ESTCP
Cost and Performance Report

(ER-0221)

Edible Oil Barriers for Treatment of Chlorinated Solvent and Perchlorate-Contaminated Groundwater

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ENVIRONMENTAL SECURITY
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COST & PERFORMANCE REPORT
Project: ER-0221

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ACRONYMS AND ABBREVIATIONS

1,1,1-TCA	1,1,1-trichloroethane
1,1,2-TCA	1,1,2-trichloroethane
1,2-DCA	1,2-dichloroethane
AFCEE	Air Force Center for Engineering and the Environment
bgs	below ground surface
BOD	biochemical oxygen demand
*c*DCE	*cis*-1,2-dichloroethene
CF	chloroform
c/t-DCE	cis/trans-dichloroethene
CT	carbon tetrachloride
CVOC	chlorinated volatile organic compound
Dhb	*Dehalobacter spp.*
Dhc	*Dehalococcoides spp.*
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOC	dissolved organic carbon
DPT	direct-push technology
DWEL	Drinking Water Equivalent Level
ENS	Environmental News Service
EOS®	Emulsified (Edible) Oil Substrate
ERD	enhanced reductive dechlorination
ESTCP	Environmental Security Technology Certification Program
gpm	gallon(s) per minute
GW	groundwater
HSA	hollow-stem auger
ISB	in situ bioremediation
ISCO	in situ chemical oxidation
ISLTT	in situ low temperature thermal
MCL	maximum contaminant level
MDE	Maryland Department of the Environment
MNA	monitored natural attenuation
NAPL	non-aqueous phase liquid
NAVFAC SE	Naval Facilities Engineering Command Southeast
NPV	net present value

NWS	Naval Weapons Station
OC	on center
O&M	operation and maintenance
OR_M	maximum oil retention
ORP	oxidation reduction potential
ppb	parts per billion
PCE	tetrachloroethene
PRB	permeable reactive barrier
psi	pounds per square inch
SCDHEC	South Carolina Department of Health and Environmental Control
SWMU	solid waste management unit
TCE	trichloroethene
TOC	total organic carbon
UIC	underground injection control
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
ZVI	zero valent iron

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Technical material contained in this report has been approved for public release.

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

This Environmental Security Technology Certification Program (ESTCP)-funded project (ER-0221) evaluated a low-cost approach for enhancing in situ anaerobic biodegradation of perchlorate and chlorinated solvents by distributing and immobilizing a slowly fermentable organic substrate in contaminated aquifers as either a permeable reactive barrier (PRB) or a source area treatment. The demonstrations involved the one-time injection of low solubility, slowly biodegradable, soybean oil-in-water emulsion to provide the primary source of organic carbon. A commercially available product, Emulsified (Edible) Oil Substrate (EOS®), was used in each demonstration. The EOS® was distributed throughout the treatment zone using either conventional wells or temporary direct-push points.

Two pilot tests were performed and each successfully demonstrated that this approach could provide good contact between the substrate and the contaminants resulting in effective rates of biodegradation. As designed, a portion of the emulsified oil was trapped within the soil pores leaving a residual oil phase to support long-term anaerobic biodegradation of target contaminants. The technology also offers the potential to substantially reduce both initial capital and long-term operation and maintenance costs.

1.2 OBJECTIVES OF THE DEMONSTRATION

The project goals were to: (1) demonstrate and evaluate use of an edible-oil-in-water emulsion as the substrate for stimulating in situ biodegradation of perchlorate and chlorinated volatile organic compounds (CVOC) in groundwater and (2) develop a protocol for its implementation. The pilot tests evaluated the distribution of the emulsion in the aquifer, the impact of substrate injection on permeability and groundwater flow paths, and the changes in contaminant concentrations and biodegradation indicator parameters. The performance objectives for each demonstration were largely achieved, and the results were used to illustrate the cost-effectiveness of the technology both as a PRB and a source area treatment.

1.3 DEMONSTRATION RESULTS

At an industrial site in Maryland, a 50-ft long by 10-ft wide by 10-ft deep emulsified oil PRB was installed perpendicular to groundwater flow and monitored to determine the cost and performance for controlling the migration of dissolved contaminants in groundwater. High perchlorate concentrations were comingled with elevated levels of 1,1,1-trichloroethane (1,1,1-TCA) and low concentrations of trichloroethene (TCE) in the shallow groundwater. The PRB reduced perchlorate to below the regulatory target, but additional contact time was needed to achieve the same results for 1,1,1-TCA and TCE. There was no adverse change in pH and no evidence of flow bypassing around the PRB. The pilot study was extended to 42 months and showed that a single application of EOS® was effective in the PRB for almost 3 years without replenishment.

At a site at the Charleston Naval Weapons Station, EOS® was used to treat a TCE source area in a shallow, low-permeability aquifer. A tightly-spaced grid of injection wells was used to

distribute EOS® in the 20-ft by 20-ft by 10-ft deep pilot test treatment cell. After 6 to 9 months, TCE degradation slowed, apparently as a result of a drop in groundwater pH to near 5. Laboratory studies evaluated potential buffering agents, and after 28 months, the treatment cell was re-injected with a buffered emulsified oil substrate formulation. After the aquifer was neutralized, TCE was rapidly reduced to *cis*-1,2-dichloroethene (*c*DCE) and vinyl chloride (VC) with some measurable ethene production. However, the absence of microorganisms with the VC-reductase enzyme appeared to limit further biodegradation. The results demonstrated the effectiveness of the technology as a source area treatment for TCE but also pointed out the importance of thorough site characterization.

1.4 COST ASSESSMENT AND IMPLEMENTATION ISSUES

The unit cost to install the 50-ft long PRB was $226/yd^3. The cost to create a 20 x 20-ft source area treatment cell ranged from $325/yd^3 for direct injection to $428/yd^3 for a recirculation design. The mass of contaminant treated in the PRB was much higher due to the rapid flow of contaminated groundwater through the barrier. Consequently, the cost per gram of contaminant treated was also less in the PRB.

Cost averages shown in the table below were calculated and ranked for several applicable in situ technologies by using literature values and costs generated for hypothetical scenarios via ESTCP-funded design tools. These costs reflect labor, equipment, and material for installation of the technology components including wells, substrates or chemicals, and the associated monitoring networks, but do not include management, design, laboratory studies, performance monitoring, and reporting.

Technology	Approach	Number of Sites/Scenarios	Average Cost
Trench biowall	Solid substrates	2 sites	$61 ± $35/yd^3
In situ bioremediation	Soluble and miscellaneous substrates	13 sites	$79 ± $73/yd^3
Low temperature thermal treatment	Electrical	6 sites	$114 ± $100/yd^3
In situ bioremediation	Emulsified oil substrate – source area cell	15 site/scenarios	$123 ± $124/yd^3
In situ bioremediation	Emulsified oil substrate – PRB	7 sites/scenarios	$161 ± $103/yd^3
In situ chemical oxidation	Chemical	13 sites	$146 ± $132/yd^3

There is a wide range associated with each technology, and actual costs are highly site-specific. In situ bioremediation using emulsified oil substrate is not the least expensive to install, but calculating the net present value (NPV) for a given scenario demonstrated that long-term costs are expected to be lower due to the lower operation and maintenance (O&M) requirements and the longevity of the substrate compared to other electron donor materials.

The major technical challenges and cost drivers identified in these demonstrations when applying emulsified oil substrate technology included:

- Contaminant type(s), concentration(s), and vertical and lateral extent

- Impact of aquifer composition and permeability on oil retention and the effective distribution of the substrate throughout the target treatment zone
- Impact of substrate on aquifer pH, which can limit biodegradation and may require buffering
- Presence of native microorganisms to biodegrade the contaminant(s) or the need to consider bioaugmentation
- Establishing a treatment zone that affords adequate contact time between the contaminant, substrate, and bacteria, especially in PRBs
- Impact of regulatory goals and monitoring requirements for the site as they affect the duration of the project.

Several technical reports were prepared as a result of this project (ESTCP, 2006b; 2008; 2009). From this work and others, ESTCP and the Air Force Center for Engineering and the Environment (AFCEE) have developed protocols (ESTCP, 2006a; AFCEE, 2007) to assist base managers and project engineers with (1) determining if the emulsified oil process is appropriate for their site and (2) designing and implementing this technology. These documents are listed in Section 8.0, References.

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2.0 INTRODUCTION

This Cost and Performance Report summarizes two demonstrations of the emulsified edible oil technology for in situ remediation of groundwater impacted with perchlorate and/or chlorinated solvents. The work was funded by ESTCP as Project No. ER-0221. The purpose of the demonstrations was to evaluate the effectiveness of this type of substrate for treating these contaminants. The first demonstration was conducted at a confidential industrial site in eastern Maryland, USA, using a PRB installed by injection EOS® to treat a commingled perchlorate/chlorinated solvent plume. The second demonstration used emulsified oil substrate to treat a small simulated source area within a chlorinated solvent-contaminated solid waste management unit (SWMU) at the Charleston Naval Weapons Station (NWS) in Goose Creek, South Carolina, USA.

Both demonstrations were originally intended for 18 months of performance monitoring. However, ESTCP afforded additional time and resources to each demonstration for additional evaluation of the technology. The pilot study in Maryland initially tested the effectiveness of the PRB to intercept and treat contamination and prevent further downgradient migration; the study was prolonged by an additional 24 months to evaluate the longevity of the substrate in the subsurface. At the Charleston NWS site, the pilot study tested the applicability of the technology for treating a source area by injecting substrate in a small grid configuration; the study was extended by an additional 11 months to test the effectiveness of a newly developed buffered-emulsified oil product for its ability to adjust pH in the aquifer and promote enhanced reductive dechlorination (ERD) that had stalled presumably because of a decline in aquifer pH.

Several technical reports were produced as a result of this ESTCP-funded project. ESTCP (2006b) and ESTCP (2008) describe the pilot study in Maryland. ESTCP (2009) describes the pilot study at Charleston NWS. ESTCP (2006a) is a protocol prepared by Solutions-IES for ESTCP based on the lessons learned during the demonstrations at these two sites. The designs, concepts, results, discussions, and conclusions provided in these project reports are used without citation in this Cost and Performance report to provide the reader a review of the performance of the technology at each site and to form the basis of the cost comparison.

2.1 BACKGROUND

Groundwater contamination by perchlorate (ClO^{4-}) has become a major environmental issue for the U.S. Department of Defense (DoD). In many cases, perchlorate has entered groundwater through the release and/or disposal of ammonium perchlorate, a strong oxidant that is used extensively in solid rocket fuel, munitions, and pyrotechnics. Perchlorate is highly soluble in water, poorly sorbs to mineral surfaces and can persist for decades under aerobic conditions. Treatment technologies applied to perchlorate contamination often include groundwater extraction with ion exchange or aboveground bioreactors to remove the contaminant (ITRC, 2005). The capital investment and O&M associated with these technologies can be very expensive compared to in situ bioremediation, which stimulates indigenous microflora to biodegrade the perchlorate. The potential for use of bioremediation is evident since a variety of studies have shown that microorganisms from a wide variety of sources (Coates and Pollock, 2003; Coates et al., 1999; Logan, 2001; Gingras and Batista, 2002) can utilize perchlorate as an electron acceptor and anaerobically biodegrade perchlorate when supplied with appropriate

organic substrates and related amendments (Logan, 1998; Hunter, 2002; Zhang et al., 2002; Waller et al., 2004; Hatzinger, 2005).

