTS				\$10,076,000	
TOTAL CAPITAL COSTS (with 20%					\$12,091,200
contingency)					
ANNUAL OPERATION, MAINTENANCE, A	ND MONI	TORING CO	STS		
Electrical utility connection to PCU:				\$40,000	\$48,000
Electrical energy usage:				\$5,429,000	\$6,514,800
Carbon usage, transportation & regeneration:				\$226,000	\$271,200
Water/condensate disposal:				\$10,000	\$12,000
Other operational costs:				\$283,000	\$339,600
Reporting	LS			<u>\$50,000</u>	<u>\$60,000</u>
TOTAL ANNUAL OM&M COSTS (Year 1)				\$6,038,000	
TOTAL ANNUAL OM&M COSTS (with					\$7,245,600
20% contingency)					
ANNUAL OPERATION, MAINTENANCE, A	ND MONI	TORING CO	STS (Years	2 through 5)	
Performance monitoring (sampling and	Sample	\$600	24	\$14,400	\$17,280
analytical)	1				
Reporting	LS			\$25,000	\$30,000
TOTAL ANNUAL OM&M COSTS (Year 2				\$39,400	
through 5)					
TOTAL ANNUAL OM&M COSTS (with					\$47,280
20% contingency)					

Table 7C. Alternative 3—Thermal Remediation Using ERH.

		T T •4			
	TT 1 /	Unit		<i>a i</i>	Cost Plus
Task	Unit	Cost	Quantity	Cost	Contingency
CAPITAL COSTS	ii		i	t	i
Amendment Wells					
Install 230 direct push wells to 20 m (assume 4	Per day	\$2,000	63	\$126,000	\$151,200
locations per day)					
Install 12 monitoring wells (2-inch PVC,	Per well	\$2,700	12	\$32,400	\$38,880
conventional drilling)					
Oversight of Drilling	Per day	\$900	63	<u>\$56,700</u>	<u>\$68,040</u>
Subtotal				\$215,100	\$258,120
Amend Modified Fentons					
Pilot test	LS	\$150,000	1	\$150,000	\$180,000
Modified Fentons (12% H202, dilute to apply at	Point	\$13,000	230	\$2,990,000	\$3,588,000
5%)					
Injection labor (assume 5 gpm injection rate,	Day	\$2,400	63	\$151,200	\$181,440
total injection per point of 11,000 gal, two					
staff required to complete work)					
Equipment for injection (tanks, containment,	LS	\$15,000	1	\$15,000	\$18,000
injection manifolds)					
Oversight (design, reporting, H&S, supervise				<u>\$250,000</u>	<u>\$300,000</u>
injection)					
Subtotal				\$3,556,200	\$4,267,440
Amend second event in year 2 (to 50% of area)				\$1,810,900	\$2,173,000
TOTAL CAPITAL COSTS				\$5,582,200	
TOTAL CAPITAL COSTS (with 20%					\$6,698,640
contingency)					
ANNUAL OPERATION, MAINTENANCE AND MONITORING COSTS (for up to 5 years)					
Performance monitoring (sampling and	Sample	\$600	96	\$57,600	\$69,120
analytical)	-				
Reporting	LS			\$25,000	\$30,000
TOTAL ANNUAL OM&M COSTS				\$82,600	
TOTAL ANNUAL OM&M COSTS (with					\$99,120
20% contingency)					

Table 7D. Alternative 4—In Situ Chemical Oxidation Using Modified Fenton's.

5.3 COST COMPARISON—LIFE-CYCLE COSTS

The estimated life-cycle costs varied for each of the technologies, as shown in Table 8. The EISB technology is based on the capital cost of the infrastructure plus O&M (including electron donor, performance monitoring, and reporting) over the period of technology implementation. Table 8 shows the total life-cycle costs of each alternative, calculated as the net present value (NPV) over time periods of:

- 30 years for P&T,
- 15 years for EISB,
- 5 years for ISCO, and
- 2 years for Thermal.

All costs are calculated at annual discount rates of 3%. Summaries of the costs of the alternatives (including both capital and annual operations and maintenance) are provided in

Table 8. The total costs over the operating period (extended for 30 years for all technologies) are provided in Figure 10.