Chlorinated solvents in groundwater are also a frequently encountered problem at DoD facilities. Although chlorinated solvents can be treated by a variety of treatment technologies such as groundwater extraction with air stripping or carbon exchange, in situ thermal desorption, or air sparging, these approaches typically require substantial capital costs and long-term O&M. In recent years, anaerobic reductive dechlorination has been shown to be an efficient microbial means of transforming more highly chlorinated species to less chlorinated species (Morse et al., 1998; USEPA, 1998; Flynn et al., 2000; AFCEE-NAVFAC ESC-ESTCP, 2004). Chlorinated solvents, or CVOCs, amenable to in situ anaerobic bioremediation include tetrachloroethene (PCE), TCE, *c*DCE, VC, 1,1,1-TCA, 1,1,2-trichloroethane (1,1,2-TCA), 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CT), and chloroform (CF). The result of complete degradation is the formation of nontoxic end products: carbon dioxide and water. Costs for in situ bioremediation are thought to be less than other traditional treatment technologies.

The key to success of in situ anaerobic bioremediation technology is to effectively deliver a biodegradable substrate to the contaminated interval within the aquifer and provide sufficient amount of material and contact time for the desired biological activity to occur. The substrate serves as a carbon source for cell growth and as an electron donor for energy generation. Many commercially available substrates can support these transformations; each has its own advantages and limitations. This project assessed an innovative, low-cost approach for distributing and immobilizing biodegradable organic substrate in perchlorate- and CVOC-contaminated aquifers to promote biodegradation for an extended period of time and provide cost information to compare with other remediation approaches.

2.2 OBJECTIVES OF THE DEMONSTRATIONS

The first goal of the project was to demonstrate and evaluate use of an edible-oil-in-water emulsion substrate for stimulating in situ biodegradation of perchlorate and chlorinated solvents. The objectives of the laboratory work and field demonstrations were to evaluate:

- Distribution of the oil emulsion in the aquifer
- Impact of the oil injection on the aquifer permeability and groundwater flow paths
- Changes in contaminant concentrations and biodegradation indicator parameters both upgradient and downgradient of the injection areas
- Data obtained during the pilot tests to demonstrate the cost-effectiveness of the approach.

The second goal of the project was to prepare a protocol to assist base managers and project engineers with determining if the emulsified oil process is appropriate for their site and to provide guidance for designing and implementing this technology. The protocol provides practitioners with an in-depth understanding of the emulsified oil process and guidance how best to apply it for their own site remediation.

2.3 REGULATORY DRIVERS

CVOCs in groundwater are regulated on a federal level by the National Primary Drinking Water Regulations, which establish maximum contaminant level (MCL) for drinking water to protect human health. MCLs have been established for 1,1,1-TCA, PCE, TCE, and their daughter products. The MCLs for CVOCs used by the Maryland Department of the Environment (MDE) and the South Carolina Department of Health and Environmental Control (SCDHEC) were used as the regulatory targets for evaluating the technology.

There is currently no federal MCL for perchlorate in drinking water (USEPA, 2005; ENS, 2006). In February 2005, the U.S. Environmental Protection Agency (USEPA) established a Drinking Water Equivalent Level (DWEL) for perchlorate of 24.5 parts per billion (ppb), which may be used by officials throughout the agency to make site-specific cleanup or interim drinking water standard decisions involving perchlorate. In January 2006, USEPA issued "Assessment Guidance for Perchlorate," identifying 24.5 micrograms per liter (µg/L) as the recommended value "to be considered" and preliminary remediation goal for perchlorate (USEPA, 2006). At the beginning of this project, MDE used a "health advisory goal" of 1 µg/L, but currently applies 2.6 µg/L as the drinking water standard. The SCDHEC has not promulgated a standard for perchlorate.

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3.0 TECHNOLOGY

The emulsified oil technology is a low-cost process for delivering a low solubility, slowly degradable organic substrate to the subsurface to enhance the anaerobic biodegradation of perchlorate and CVOCs among other reducible compounds. Early studies showed promise for the use of edible vegetable oils to promote ERD (Boulicault et al., 2000; AFCEE-NAVFAC ESC-ESTCP, 2004; Parsons, 2002; Borden and Rodriguez, 2005). However, inherent limitations to this substrate included the need for large amounts of oil injected at close spacing, limited spreading ability, potential for floating out of the treatment zone, and loss of aquifer permeability (AFCEE, 2007). To enhance the distribution of the oil throughout the target zone, a stable, non-coalescing oil-in-water emulsion was developed (Lieberman et al., 2005; Borden, 2005, 2007; Zawtocki, 2005) with uniform droplet size and negative surface charge to allow transport in most aquifers. Using this material, the sediment surfaces gradually become coated with a thin layer of oil droplets that provides a carbon source for long-term reductive dechlorination.

3.1 TECHNOLOGY DESCRIPTION AND APPLICATIONS

Emulsified oil substrate is available commercially as a pre-blended mixture that provides the end-user with a reliable, consistent, and uniform product to use. The amount of emulsified oil injected into the subsurface is determined based on the concentrations of the target compounds, the concentrations of various biodegradation and geochemical parameters, the concentrations of competing electron acceptors, and soil retention coefficients as determined by the geologic and hydrogeologic conditions.

The processes by which emulsified oil substrate enhances in situ biodegradation of perchlorate and chlorinated ethanes and ethenes are similar, although the microbial populations and metabolic pathways differ. In both cases, emulsified oil substrate introduced into the contaminated aquifer is gradually fermented over time by indigenous microflora, providing a slow, continuous source of dissolved organic carbon (DOC) and hydrogen (H_2) to support anaerobic biodegradation of the target contaminants. The efficacy of using soybean oil for this process is that one mole of edible oil (i.e., soybean oil) can be fermented and produce 156 moles of hydrogen equivalents, or 82 moles of hydrogen equivalents per pound of soybean oil (Equation 1). By comparison, as shown in Equation 2, a mole of lactate would be expected to produce only 6 moles of hydrogen equivalents (or 30 moles of hydrogen per pound of lactate).

(Eq. 1) $C_{56}H_{100}O_6$ (**oil**) + 106 H_2O – ***Fermenting Bacteria*** → 56 CO_2 + 156 H_2

(Eq. 2) $C_3H_6O_3$ (**lactate**)+ 3 H_2O --***Bacteria***--> 3 CO_2 + 6 H_2

Perchlorate-reducing microorganisms use the organic substrate directly as a carbon and energy source. Perchlorate serves as an electron acceptor, and more than 50 perchlorate-reducing anaerobic and facultative anaerobic bacteria have been cultured (Coates and Achenbach, 2006). The substrate-enhanced, enzyme-mediated metabolism of perchlorate proceeds by the sequential removal of oxygen atoms from the anion as shown in Equation 3.

(Eq.3) ClO_4^- → ClO_3^- → ClO_2^- → $Cl^- + O_2$
Perchlorate Chlorate Chlorite Chloride + Oxygen

By contrast, the degradation of 1,1,1-TCA and TCE is a two-step process that first requires the fermentation of the oil to generate acetate and hydrogen (Eq. 1). In the second step, these products can be used by the specific population of bacteria capable of carrying out the desired sequential dechlorination steps.

Far fewer microbial species can biodegrade 1,1,1-TCA, PCE, and TCE, and dehalorespiring microorganisms are generally more fastidious about their substrate and environmental conditions. The initial microbially mediated conversion step of 1,1,1-TCA and TCE is a sequential reduction of the chlorinated molecule requiring the presence of H_2 as shown in equations 4a and 4b. Diagrams of the metabolic pathways for the breakdown of CVOCs can be found in many publications including AFCEE-NAVFAC ESC-ESTCP (2004), Morse et al. (1998) and USEPA (1998), among others.

(4a) $C_2H_3Cl_3$ (**1,1,1-TCA**) + H_2 – ***Dehalorespiring Bacteria*** → $C_2H_3Cl_2$ (**1,1-DCA**) + Cl^- + H^+

(4b) C_2HCl_3 (**TCE**) + H_2 - ***Dehalorespiring Bacteria*** →$C_2H_2Cl_2$ (***cis/trans*-1,2-DCE**) + Cl^-+H^+

The formation of hydrogen from the fermentation of edible oils, carbohydrates, alcohols, short-chain fatty acids, and lactate-based substrates is recognized as a desirable outcome of the technology (Morse et al., 1998; Ellis et al., 2000; AFCEE-NAVFAC ESC-ESTCP, 2004). Fermentation of vegetable oils also leads to the formation of short-chain metabolic acids (e.g., acetic, formic, propionic, butyric acids), and successful reductive dechlorination also releases chloride that can react to form hydrochloric acid (HCl). Together these effects can result in a decrease in the pH of the aquifer, especially when chlorinated solvent concentrations are high and alkalinity is low. Maes et al. (2006), Tillotson (2007), Vainberg et al. (2006) and Rosner et al. (1997) demonstrated the sensitivity of dehalorespiring species to a decline in pH, particularly below pH 5.5. Recent work has been directed to developing a product that could simultaneously buffer the aquifer while providing substrate. The pilot study in Charleston NWS was useful for understanding and developing this process.

There are several applications for emulsified oil substrate. In addition to degradation of perchlorate and CVOCs, emulsified oil substrate can be used to promote degradation of chlorobenzenes, chlorophenols, chlorinated pesticides (e.g., chlordane), explosive and ordnance compounds (e.g., TNT, RDX, HMX), nitrate and sulfate, and the transformation of hexavalent chromium. The distribution of the oil throughout the target zone is enhanced by the use of emulsifying agents that reduce the viscosity of the substrate and improve its handling characteristics. Using conventional wells or direct-push injection points, emulsified oil can be injected into “hot spots” as a source area treatment, throughout a contaminant plume, or as a PRB to intercept contaminant flow. Recirculation can also be used to aid in the spread of the substrate.

3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

3.2.1 In Situ Anaerobic Bioremediation

The advantages of enhanced reductive in situ bioremediation are well documented (AFCEE-NAVFAC ESC-ESTCP, 2004; USEPA, 1998). In situ anaerobic bioremediation can be used to treat soil and groundwater contaminated with many types of contaminants, as noted above. Approaches using soluble substrates, slow-release, and solid substrates to treat CVOCs and perchlorate are all based on microbial processes, and none of these substrates is inherently more or less effective in degrading perchlorate, PCE, TCE, or 1,1,1-TCA. The technology is relatively simple and inexpensive to apply. Common advantages of in situ bioremediation include:

- Lower capital and O&M costs.
- Minimal impact on site infrastructure.
- No secondary waste stream to treat.
- Variety of organic substrates can be utilized, including soluble substrates (e.g. lactate, molasses), slow-release substrates (e.g., polymerized-lactate, vegetable oil, emulsified oils), and solid substrates (e.g., mulch, chitin).
- Substrates are relatively inexpensive.
- Substrates can be applied in various configurations to remediate source areas (grid), contain plumes (PRBs), and provide plume-wide treatment (combination).
- Lower life-cycle costs.

There are also some potential limitations to use of in situ anaerobic bioremediation that need to be carefully considered.

- The introduction of organic substrates can affect adversely affect secondary water quality in any of the following ways:
    - Increasing the biochemical oxygen demand (BOD) and total organic carbon (TOC) in the groundwater potentially imparting undesirable taste and odor
    - Anaerobic metabolic processes resulting in increased levels of dissolved manganese, iron, and sulfide downgradient from the treatment zone
    - Strong reducing environment that may result in mobilizing toxic metals such as arsenic
    - Incomplete reductive biodegradation of the contaminants leading to accumulation of potentially toxic intermediate daughter products (e.g., cis/trans-dichloroethene [c/t-DCE] and VC) in the downgradient aquifer
    - Release of carbon dioxide and methane to the vadose zone

- Risk of vapor intrusion to buildings or underground utilities if the water table is shallow or the treatment zone is in close proximity, especially if dechlorination is incomplete.

- Variations in aquifer permeability may affect injection rates and the spatial distribution of substrate. Depending on the substrate selected, special methods may be needed to help distribute substrate throughout aquifer (e.g., trenching, hydraulic fracturing, high pressure injection, or mechanical mixing.) These affect cost.
- Changes in permeability can also be a result of substrate injection due to biomass growth and/or gas bubble accumulation.
- The depth of the contaminated interval can serve as a physical limitation to applying the technology. The choice of method of injection, associated costs for drilling, and additional time needed to inject to greater depths all influence overall project costs, regardless of the type of substrate selected.
- Reliance on indigenous microbial populations. The appropriate microorganisms must be present. Microorganisms capable of completely degrading the CVOCs to nontoxic end products may not be present at sites (Bradley, 2000). Perchlorate-reducing microorganisms are more widespread and may not pose as difficult a hurdle to overcome.

3.2.2 Emulsified Oil Substrate Technology

There are additional advantages for using emulsified oil substrate as the technology of choice for in situ anaerobic bioremediation. These include:

- Provides a long-lasting substrate which typically requires fewer re-injections or replenishments of the treatment zone. A single application of emulsified oils often lasts 3 to 5 years.
- Provides more reducing equivalents per mole of substrate resulting in need for less substrate.
- Substrate costs are lower over the project life. Unit costs are slightly higher for emulsified oils than for soluble substrates such as carbohydrates and lactate. However, soybean oil contains more reducing equivalents per gram than soluble substrates so the cost per reducing equivalent may be lower. More importantly, the greater longevity of oil in the subsurface requires less frequent substrate addition and greatly reduces labor costs for substrate reinjection.
- Provides for effective transport throughout the contaminated zone. Emulsified oils can be distributed over relatively large areas by flushing the oil droplets through the aquifer material with water, allowing treatment of larger aquifer volumes with fewer injection points, reducing costs.
- Provides an effective approach for maximizing the contact time between bacteria, substrate and contaminants. As the oil droplets migrate through the treatment zone, hydrophobic contaminants (e.g., chlorinated solvents) will partition into the

oil droplets forming a new mixed non-aqueous phase liquid (NAPL). This mixed NAPL provides an ideal environment for growth of dechlorinators since it contains both electron acceptor and electron donor. Once this mixed NAPL is formed, there is no opportunity for the substrate to be fermented to methane before it reaches the contaminant (Yang and McCarty, 2002), thus assuring prolonged contact time and maintaining conditions conducive for reductive dechlorination for years.

Many of the limitations of the emulsified oil technology are similar to other substrates used for in situ anaerobic bioremediation. However, because of the nature of the substrate certain other conditions may develop such as:

- Release of short-chain volatile fatty acids that could potentially decrease pH.
- Oil retention by the aquifer material and the rate that water can be injected. Aquifer material with high clay content retains more oil droplets, requiring injection of more emulsion to achieve the same radius of influence. Aquifer material with high clay content will also have a lower permeability, making it more difficult to inject large volumes of water to distribute the oil droplets. Although overcoming these limitations with more substrate may increase initial costs, greater amount of oil may increase longevity, reducing future costs.

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4.0 EMULSIFIED OIL PRB DEMONSTRATION

Emulsified oils can be used to treat contaminated groundwater in a PRB configuration by injecting the emulsion through a series of temporary or permanent wells installed perpendicular to groundwater flow. As groundwater moves through the emulsion treated zone under the natural hydraulic gradient, a portion of the trapped oil dissolves, providing a carbon and energy source to accelerate anaerobic biodegradation processes. A diagram of the concept is shown in Figure 1.

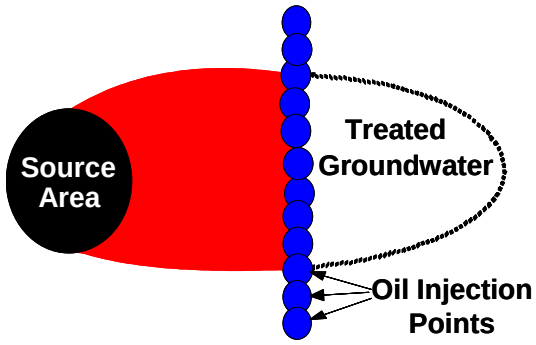

Figure 1. Conceptual diagram of a PRB for treating contaminated groundwater.

4.1 PRB PERFORMANCE OBJECTIVES

The overall goal of the PRB demonstration project in Maryland was to evaluate the cost and performance of an emulsified oil PRB for remediating perchlorate and chlorinated solvents in groundwater. The performance of the barrier was evaluated by monitoring changes in the distribution of EOS® in the subsurface, contaminant concentrations and mass, and the impact of the emulsion injection on aquifer permeability and groundwater flow. The project was also extended to evaluate the effective longevity of the substrate in the aquifer. The performance metrics for the project and corresponding statement of success at meeting each objective are summarized in Table 1. The performance assessment is summarized in Section 4.3.

Table 1. Performance objectives for Maryland permeable reactive barrier pilot study.

Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)
Qualitative Performance Objectives		
1. Reduce risk	Reduce concentrations and mass flux of regulated contaminants.	Yes
2. Capital costs	Capital costs are significantly lower than other barrier technologies.	Yes
3. Maintenance	Re-injection is not required for at least 5 years.	No[a]
4. Ease of use	Installation of PRB using readily available equipment.	Yes
5. Compatible with MNA[b] approaches	Chemical changes in downgradient groundwater do not adversely impact any ongoing MNA processes.	Yes
6. Minimal adverse impacts	Groundwater quality over 100 ft downgradient is not severely impacted by remediation technology.	No[c]

Table 1. Performance objectives for Maryland permeable reactive barrier pilot study (continued)**.**

Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)
Quantitative Performance Objectives		
1. Reduce perchlorate concentrations	Primarily, >90% reduction in perchlorate concentration in one or more downgradient wells and secondarily, achieve reductions that will meet the assumed 4 ppb regulatory standard.	Yes, based on data from well SMW-6 along the centerline of the barrier
2. Reduce 1,1,1-TCA concentrations	>75% reduction in average 1,1,1-TCA concentration in downgradient wells.	Yes
3. Reduce mass flux of perchlorate	Reduce mass flux of perchlorate by over 75%.	Yes
4. Reduce mass flux of chlorinated ethanes	Reduce mass flux of total chlorinated ethanes by over 75%.	Yes
5. Emulsion injection does not reduce aquifer permeability to the extent that it compromises the performance of the barrier	Hydraulic conductivity testing will be performed before and after injection to evaluate potential changes. A bromide tracer test will also be performed to evaluate flow through the barrier.	Yes
6. Contaminant bypassing around the barrier is not excessive and does not compromise performance of the barrier	Tracer injected in upgradient monitor well is detected in barrier well and downgradient wells but not side-gradient wells.	Yes
7. Meet regulatory standards	Contaminant concentrations in one or more downgradient wells are below the standards.	Yes[d]

Notes:

[a] System operated without maintenance for 1.5 years. Extended monitoring showed good bioactivity for close to 3 years with some decline thereafter until the monitoring was stopped.

[b] MNA = monitored natural attenuation.

[c] Extraction trench was located 50 ft downgradient of the PRB. Increased concentrations of dissolved iron and manganese entering the trench increased maintenance costs for the air stripper.

[d] Standard at the time objective was set was considered the Method 314 detection limit of 4 µg/L.

4.2 PRB DEMONSTRATION DESIGN AND IMPLEMENTATION

4.2.1 Site Location and Background Conditions

The site was located at an industrial facility in northeast Maryland where a commingled perchlorate and chlorinated solvent plume extended downgradient of a closed surface impoundment. The former impoundment was operated at the site from 1976 through 1988 for the storage of an aqueous solution of ammonium perchlorate and waste solvents as part of former industrial operations including manufacture of fireworks, munitions, pesticides, and solid propellant rockets. The rubber liner failed and was replaced with a plastic liner material after groundwater impacts were discovered in 1983. The impoundment was permanently closed in

1988. The pilot test PRB was constructed in an open grassy area approximately 150 ft downgradient from the former impoundment.

Prior to injection of the EOS® substrate to form the PRB, a thorough hydrogeologic and contaminant baseline characterization of the pilot study site was prepared. The results are discussed in detail in the Final Report (ESTCP, 2006b). The site hydrogeology was characterized as a shallow water table aquifer composed of silty sand and gravel to approximately 15 ft below ground surface (bgs) that is underlain by silty clay. The water table varies between approximately 1 and 8 ft bgs with groundwater in the pilot test area generally flowing westward with a shallow hydraulic gradient of .003ft/ft. Hydraulic conductivities averaged 22 to 40 ft/day and, assuming 30% porosity, the groundwater velocity was approximately 80+ ft/yr. Although this value was used in design of the field demonstration, the average groundwater velocity in the pilot test area during the demonstration period was calculated to be 400 ft/yr. The injection test showed that flow rates of approximately 1 gallons per minute (gpm) could be maintained with less than 10 pounds per square inch (psi) of pressure.

Perchlorate concentrations ranged from 3100 to 20,000 µg/L; 1,1,1-TCA ranged from 5700 to 17,000 µg/L; TCE ranged from 28 to 210 µg/L. The pH was close to 6.0, and the aquifer was generally in the oxidative range for dissolved oxygen (DO) and oxidation reduction potential (ORP) with low concentrations of TOC, nitrate, and sulfate. Historical data indicated there had been a decrease in CVOCs over time as a result of many years of groundwater pump-and-treat with air stripping. However, there was little evidence of perchlorate reduction during the same period.

4.2.2 Laboratory Studies

Before deciding to use the Maryland site for the demonstration, laboratory studies were performed. As part of the characterization activities, soil and groundwater was collected for microcosm and column studies. The studies were conducted in the Department of Civil, Construction, and Chemical Engineering at North Carolina State University.

The microcosm studies were performed to (1) identify an appropriate edible oil substrate that would support complete biodegradation of perchlorate and 1,1,1-TCA in the groundwater with minimal methane production and (2) determine whether bioaugmentation was needed to achieve complete conversion of 1,1,1-TCA to nontoxic end products. Results showed that perchlorate degradation was rapid and complete in the microcosms treated with EOS® compared to other oils and no bioaugmentation was needed to degrade perchlorate. Chlorinated solvent degradation results were more variable. In some incubations, 1,1-DCA was produced during biodegradation of 1,1,1-TCA but did not degrade further. However, in other incubations, 1,1-DCA was extensively degraded.