	P&T	EISB	ISCO	Thermal
Capital cost	\$564,400	\$3,255,900	\$5,432,500	\$10,076,000
O&M	\$302,000	\$82,600	\$82,600	\$6,038,000
NPV	\$9,216,300	\$4,465,700	\$5,841,800	\$16,095,900
Discount rate	0.003	0.003	0.003	0.003
Period (year)	30	15	5	1
P/A, i%, n	28.6486	14.6460	4.9553	0.9970

Table 8. Summary of Life-Cycle Costs.

NPV = capital costs + O&M costs* (P/A, i%, n)



Figure 10. Summary of Cumulative Costs by Alternative.

As shown in Table 8, the highest cost was the thermal remedy and the lowest cost EISB. For the EISB configuration, there would be three applications of electron donor to the source area to enhance the remediation. Capital costs to amend electron donor are more than the capital costs to install a conventional (i.e., off-the-shelf) air stripper/GAC treatment system. The cost savings

for the EISB remedy relate to lower annual O&M costs for those years when electron donor reamendment is not completed. In this evaluation an enhancement factor of 2 was used.

The EISB analysis is sensitive to enhancement factors as changes in these will adjust remediation time frames, but there are other factors that will also impact the remediation time frames for other technologies, such as the amount of heating time required (which can be dependent on the geologic medium). Similarly, the need for long-term monitoring or monitored natural attenuation (MNA) polishing is going to be dependent on many factors (including the treatment goals and the geologic medium). Rather than focus on just enhanced bioremediation, we opted to assess source remediation time frame using source decay terms as described by Rao et al. (2001) and Falta et al. (2005).

The table below presents an analysis to assess the remediation time frame using the source configuration developed for the cost comparison. This table shows the time to reduce the source concentration to a remedial goal (e.g., the MCL, or a 90% reduction of the original source area concentration), assuming:

- Either no mass flux enhancement (e.g., P&T), a mass flux enhancement of two times or four times higher, which represents the lower and mid-level mass discharge enhancement achieved in the test plot
- Three different mass flux relationships to source depletion as described by gamma (Γ), an empirical fitting parameter
- That Γ and mass flux enhancement remains constant over the time frame of treatment.

	Source Target (Concentration)					
-		90%		90%		90%
	MCL	reduction	MCL	reduction	MCL	reduction
				Г		
Treatment Affect on Mass Flux		0.5		1		2
		Approxima	ate Time t	o Achieve Targ	et (Years)	
No Mass Flux Enhancement	22	20	85	25	470	24
Biodegradation Enhances Mass Flux 2X	11	10	45	17	345	19
Biodegradation Enhances Mass Flux 4X	6	5	25	10	245	15
Remove 80% of Mass - No Mass Flux Enhancement	4	4	17	5	95	5
Remove 80% of Mass-Biodegradation Enhances Mass Flux 2X	2	2	9	3	69	4
Remove 80% of Mass-Biodegradation Enhances Mass Flux 4X	1	<1	5	2	49	3

MCL is set to 5µg/L

 Γ is a function of the heterogeneity of the subsurface and DNAPL architecture, and describes the relationship between source mass removal and change in mass flux from a source over time as described by Rao et al. (2001) and Falta et al. (2005). In all cases, even a small increase of twofold in the mass flux will reduce the time to achieve MCL compared to the P&T scenario. The difference is not as pronounced if the objective is to reduce the source concentrations by 90%, but there is still a reduction in time.

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6.0 IMPLEMENTATION ISSUES

6.1 COST OBSERVATIONS

A number of factors influence the full-scale implementation cost of bioaugmentation. Primary factors affecting the cost of the technology include the time required for remediation, the maximum depth at which the contaminants are present, and the presence of available infrastructure.

The duration of remediation is a function of the performance of the technology also controlled by a number of factors. The spatial extent of the DNAPL can add significant cost to total implementation costs. Since enhanced bioremediation relies on the delivery of amendments (e.g., electron donor, nutrients, and biomass) through injection wells to promote contaminant degradation, the volume of the aquifer defined by the horizontal and vertical extent of the DNAPL will control the amendment flow rate, the size of the amendment dosing system, and the number of wells required to circulate the amendments through the treatment zone.