Small diameter column experiments (2.5 cm dia. x 80 cm long) were conducted using aquifer material to verify that EOS® could be effectively distributed through the aquifer material and to estimate model parameters for simulating emulsion transport and retention. A pulse of EOS® was injected into the columns followed by chase water. The results showed that 97% of the volatile solids were retained throughout the column, although higher concentrations were

measured at the inlet. The data were used to develop model parameters to simulate the distribution of EOS® at the site in preparation for the field study.

4.2.3 Pilot Study Design

The results of the site characterization activities, microcosm studies and column tests were used to aid in the design of the EOS® biobarrier. The primary design components were 1) screen interval of the injection wells, 2) spacing of the injections wells, 3) amount of substrate to inject, and 4) total injection volume (substrate and chase water) needed to form the PRB. The layout of the monitoring network was designed based on groundwater flow direction and velocity.

The optimal screen interval of the injection wells was determined to be 5 to 15 ft bgs. The pilot test barrier was designed as a 50-ft long barrier perpendicular to groundwater flow. Due to uncertainties regarding the permeability of the aquifer, a conservative injection well spacing of 5 ft on-center was utilized. The well layout is shown in Figure 2.

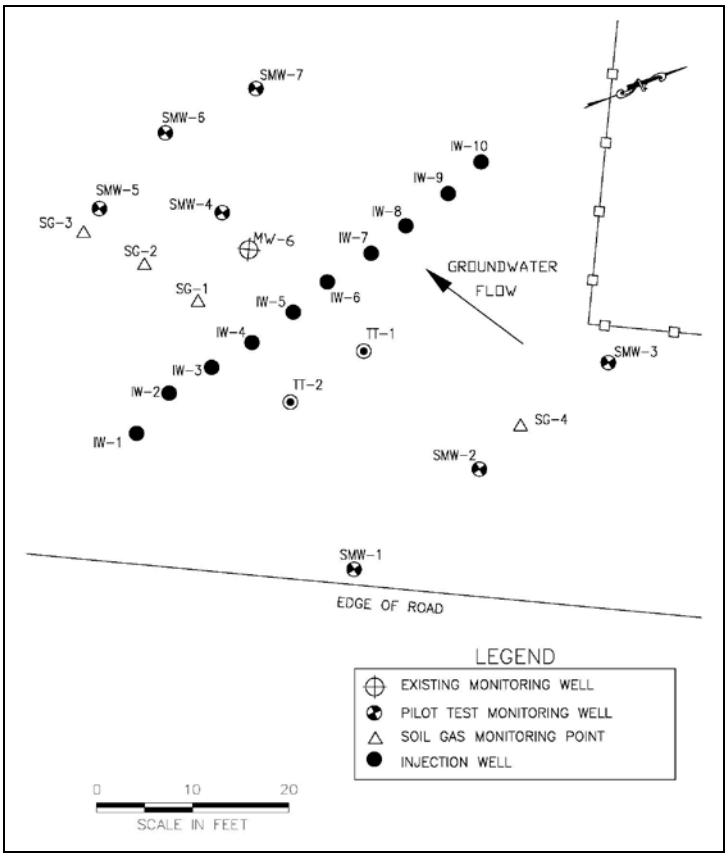

Figure 2. Layout of permeable reactive barrier and monitoring points.

Seven monitoring wells, four soil gas monitoring points, and two tracer test wells were installed as part of the site characterization activities and constituted the network to monitor the emplacement of EOS® and its effectiveness in reducing contaminant concentrations.

4.2.4 Substrate Injection

Solutions-IES determined the amount of EOS® to inject based on two factors: (1) the oil required for biodegradation and (2) the oil retention by the sediment. As discussed in the Final Report (ESTCP, 2006b), using these values gave similar results, and the amount of oil required to support contaminant biodegradation was approximately 500 to 600 lb, i.e., two 55-gallon drums of EOS® (EOS® is approximately 60% soybean oil). Based on these calculations, Solutions-IES injected two drums and 2200 gallons total volume (water and emulsion) evenly among the 10 injection wells to create the PRB. Injecting additional EOS® could have improved contact efficiency and remediation system performance. However, the additional EOS® would likely have lasted beyond the end of the planned 18-month monitoring period.

The PRB was created in October 2003. The temporary equipment required for the injection included a solution mixing/holding tank or pool, a gasoline powered transfer pump, injection hoses, flow meters, pressure gauges, and valves. The mixing equipment and hoses leading to the injection wells are shown in Figure 3. Utility requirements were limited to a source of water for diluting the concentrated emulsion and for use as chase water. Treated water was obtained from an air stripper located approximately 150 ft south of the PRB.

Figure 3. Injection of EOS® to form the permeable reactive barrier.

4.3 PRB PERFORMANCE ASSESSMENT

Performance monitoring was initiated after the oil emulsion was injected (October 13-14, 2003) and then approximately 1 month, 2 months, 4 months, 11 months, and 18 months thereafter. The evaluation focused on 1) the distribution of EOS® in the aquifer; 2) the ability of the technology to promote degradation of perchlorate, 1,1,1-TCA, and TCE; 3) the impacts of the EOS® injection on the hydraulic conductivity of the aquifer and groundwater flow in the vicinity of the barrier; and 4) secondary water quality impacts. Four additional semi-annual monitoring events were conducted in the 24 months following the initial performance period to evaluate 1) the

longevity of the emulsified oil in the subsurface and 2) the long-term effectiveness of the PRB. The discussion of data obtained during the original 18-month demonstration project can be found in the Final Report (ESTCP, 2006b). The discussion of the extended monitoring portion of the test is presented in the Final Report Addendum (ESTCP, 2008).

4.3.1 Total Organic Carbon and Distribution of EOS®

During injection, milky emulsion was quickly observed 5 ft from the nearest injection point. TOC quickly increased in the monitor well 12.5 ft downgradient from the PRB and leveled off at 20 to 50 mg/L. A smaller increase in TOC was observed 20 ft downgradient, and little change was observed upgradient. These results indicate that the initial injection spread emulsion up to 12.5 ft from the injection wells. However, most of the emulsion was sorbed to the aquifer sediment shortly after injection, with TOC slowly being released from the barrier over time, as desired. The 6-month post-injection Geoprobe® sampling event revealed elevated TOC levels in a wide area downgradient of the PRB, extending as far as 35 ft in the direction of groundwater flow.

The distribution of EOS® in the aquifer was evaluated through soil and groundwater TOC data. The average TOC concentrations in the pre-injection and background soil samples were 172 mg/kg (5 to 10 ft bgs) and 648 mg/kg (10 to 15 ft bgs). Soil samples collected at 6 and 9 months post-injection from within the PRB had average TOC concentrations of 829 mg/kg (5 to10 ft bgs) and 1274 mg/kg (10 to 15 ft bgs) suggesting the presence of emulsion.

4.3.2 Groundwater Geochemistry

Geochemical data confirmed that anaerobic conditions favorable for biodegradation of these compounds were established in the treatment area and remained for the 42-month life of the project.

- **DO and ORP.** DO concentrations decreased across the entire pilot test area, although not as strongly as might be expected. ORP decreased in all of the site monitoring and injection wells following EOS® injection and remained conducive to perchlorate and chlorinated solvent biodegradation for the full 42-month duration of the study.
- **Nitrate and Sulfate.** Immediately after EOS® injection, the pre-injection average nitrate and sulfate concentrations decreased and stayed very low to non-detect through 24 months. Low, but measurable, concentrations of nitrate and sulfate began to rebound after 30 months.
- **Iron and Manganese.** Dissolved iron increased from non-detect in the injection and downgradient wells to concentrations as high as 78 mg/L; manganese also increased. This may have contributed to fouling of the air stripper recovery trench approximately 50 ft downgradient.
- **Methane.** Methane increased in the injection wells from non-detect to >1000 mg/L by 11 months post-injection and remained elevated throughout the entire 42 months, indicating anaerobic reducing conditions were being maintained.

- **pH.** The EOS® substrate used in the injection has a low pH (~3.5); however, over the course of the pilot test, the pH levels in the injection and downgradient monitor wells increased slightly from pre-injection levels around 6.0 to post-injection values near 6.5.
- **Chloride.** There were no changes or trends associated with chloride concentrations in the pilot test area.

4.3.3 Perchlorate

The EOS® PRB was very effective at degrading perchlorate throughout the duration of the pilot study. Perchlorate concentrations in all the injection wells were non-detect (<4 µg/L) within 5 days of injection (Figure 4). Perchlorate removal efficiency remained greater than 93% for 133 days in the five injection wells that were measured.

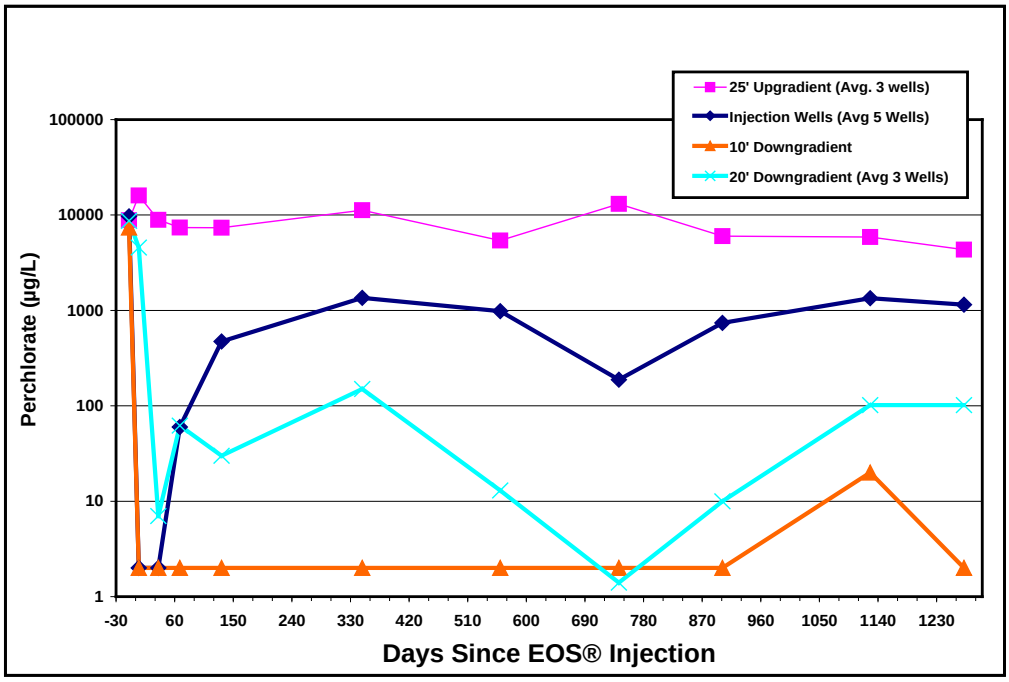

Figure 4. Perchlorate concentrations versus time.

Figure 5 shows perchlorate concentrations in groundwater 9 months after installation. Downgradient of the PRB, concentrations are <4 µg/L along almost the entire face of the barrier. The elevated concentrations near the ends of the PRB are a result of its placement in the middle of the plume, not flow bypassing. The data suggest that the effectiveness of perchlorate degradation may have been starting to decline by 18 months (Day 560) post-injection. By 42 months (Day 1272), the average perchlorate concentration in the downgradient wells was 128 µg/L, indicating an average removal efficiency of 97%.

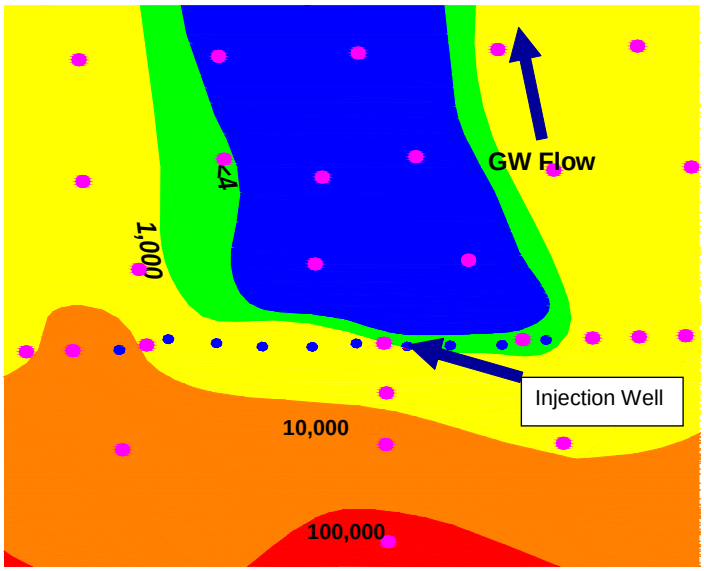

Figure 5. PRB effectiveness 9 months after EOS® injection.
Blue points are injection wells along the PRB; pink points are groundwater monitoring locations; values are perchlorate concentrations in µg/L.

As shown in Figure 4, the beginning of a perchlorate "rebound" in the injection wells was observed after about 4 months (Day 132), but concentrations stabilized and removal efficiency remained high for the following 7 months. Some injection wells performed better and longer than others, demonstrating the effectiveness of the technology but emphasizing the importance of the layout and design. Depletion of TOC in the injection wells by 42 months may have contributed to the further drop in effectiveness measured during the last sampling event. Additional sampling events would be required to definitively determine if perchlorate concentrations were beginning to climb toward pre-test levels suggesting that the PRB had totally exhausted its useful life and EOS® needed to be re-injected to re-establish the earlier level of effectiveness.

The mass flux calculations indicated approximately 61 lb of perchlorate was removed over the entire 42-month demonstration. Average perchlorate concentrations in the three monitoring wells located 20 ft downgradient of the barrier were two to three orders of magnitude lower than concentrations upgradient of the PRB for over 3 years following EOS® injection. This demonstrates the effectiveness and longevity of the emulsified oil treatment process for treating perchlorate contaminated groundwater.

4.3.4 Chlorinated Ethanes

The concentration changes of chlorinated ethane compounds in the injection and downgradient were similar. Changes in groundwater contamination treated in the PRB are reflected 20 ft downgradient approximately 2 months later as a result of groundwater flow velocity and travel time of contaminants in the aquifer. After 42 months, 1,1,1-TCA was still reduced by 91% 20 ft downgradient of the barrier. Figure 6 shows the changes in 1,1,1-TCA and its daughter products in SMW-6 located approximately 20 ft downgradient of the injection wells forming the PRB.

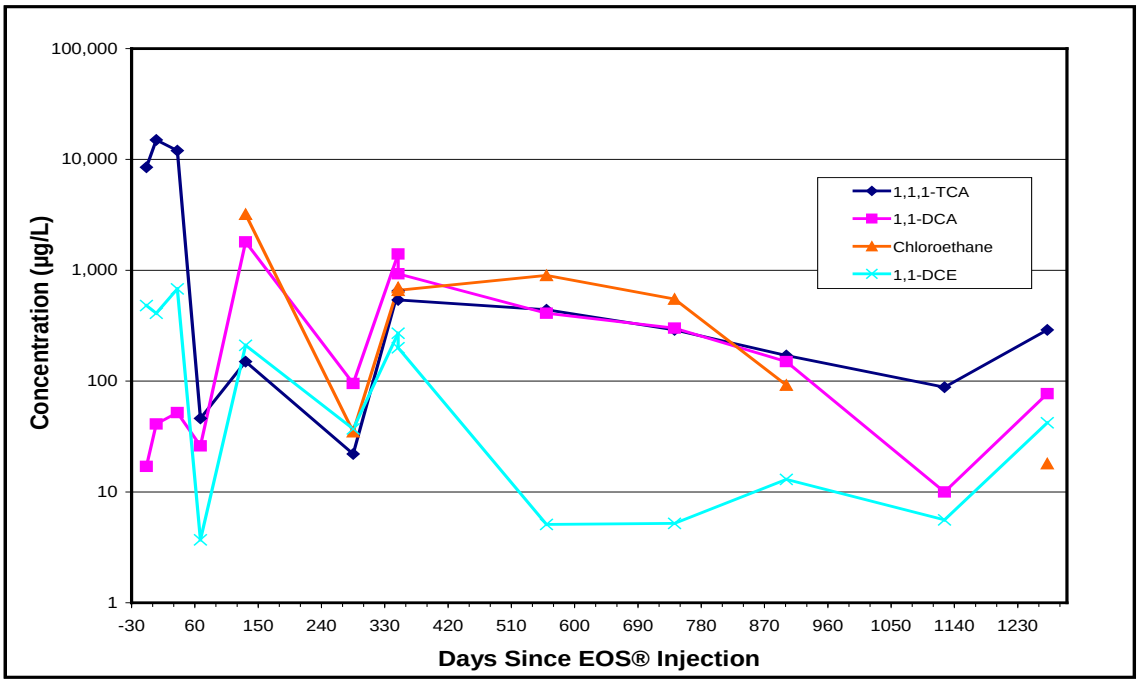

Figure 6. Chlorinated ethane concentrations versus time in downgradient monitor well SMW-6.

Although the concentrations of the parent molecule 1,1,1-TCA were dramatically reduced by passage through the PRB and averaged better than 75% lower both in and downgradient of the barrier for over 2.5 years (~30 months), the lowest concentrations achieved did not meet the Federal MCL of 200 µg/L. During a period of increased contact time (when the downgradient interceptor trench was taken out of service), the treatment came closest to meeting the standard. In addition, the active biodegradation of 1,1,1-TCA resulted in the formation of 1,1-DCA at concentrations greater than the MDE Cleanup Standard of 80 µg/L and chloroethane at concentrations greater than the Cleanup Standard of 3.6 µg/L. To achieve these lower target concentrations would require additional contact time in the PRB for further biodegradation of the parent and daughter compounds to continue.

4.3.5 Permeability Impacts of the EOS® Injection

Despite the injection of EOS®, the hydraulic conductivity in the biobarrier was never less than the conductivity measured upgradient of the barrier. The pre-injection and post-injection bromide tracer test results were similar, indicating that EOS® injection did not result in flow bypassing around the barrier. The average hydraulic conductivity downgradient of the biobarrier was typically higher than both the upgradient and injection wells. In general, hydraulic conductivity was not adversely affected by the introduction of emulsified oil.

4.4 PRB PILOT STUDY COST ASSESSMENT

A brief cost breakdown and performance analysis was provided in the Final Report for this site (ESTCP, 2006b). That information was expanded and used to refine and determine costs to implement the Maryland pilot test. Large portions of the costs were associated with site characterization, laboratory studies, engineering design, and modeling due to the rigorous planning of the evaluation. The main technology-related costs were associated with the actual injection process, including costs for installing the injection and monitoring wells, purchasing the substrate for injection, mobilizing to the site, and performing the injection. After the injection was completed, the only ongoing costs were for performance monitoring.

Technology Demonstration Plan development, long-term project management, reporting costs and technology transfer costs were not figured in. The revised total cost of the barrier pilot test demonstration was approximately $264,700, which was slightly higher than the $216,000 cost shown in the Final Report. Primary cost elements included:

a) Site characterization and design: ~$54,750 (21%)
b) Laboratory treatability study: ~$30,000 (11%)
c) PRB construction: ~$8900 (3%)
d) Monitoring well network consisting of 14 additional wells: ~$10,130 (4%)
e) Substrate and shipping: $2870 (1%)
f) Labor and equipment to inject PRB: ~$20,000 (8%)
g) Performance monitoring: ~$124,500 (~47%)
h) Extra specialized analyses: $13,550 (5%)

The combined cost to install the PRB and the monitoring network and to manage the one-time injection of substrate to create the PRB (items c, d, e, and f) was $41,900, which calculates to $8.39/ft^3 or $226/yd^3.

5.0 EMULSIFIED OIL SOURCE AREA TREATMENT

The demonstration was designed as a pilot test to evaluate the effectiveness of emulsified oil substrate for enhancing the biodegradation of CVOCs in a simulated source area. The project was conducted in two phases within a small area within SWMU 17 at the Charleston NWS.

Phase I was performed as prescribed in the original Technology Demonstration Plan and included site characterization, baseline sampling, injection of emulsified oil substrate and performance monitoring for 28 months. Solutions-IES and ESTCP expanded the project to include Phase II after the performance monitoring results from Phase I indicated that low pH was limiting further biodegradation of the target CVOCs. Phase II included a bench-scale treatability study, development and injection of a newly formulated pH-buffered substrate to overcome the pH problem, and an additional 11 months of performance monitoring in the field to measure the effect of the second substrate on enhanced reductive dechlorination.

5.1 SOURCE AREA TREATMENT PERFORMANCE OBJECTIVES

The goal of this demonstration project was to evaluate the performance of EOS® for remediating TCE in groundwater. The performance was evaluated by monitoring changes in contaminant concentration and mass flux, the distribution of EOS® in the subsurface, and the impact of the emulsion injection on aquifer permeability and groundwater flow. The Phase I performance metrics and results are summarized in Table 2.

Table 2. Performance objectives for South Carolina source area treatment pilot study.

Primary Performance Criteria	Success Criteria	Results
Qualitative Performance Objective		
1. Reduce risk	Reduce mass of contaminants in treatment zone and downgradient mass flux of regulated contaminants.	Yes
2. Capital costs	Capital costs are significantly lower than other zone treatment technologies.	Yes
3. Maintenance	Re-injection is not required for at least 5 years.	Not determined*
4. Ease of use	Installation of treatment zone using readily available equipment.	Yes
5. Compatible with MNA approaches	Chemical changes in downgradient groundwater do not adversely impact any ongoing MNA processes.	Yes
Quantitative Performance Objective		
1. Reduce TCE levels	>90% reduction in average TCE concentration in monitoring wells in treatment zone.	Yes
2. Convert TCE to nontoxic end-products	>50% reduction of TCE is converted to ethene or ethane.	Yes. CVOCs reduced by >80%
3. Reduce contaminant mass flux	Reduce mass flux of chlorinated ethenes by over 75%.	Yes
4. Reduce mass of TCE in soil	Reduce average TCE concentration in treatment zone by >80%	Yes

*Measureable TOC was present in the aquifer after 28 months. Addition of pH buffered substrate replenished the TOC, but the longevity was only measured for an additional 11 months before terminating the study. This precluded measuring when re-injection would eventually be needed to replenish the treatment zone.