Another limitation of the technology will be the costs associated with locating a DNAPL source zone for treatment. At some sites, it may not be cost-effective to accurately locate the DNAPL; instead, the design of the treatment system should be sufficiently large to encompass the entire DNAPL source zone. This may increase the annual treatment costs (i.e., O&M) of a bioaugmentation system; however, this may be offset by the reduction in the cost of site investigation activities.

6.2 **PERFORMANCE OBSERVATIONS**

While an enhanced removal rate of the DNAPL may be achieved through bioaugmentation, the rate of mass removal may still be small in comparison to the mass of DNAPL initially present, suggesting that sites where a large mass of DNAPL is present may limit the measurable effectiveness of the technology. Because the technology requires the establishment of anaerobic and reducing conditions in the source zone, the ability to support reductive dechlorination while maintaining intrinsic (background) oxidation reduction reaction (redox) conditions will also improve the performance of this technology.

During the course of the demonstration technology, biofouling and precipitate accumulation within the extraction, circulation, and injection system negatively affected the performance of the technology. The distribution of the electron donor was significantly lowered due to poor permeability and, as a result, reduced the DNAPL reduction rate. As a result of the increasing biofilm growth, the extraction, circulation, and injection system was augmented in stages to deal with each rising issue. A GAC treatment system and a filtration system were later installed in order to remove the persistent biofilm growth and increasing precipitation of suspected iron sulfides within the circulation system.

Geological heterogeneity will strongly influence the performance of bioaugmentation by limiting the delivery of the amendments to the microorganisms adjacent to the DNAPL. In particular, the delivery of a sufficient concentration of electron donor to support the microbial activity may limit the maximum concentration of the target contaminant that can be degraded. This limitation will depend on the type and concentration of the electron donor added into the source zone, the utilization rate by the microorganism, and the design of the nutrient delivery system.

6.3 SCALE-UP

All the equipment used in the demonstration was commercially available, off-the-shelf equipment. There were a number of design components installed at an added cost just for this demonstration that would not need to be applied at other sites. These include:

- The efforts to track mass balance need not be as rigorously applied to other sites as starting mass unlikely to be quantified
- GAC treatment prior to re-injection (which was used during this demonstration to facilitate mass balance)
- The extent of water table manipulation was an added effort that would not be required in a non-sheet pile test cell setting
- The number and frequency of multilevel monitoring wells can be decreased for an expanded setting. This demonstration used a higher degree of instrumentation for proof-of-concept purposes.

6.4 OTHER SIGNIFICANT OBSERVATIONS

SCIA is a technique that measures the ratio of ¹³C to ¹²C for an individual compound in a sample. SCIA has the potential to differentiate between chlorinated ethene biodegradation and nondegradative, physical processes (Morrill et al., 2005). Preferential biodegradation of ¹²C-containing compounds results in an enrichment of the heavy isotope (¹³C) in the remaining substrate, which changes the isotope value of the parent compound. The fact that biodegradation changes the isotope value makes it an isotopically fractionating process. In contrast, nondegradative processes such as dissolution, volatilization, and sorption do not cause a significant change to the isotope values (they remain within \pm 0.5 per mil [‰], which is the analytical error associated with this method) and are therefore non-isotopically fractionating processes.

Groundwater samples were collected from the test cell and analyzed for SCIA at the University of Toronto. This work was the component of a doctoral thesis (Morrill et al., 2005). The results of the SCIA sampling for the field demonstration indicated that biodegradation of some compounds was detected before conventional groundwater analytical results confirmed biodegradation was occurring. This was most pronounced in the observation of cis-1,2-DCE and VC isotopic fractionation, indicating biodegradation of cis-1,2-DCE to VC and VC to ethene within the test cell (NAVFAC-ESC/Geosyntec, 2007). This suggests that in cases where a variety of processes may be occurring, SCIA can be used to demonstrate if biodegradation processes are significant contributors via reductive dechlorination mechanisms.

6.5 LESSONS LEARNED

There are no standard protocols for measuring the performance of DNAPL source zone treatment technologies, but there are a variety of assessment tools, including groundwater sampling, soil

collection, enhancement factors and, stable compound isotope ratios that can provide information about the changes in concentration of contaminants in groundwater or the amount of mass remaining in the source zone.