After reviewing the performance monitoring results for up to 24 months after implementing Phase I, it appeared that low groundwater pH was inhibiting reductive dechlorination. ESTCP funded supplemental laboratory and field studies to test this hypothesis and seek ways to overcome this apparent limitation. The objectives of Phase II were to evaluate the ability to increase the pH of the aquifer into the optimal range for dehalorespiring bacteria to thrive using an injectable, pH-buffered emulsion and determine the effectiveness of the approach for improving in situ reductive dechlorination of TCE.

5.2 SOUTH CAROLINA SITE DESCRIPTION AND HYDROGEOLOGY

The project was performed within a TCE plume in an area designated as SWMU 17 at the Charleston NWS in Goose Creek (near Charleston), South Carolina. The hydrogeology of the area consists of 20 to 25 ft of undifferentiated Quaternary age sands, silts, and clays of the Wando Formation that rest on undifferentiated Tertiary age marine sediments of the Cooper Group. The Cooper River marl (top of the Cooper Group) defines the base of the surficial aquifer; its high fines content acts as a regional aquiclude and restricts further downward movement of shallow groundwater.

The groundwater potentiometric surface beneath SWMU 17 is relatively flat with some tidal influence resulting in fluctuating groundwater flow directions. The depth to the water table varies seasonally in response to precipitation and evapotranspiration and typically ranges between 0.5 ft and 6 ft bgs. Aquifer tests nearby suggest the hydraulic conductivity of the surficial aquifer is low, on the order of 1 to 10 ft/d (Vroblesky, 2007). The relatively low hydraulic conductivity combined with a nearly flat gradient suggest groundwater flow velocity is also low, on the order of <10 ft/yr.

The geochemistry of the groundwater was not optimal for biodegradation to occur. Initial pH was neutral, and groundwater was generally oxidative. There was virtually no measureable TOC in the groundwater, but elevated sulfate was detected. The concentrations of TCE within the treatment cell ranged from 9800 to 28,000 µg/L, with very little *c*DCE and no VC or ethene detected.

5.3 PHASE I TEST DESIGN AND INJECTION

The target treatment zone consisted of a 20 x 20 ft test cell (Figure 7). The treatment cell was characterized by up to 16,000 mg/kg TCE in soil and up to 1,000,000 µg/L in groundwater. Contaminant concentrations were highest at between 8 and 16 ft bgs in this cell, in a moderate to lower permeability silty sand layer. The volume of contaminated aquifer material within the pilot test cell was 4000 ft^3 (148 yd^3). The injection design consisted of a grid of 16 temporary 1-inch diameter injection/extraction wells installed using direct-push methods, approximately 5 ft on center (OC) across the test cell.

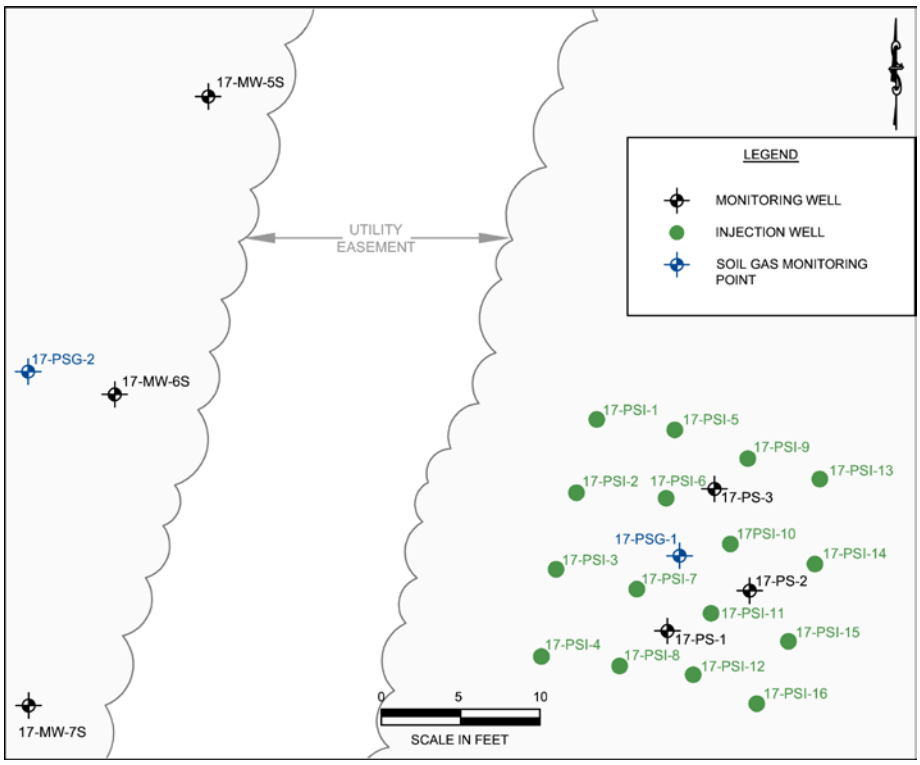

Figure 7. Treatment cell layout for Phase I.

The substrate was prepared by mixing and diluting the EOS® concentrate with groundwater obtained by pumping from each of the three permanent monitoring wells located in the test cell (17PS-01, 17PS-02 and 17PS-03). The low groundwater velocity posed concern that the introduction of large amounts of diluted substrate could result in a dilution effect that could persist for an extended time period and complicate data interpretation. Consequently, a recirculation system was used to help distribute emulsion throughout the target treatment zone to minimize injection of off-site water. During the injection process, groundwater was extracted from eight of the wells, amended with EOS® concentrate, and injected into the other half. After half the EOS® was injected, the former injection wells were converted to extraction wells and the process was reversed. A final volume of 684 gal of diluted EOS® mixture (i.e., 156 gallons of EOS® concentrate (1260 lb) diluted with 528 gal of groundwater) was injected. Following the final injection, 125 mL of a vitamin B-12 (cobalamin) solution were added to each of the 16 injection wells. Vitamin B-12 has been shown to optimize growth of *Dehalococcoides ethenogenes* and improve reductive dechlorination (He et al., 2007).

5.4 LABORATORY STUDIES

TCE degradation slowed approximately 6 months after EOS® injection, and limited reductive dechlorination to VC and ethene was observed. Laboratory studies were conducted concurrent with the final performance monitoring events of Phase I to diagnose and improve the performance, apparently limited by acidic groundwater conditions in the target treatment zone. The key findings from these studies are described below and were used to design the Phase II portion of the field demonstration.

- **Subsurface pH.** The pH of the soils and groundwater were similarly acidic, ranging from pH 4.3 to pH 5.2. This range is considered unfavorable for optimal bioactivity of many dehalorespiring bacteria including *Dehalococcoides ethenogenes*.

- **Microbial Characterization**. *Dehalobacter spp.* (Dhb) numbers were high in matrices from both outside and inside the test cell, indicating there was a native population of bacteria that could convert TCE to *c*DCE. However, *Dehalococcoides spp.* (Dhc) numbers were very low in the same samples, indicating that further conversion of *c*DCE to ethene might be limited by the absence of this important dechlorinating population. Dhc are the only organisms known to be capable of gaining energy from the complete dechlorination of PCE and TCE, and are known to be acid-sensitive. Dechlorination activity of cultures is strongly inhibited below a pH of 5.5 to 6.0.

- **Microcosm Studies.** Anaerobic microcosms were constructed with site matrix soil and groundwater and provided with pH buffer and EOS® with and without the SDC-9 bioaugmentation culture provided by Shaw Environmental, Inc. Amending the microcosms with pH buffer alone increased reduction of TCE to *c*DCE, but further reduction of *c*DCE did not occur indicating the indigenous microbial community may not be capable of complete dechlorination of TCE to ethene. Buffered and bioaugmented microcosms with matrices from the treatment cell completely reduced TCE to ethene in 19 days suggesting that the combination of low pH (i.e., <6.0) and absence of appropriate microorganisms were responsible for the inability of the metabolism to go to completion (Tillotson, 2007).

- **Buffering Studies.** Several different alkali materials were evaluated to find a reagent that could be injected to provide a large amount of alkalinity per pound but not result in an excessively high pH near the point of injection. $Mg(OH)_2$ was chosen because the pH of pure $Mg(OH)_2$ in solution is ~10, so after its application, the pH within most of the aquifer would be expected to vary between background (~5) and 9. A titration experiment determined that approximately 1200 lb of $Mg(OH)_2$ would be required to raise the pH of the pilot test cell to approximately pH 7.

5.5 PHASE II TEST DESIGN AND INJECTION

In Phase II, the amount of buffered-EOS® was determined by the laboratory testing scaled up to the field. Approximately 28 months after beginning Phase I, eight drums (3030 lb) of pre-mixed $Mg(OH)_2$/EOS® material (buffered-EOS®) were obtained from EOS Remediation, Inc. and shipped to the site. The Phase II injection design called for diluting buffered-EOS® with potable water and injecting approximately 7 gal of dilute mixture per ft evenly over the entire saturated zone (6 to 16 ft bgs) at 20 injection points spaced throughout the treatment cell. The injection of the buffered-EOS® mixture into the aquifer was performed as pressurized direct injections directly through standard Geoprobe® rods.

During injection, milkiness was observed and increases to TOC were measured in monitor wells within the treatment cell. Groundwater mounding occurred and some substrate "daylighted" at several locations. Reducing the injection pressure minimized these occurrences, and splitting the injections into two events helped control these conditions. The natural gradient was quickly re-established after the injection process was completed. There was some reduction in hydraulic conductivity in the treatment cell after the injection of emulsified oil substrate, but this appeared to have little measureable effect on the relatively slow groundwater flow velocity through the treatment cell.

5.6 SOURCE AREA TREATMENT PERFORMANCE ASSESSMENT

5.6.1 Substrate Effectiveness for Enhanced Reductive Dechlorination

As early as 6 months after the Phase I injection of EOS® substrate, data showed evidence of enhanced reductive dechlorination in the treatment cell compared to the surrounding environment. By 28 months, the TCE concentrations were routinely 76 to 86% lower throughout the test cell groundwater than in the background groundwater. Three months after buffered-EOS® injection, soil samples collected from 8 to 16 ft bgs throughout the test cell showed that the soil pH had increased from pH 4.9-5.3 to pH 6.4-7.7. After the pH was adjusted, the concentrations of TCE were further reduced to less than 96 to >99% of the background concentrations. The decrease in concentration of TCE and formation of *c*DCE, VC, and ethene in one of the three monitor wells situated within the treatment grid are shown in Figure 8.

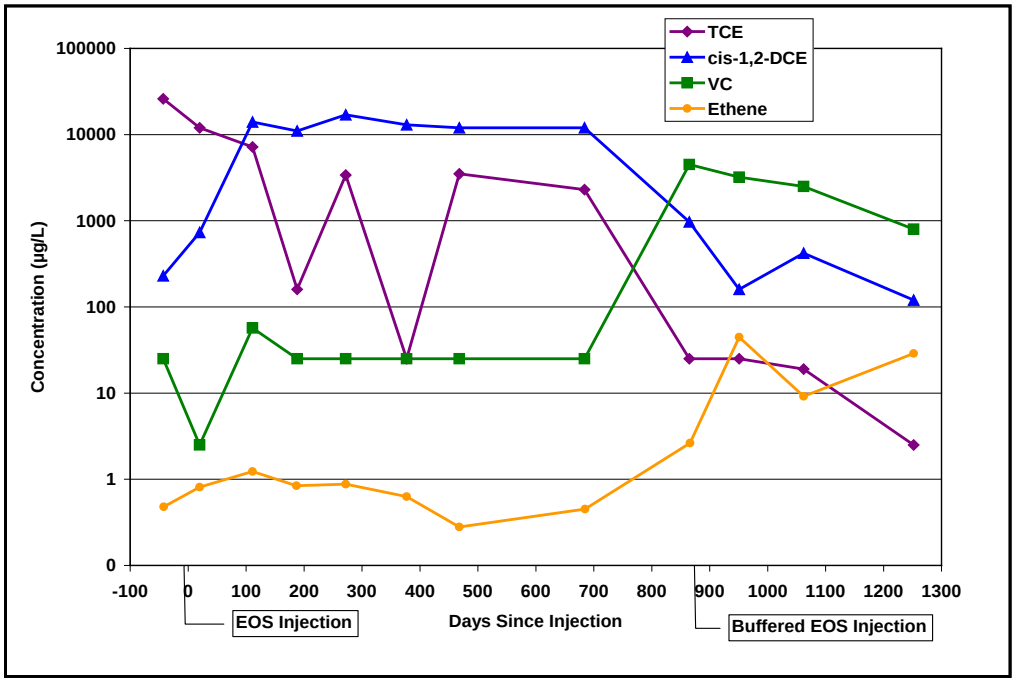

Figure 8. Changes in concentration of TCE and biodegradation daughter products in monitor well 17PS-03.

The groundwater concentrations were converted to molar concentrations to evaluate the stoichiometric change from TCE to its metabolic daughter products. Before the addition of

buffered–EOS® (up to Day 685), the molar ratio in each of the three monitor wells in the test cell reflected some conversion of TCE to *c*DCE. The addition of buffered-EOS® on Day 866 reduced the pH inhibition in the treatment cell, enhancing conversion of *c*DCE to VC and ethene. At the end of the 41-month monitoring period, VC and ethene were the primary metabolic daughter products present.

5.6.2 Microbial Activity

The biotransformation of TCE to *c*DCE suggested an active population of Dhb in the aquifer, although the enumeration of Dhb showed the population was below detection in the treatment cell at the end of the performance monitoring period. Before treatment, there was little indication of background Dhc activity, and the addition of substrate resulted in only marginal formation of VC and ethene. Dhc is sensitive to acidic pH conditions with little activity documented near or below pH 5.5. The addition of buffered-EOS® during Phase II resulted in an increase in pH and rapid biodegradation of TCE and *c*DCE with some conversion of VC. However, there was limited further conversion to ethene, which was surprising since at the end of Phase II, the Dhc population density was 4 to 5 orders of magnitude greater in the treated soil and groundwater compared to the untreated background matrices. Enzyme assays for VC-reductase (VC R-dase) and BAV1 VC-Dase suggested an absence of this capability in the population.

5.6.3 Substrate Longevity

Three drums (165 gal; 1260 lb) of EOS® concentrate provided for elevated TOC in groundwater for the entire 28 months of Phase I. After 377 days (~12 months) the average TOC concentration was still 57.4 mg/L, but by 468 days (~15 months), the concentration had dropped to 9.6 mg/L. The TOC in soil 9 months after injection was elevated compared to pre-injection concentrations of native background TOC. These observations support the hypothesis that even after prolonged exposure to bioactivity residual TOC is sorbed to the aquifer sediments. However, this reserve organic carbon may not be apparent by simply measuring TOC in groundwater.

The treatment grid was then replenished with an additional 330 gal (3030 lb) of buffered EOS® and monitored for an additional 13 months (Phase II). The presence and effectiveness of this second injection beyond 13 months was not tested. The availability of excess TOC was evident by the level of methane production throughout the entire 41-month pilot study.

5.6.4 Geochemical Changes to the Aquifer

DO decreased very soon after injection of substrate and stayed low during the course of the study. There was an immediate reduction in ORP in the treatment grid from mostly positive to negative, but there was some rebound and fluctuations in ORP observed over time. The ORP in the pilot test monitor wells stayed more consistently below 0 mV than the ORP in the injection wells. After buffered-EOS® was added, the ORP in the pilot test monitor wells steadily decreased approaching -160 mV. It is possible that some of the inability to achieve high rates of reductive dechlorination may have also been a result of not reaching optimal ORP during Phase I of the pilot study. Methane and H_2S were formed as noted in the headspace of the wells, but were not measurable in the vadose zone via the soil gas monitoring points. The increasing

concentrations of dissolved methane in groundwater during the pilot test suggest that lower ORPs are being achieved than have been measured.

Nitrate was not present in the aquifer and was not an issue during this study. Sulfate was not extraordinarily high in the aquifer, and the addition of emulsified oil quickly reduced the concentrations to below 20 mg/L where they remained for the balance of the study. Dissolved iron concentrations increased substantially after the injection of substrate. This is another indicator of the creation of a strongly reducing environment. The addition of buffered EOS® resulted in a drop in dissolved iron, presumably due to precipitation of $FeCO_3$.

5.6.5 Effect of pH

The aquifer pH in the pilot test cell decreased to below pH 5.5 resulting in cessation or slowing of reductive dechlorination. Injecting the buffered-EOS® blend developed in the laboratory successfully adjusted the pH of the aquifer effectively stimulating rapid biodegradation of TCE and *c*DCE with continuing conversion to ethene.

5.7 SOURCE AREA TREATMENT PILOT STUDY COST ASSESSMENT

The cost breakdown for the source area treatment pilot study was provided in the Final Report (ESTCP, 2009). Technology Demonstration Plan development, long-term project management, reporting costs and technology transfer costs were not figured in. The revised total cost of the source area treatment demonstration was approximately $377,800. Primary cost elements included:

a) Site characterization and design: ~$37,900 (10%)
b) Treatment cell construction with monitoring wells: ~$27,800 (8%)
c) Phase I substrate and shipping: ~$3100 (1%)
d) Labor and equipment to inject Treatment Cell – Phase I: ~$38,400 (10%)
e) Laboratory treatability study: ~$43,100 (11%)
f) Phase II substrate and shipping: ~$10,500 (3%)
g) Labor and equipment to inject treatment cell – Phase II: ~37,650 (10%)
h) Performance monitoring: ~$128,250 (34%)
i) Extra specialized analyses: ~$51,100 (14%)

The combined cost to install the treatment grid, the monitoring network, and manage the injection of substrate using the temporary injection/recovery recirculation approach was $69,300 (items b, c and d), which calculates to $17/ft^{3}or $468/yd^3 to impact the 4000 ft^3 (148 yd^3) treatment zone.

In Phase II, just under three times as much material was introduced into the aquifer as in Phase I, and the unit cost of the substrate was slightly higher because of the blend of emulsified oil concentrate with alkaline buffering agent. Nonetheless, the cost for purchase and application of the buffered EOS® substrate was slightly less at approximately $48,150 (items f and g), which calculates to $12/ft^3 or $325/yd^3. The largest portion of the total cost (~34%) was due to the extended performance monitoring of both phases that comprised 41 months of the demonstration (i.e., ~$9900 per event).

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6.0 COST SUMMARY OF EMULSIFIED OIL TECHNOLOGY

The pilot studies at the Maryland and Charleston sites clearly demonstrated the strength and versatility of the emulsified oil technology. They also pointed out some of the issues that users must be aware of when considering using the approach. The following sections discuss the costs associated with applying the technology, offer a comparison between the use of the technology as a PRB and a source area treatment, and compare costs to some other technologies typically used to remediate perchlorate and CVOCs in groundwater.

6.1 COST DRIVERS

The many inter-related components of the emulsified oil substrate technology that impact cost are discussed in the following sections.

6.1.1 Contamination Type, Concentrations, and Biodegradability

The emulsified oil technology has the potential for remediating many types of groundwater contamination, including CVOCs and perchlorate. Although the microbial pathways may vary, the contaminants serve as the electron acceptor while the substrate functions as the electron donor. Competing electron acceptors for CVOC degradation include DO, nitrate, iron(III) and sulfate. Competing electron acceptors for perchlorate degradation are primarily DO and nitrate. These electron acceptors must be consumed before the desired reduction of the target contaminant can proceed effectively. Although these conditions are important, contaminant concentration has relatively little impact on the design and amount of substrate needed at many sites. In source zones with dense non-aqueous phase liquid (DNAPL), concentrations will have more relevance than in a dissolved plume formed downgradient.

6.1.2 Plume Size and Depth

The total cost to treat large areas is greater than for small areas. However, costs per unit volume to treat a large area can be significantly lower due to economies of scale during injection and the relatively lower design, permitting, and monitoring costs. Deeper contamination zones are somewhat more expensive to treat due to the higher costs for injection wells. However, other costs are not significantly impacted.

6.1.3 Injection Network

Injection costs depend on the method used to install injection points, labor for injection, the flow rate per point, and the number of points injected at one time. Emulsified oils can be injected through direct-push points, temporary injection wells, or conventional monitor wells. The effect of injection point spacing on cost is primarily a trade-off between well installation, labor, and substrate costs. If the intent of the injection is to "smear" the entire zone between the wells with substrate during the injection process, wider spacing of the injection points will reduce injection well installation costs, but may increase the time/labor required for injection. If less than total coverage is acceptable, labor and equipment costs may be adjusted accordingly. Similarly, the well installation costs are affected by the geology and depth to groundwater, while the labor costs are determined by the time required for fluid injection. In a high permeability aquifer, fluid

injection will be easier and will take less time. Often, multiple wells can be injected simultaneously by manifolding pumps and delivery lines or using commercially available dosing equipment to reduce the time required to complete the injections.

6.1.4 Substrate Costs

The amount of emulsified oil substrate required at a specific site will depend on two different factors: 1) the mass of contaminant and competing electron acceptors to be degraded and 2) the oil retention by the aquifer material. Material costs for anaerobic bioremediation using emulsified oils are generally higher than for soluble substrates such as carbohydrates and lactate. It takes 26 times as many moles of lactate to obtain the same reducing equivalents as one mole of soybean oil, the primary ingredient in emulsified oil substrate (ESTCP, 2006a). Consequently, total costs for emulsified oil are generally lower because of the additional amount of lactate required and the additional labor associated with repeated lactate additions to replenish spent substrate. The greater longevity of oil in the subsurface generally results in lower total costs because of the much less frequent substrate injection.

6.1.5 Emulsified Oil Distribution

To be most effective, emulsified oil substrate should be distributed vertically and horizontally throughout the treatment zone. If the emulsified oil is not effectively distributed, contact between contaminated soil and groundwater may be delayed as either soluble components of the substrate migrate away from the injection zone or contaminated groundwater migrates to the injection zone. For optimum contaminant removal, emulsified oil treatments should be designed to achieve the highest contact efficiency that can be cost-effectively achieved. Modeling studies by Clayton and Borden (2008) showed that injecting more oil with more water while using more closely spaced wells will improve emulsion distribution. However, injecting more oil with more water and more wells will increase costs.