Several studies, including this ESTCP project (ER-0008) have proven that bioaugmentation of source areas is technically feasible. The enhanced dissolution rate of a single compound DNAPL will be substantially enhanced by the first dechlorination step (e.g., PCE to TCE and TCE to cis 1,2 DCE). However, if further dechlorination is not achieved, there will be an increase in the mass flux of partially dechlorinated solvents that can cause plumes to expand. Complete dechlorination is necessary to contain the increase in mass flux.

Bioaugmentation of DNAPL source zones is feasible. To date, bioaugmentation has been applied at over 100 sites in the United States where groundwater contains chlorinated ethenes. Factors to consider for the application of bioaugmentation include:

- Lack of appropriate dechlorinating microorganisms that function at high concentrations or where requisite *Dehalococcoides* organisms are absent or poorly distributed. At these sites, bioaugmentation may be used to ensure that the necessary microorganisms to achieve complete dechlorination to ethene are present or to supplement the activity of the existing dechlorinating population.
- **Reduction of lag times to meet goals.** The presence of *Dehalococcoides* organisms at a site suggests that bioaugmentation may not be required for complete degradation of chlorinated ethenes. Nevertheless, some sites where *Dehalococcoides* is present may benefit from bioaugmentation to decrease the lag time prior to the onset of dechlorination. A benefit that may be significant is when travel times to compliance points are insufficient, an increase in mass flux will cause expansion of a plume of partially dechlorinated products, or where there are stringent regulatory or commercial deadlines. Some sites may have long treatment times (e.g., 30 years) and, in these cases, the benefit of bioaugmentation will need to be considered over the lifetime of the project.
- **Relatively low cost.** Bioaugmentation costs are often low relative to the life-cycle costs of the remedy (including capital costs, electron donors and their addition, and routine operation and monitoring costs), and it will improve dechlorination rates in the areas of interest.

Issues to be considered in the application of a bioaugmentation culture to a source zone include (1) factors impacting *Dehalococcoides* with various groundwater conditions (such as pH, redox conditions, temperature); (2) designing the electron donor and bioaugmentation application methodology (passive versus induced gradient/recirculation); (3) tracking bioaugmentation performance; and (4) tools to track bioaugmentation performance.

6.6 END-USER ISSUES

Bioaugmentation is potentially widely applicable at chlorinated solvent sites throughout North America. Recently, a bioaugmentation white paper (ESTCP, 2006) was released, and this paper

documents the status of development of bioaugmentation as a tool for remediation of chlorinated solvents and also discusses the current status and research needs for bioaugmentation in this area. In the spring of 2006, the DNAPL Bioremediation ITRC team sponsored a Case Study Forum, in which remedial performance was evaluated at six DNAPL source zone sites, including this demonstration. Close coordination with the ITRC for communication to the environmental industry and to insure rapid acceptance by industry and local governments will continue beyond the case study forum.

Furthermore, periodic presentations have been delivered at conferences (e.g., Battelle Conferences in 2002, 2003, and 2004) and workshops (NAVFAC-ESC, Dover National Environmental Technology Test Sites [NETTS], Amherst Soil and Remediation Conference in October 2003) and will continue to be delivered. This data has been presented at the Remediation Technologies Development Forum (RTDF) bioremediation working group. A peer-review publication will be prepared and submitted in the coming months. Other future efforts will include dissemination of the Implementation Guidance Document (the protocol), presentations during training seminars, and sessions currently offered through organizations such as NAVFAC-ESC, the RTDF, and the ITRC.

6.7 APPROACH TO REGULATORY COMPLIANCE AND ACCEPTANCE

The necessary permitting and compliance issues are described below.

- 1. Permit to Release DNAPL.
 - a. DNTS has a unique permit (Permit to Operate and Maintain a Groundwater Remediation Field Laboratory at DAFB, DE, State of DE Department of Natural Resources and Environmental Control Permit #98-PRP-03) that allows the use of up to 100 L of PCE within each test cell provided; there is strict adherence to the constraints imposed by the permit. All operations must comply with all applicable federal, state, and local regulations for which permits would normally be required. Additionally, all operations must be subject to all applicable DAFB requirements.
- 2. Approval from local and state authorities to release microbial consortium.
 - a. DNTS obtained the necessary approvals for the release of a natural consortium of microorganisms into the test cell.
 - b. DNTS maintained compliance with their permits by monitoring the system on a routine basis.

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APPENDIX A

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