6.1.6 Maximum Oil Retention

Maximum oil retention (OR_M) is one of the most important factors controlling system performance and costs, but also one of the most poorly known. Common practice is to select an oil retention value from a table of previously measured values for different aquifer materials (i.e., sand, clay, silty sand, etc.). However, there is tremendous variation in OR_M between different materials. Consequently, it would be very easy for the estimated value to differ from the actual value at the site by a factor of two to four. Given the importance of this parameter, whenever possible, OR_M should be directly measured on field or lab samples so site-specific values can be used in the design.

6.1.7 Emulsified Oil Biodegradation

Little is known about the factors controlling substrate consumption in area treatment and how this influences performance over time. In source areas, contaminant biodegradation rates are often limited by slow mass transfer, and maintaining high biodegradation rates may not be critical. However, maintaining high biodegradation rates could possibly reduce the required operating life of the source area treatment, reducing costs. If the edible oil emulsion is biodegraded too rapidly or depleted by high groundwater flow, then more frequent injection will

be required to maintain performance, thus increasing overall project costs. Operating experience at other sites indicates that a single emulsion injection will be effective in stimulating biodegradation for 3 to 5 years. Increasing the time period between re-injections from 2 to 5 years for area treatment can be expected to significantly reduce costs. Increasing substrate longevity beyond 5 years has only a modest impact on life-cycle costs.

6.1.8 Contact Time

Contact time is an important variable in determining substrate volumes, especially for a PRB. At the Maryland site, the emulsified oil PRB was installed to intercept groundwater contaminated with perchlorate, 1,1,1-TCA and TCE. Perchlorate was degraded very quickly on contact with the substrate, and the required contact time for essentially complete perchlorate degradation was only a few weeks. By contrast, the required contact time for high levels of TCA and TCE degradation was estimated to be between 3 and 6 months. However, there is currently no reliable method to estimate the required contact time for source area treatment. For area treatment, estimated costs increase approximately linearly with target contact efficiency (Weispfenning and Borden, 2008; Borden et al, 2008a).

6.1.9 Absence of Appropriate Microorganisms

Available information indicates that the indigenous microbial population may not be capable of complete reductive dechlorination of PCE and TCE to ethene at all sites. The pilot study at Charleston NWS showed that TCE dehalorespiring bacteria were present in the aquifer and that the addition of substrate could stimulate microbial growth and result in biodegradation of TCE to *c*DCE. However, as the pH decreased in the aquifer, the ability to continue reductive dechlorination diminished. Re-establishing pH neutral conditions re-started the reductive dechlorination process resulting in almost complete removal of TCE and more *c*DCE. However, VC was formed and only slowly disappeared, likely a result of the apparent absence of VC reductase enzymes in the environment.

Additional information on aquifer bioaugmentation can be found in ESTCP (2005). At sites where the required microorganisms are not present, commercially available bioaugmentation cultures may be added to the aquifer for improved treatment. The percentage of costs associated with bioaugmentation is often small compared to the overall project costs. For this reason, pre-design testing for the presence of appropriate dehalorespiring populations is warranted and can be valuable for predicting project success. Bioaugmentation should be considered if there is doubt.

6.1.10 Regulatory Framework

The costs for employing the technology may vary from state to state. In this project, the MDE asked to review the work plan and approve the pilot test but did not issue an underground injection control (UIC) permit. SCDHEC, on the other hand, required following its formal UIC permit application and approval process before proceeding.

Different states and regulators also may consider the potential impact of secondary water quality in their approval process. These decisions may cause practitioners to alter their choice of

substrate, control the amount of substrate used, and modify the location of the application relative to site features and possible receptors. Additional monitoring may also be required. Any of these issues could further increase cost.

6.2 COST COMPARISON—MARYLAND PRB VERSUS SOUTH CAROLINA SOURCE AREA TREATMENT CELL

Although costs for implementing each of the pilot tests cannot be directly compared due to differences in site conditions and design, the target subsurface treatment zones that were created were similar in volume:

- PRB Dimensions – 50 ft long x 10 ft wide x 10 ft deep = 5000 ft^3 (185 yd^3)
- Source Area Dimensions – 20 ft long x 20 ft wide x 10 ft deep = 4000 ft^3 (148 yd^3).

A comparison of costs to implement the design at the two sites was performed using the cost information provided in Sections 4.4 and 5.7, respectively (Table 3). The cost to construct the PRB in Maryland was approximately \$8.38 /ft^3 (\$226/yd^3). The cost to create the treatment cell with EOS® at Charleston NWS was \$17.32/ft^3 (\$468/yd^3). If buffered-EOS® alone had been used from the beginning, the cost would have been \$12.05/ft^3 (\$325/yd^3).

Table 3. Cost comparison for PRB and treatment cell pilot tests.

Site	Maryland	South Carolina
Configuration	50 x 10 x 10 ft PRB	20 x 20 x 10 ft cell
Treatment zone volume	5000 ft^3 = 185 yd^3	4000 ft^3 = 148 yd^3
Volume of groundwater treated	3.8 x 10^6 L	Not applicable
Contaminant mass treated	40,900 g	1500 g
Cost to construct	\$41,900 (**Section 4.4**)	\$69,250 (**Section 5.7**)
Unit cost to construct treatment zone with EOS® or buffered EOS® (*)	\$8.38/ft^3 = \$226/yd^3	\$17.32/ft^3 = \$468/yd^3 \$12.05/ft^3 = \$325/$yd^{3(*)}$
Cost per unit volume groundwater treated	\$0.011/L = \$0.04/gal	Not applicable
Cost per gram contaminant	\$1.02/g	\$46.17/g

A comparison of the treatment approaches was then prepared to estimate the cost per unit volume of contaminated groundwater and the cost per unit mass of contaminant that was remediated. Several assumptions were used. Based on both studies, longevity of the substrate in the aquifer was assumed to be 3 years, which is just less than the length of each pilot study. At Charleston NWS, groundwater velocity was assumed to be less than 10 ft/yr and there was some evidence of fluctuating groundwater flow direction. Thus, movement of TCE-contaminated groundwater into and out of the treatment zone was considered negligible over the life of the pilot study. Over the duration of the Charleston pilot test, total CVOCs were reduced from 7564 µg/kg to 768 µg/kg (see ESTCP, 2009). Assuming a bulk density of 120 lb/ft^3 (1.92 kg/L), this results in a net CVOC removal of 1500 g.

At the Maryland PRB, the average groundwater flow velocity was approximately 500 ft/yr resulting in treatment of over 1500 pore volumes of groundwater over the 3-year duration of the project. Mass removals in the Maryland PRB were estimated based on observed changes in contaminant concentrations during passage through the barrier and measured groundwater flow velocities (ESTCP, 2008). Over the 3.5 year performance monitoring period, 27.7 kg of perchlorate and 13.2 kg of 1,1,1-TCA were degraded. The results of these analyses are summarized in Table 3.

The contact time in the treatment cell in South Carolina was believed to be sufficient for complete biodegradation of TCE to nontoxic end products. However, absence of dehalorespiring bacteria with VC-reductase capability limited complete reduction of VC to ethene. In full scale, bioaugmentation of the aquifer would increase the unit costs but presumably would lead to better overall performance. In Maryland, perchlorate-contaminated groundwater was effectively treated to the regulatory limit through the 10-ft wide PRB. However, 1,1,1-TCA and TCE appeared to need additional contact time. In full scale, this could be achieved by emplacing additional barriers or increasing the well spacing to achieve a wider radius of influence around each point. Either approach would increase unit cost.

6.3 COST COMPARISONS AND SENSITIVITY ANALYSIS

Because subsurface conditions can widely vary among sites, Borden et al. (2008a, 2008b), with funding from ESTCP, created a spreadsheet-based design tool (Design Tool) to assist engineers and project scientists in planning emulsified oil injection systems. Design Tool can be applied to injection-only systems for distributing emulsified oils in barriers and area treatments. It allows users to quickly compare the relative costs of different injection alternatives and identify a design that is best suited to the site-specific conditions. The relative costs and performance of different injection alternatives can be evaluated using Design Tool to identify a design that is best suited to the site-specific conditions.

Capital and life-cycle costs directly relate to the size of the treatment area but are relatively insensitive to site conditions. Total costs are often higher for large, wide, deep sites. However, unit costs may be lower also for large sites due to the proportionately lower fixed costs associated with planning, design, and monitoring.

Design Tool was utilized in developing the cost comparisons presented in this section. A sensitivity analysis is presented to illustrate how areal extent and depth of the contamination zone can impact costs. Additional factors such as contaminant concentrations, injection well spacing, proposed radius of influence of substrate around each injection well, site hydrogeology, and substrate costs were kept constant except as noted.

6.3.1 Emulsified Oil Bioremediation Sensitivity Analysis

The prevailing site characteristics at the Maryland PRB and South Carolina area treatment were used as the basis of comparisons with various configurations of PRBs and source area treatment cells. These site-specific conditions that were used in Design Tool are shown in Table 4.

Table 4. Site characteristics used in Design Tool scenarios.

	Permeable Reactive Barrier	Source Area Treatment
Soil type	Silty sand	Clayey sand
Maximum oil retention	.0085 lb oil/lb soil	.0085 lb oil/lb soil
Hydraulic gradient	.003	.001
Hydraulic conductivity	22 ft/day	7.2 ft/day
Total porosity	0.30	0.30
Effective porosity	0.24	0.24
Seepage velocity	0.28 ft/day = 100 ft/yr*	0.03 ft/day = 11 ft/yr
Contaminant loading	11 mg/L 1,1,1-TCA; 8.6 mg/L perchlorate	20 mg/L TCE
Injection rate	0.3 gpm (shallow 1-inch) or 3 gpm (deep 2-inch)	0.2 gpm (shallow 1-inch) or 1 gpm (deep 2-inch)

* A seepage velocity of 100 ft/yr was used in the PRB analysis. The high seepage velocity at the Maryland PRB was not believed to be representative of typical site conditions.

These conditions were used in a variety of hypothetical scenarios constructed by varying the size of the treatment area and depth. The conditions established for the analysis are summarized in Table 5. The first five scenarios represent PRB installations. The barrier length in the first three scenarios is 50 ft, but the width of vertical layer of contamination is either 10 or 25 ft. Scenarios 4 and 5 represent barriers that are 200 ft long that would be installed to intercept wider plumes. Scenario 4 impacts shallow contamination while Scenario 5 impacts deeper contamination. For evaluating cost, is it assumed that the PRBs installed in shallower contamination conditions are created using 1-inch diameter injection wells installed by direct-push methodology such as Geoprobe®. Deeper PRBs would be installed using hollow-stem auger drilling equipment to set the injection wells.

Table 5. Treatment design scenarios used for sensitivity analysis.

Scenario	Name	Length (ft)	Vertical Interval (ft)	Treatment Zone Width (ft)	Well Installation/ Injection Method/Rate	Notes
Permeable Reactive Barrier Configurations						
1	Narrow, shallow GW* plume (10,000 ft^3)	50	10	5 ft/PRB x 4 PRBs	40 DPT** injection wells 5-ft OC	4 parallel 50-ft long barriers
2	Narrow, shallow GW* plume, high contamination (12,500 ft^3)	50	10	5 ft/PRB x 5 PRBs	50 DPT** injection wells 5-ft OC	5 parallel 50-ft long barriers
3	Narrow, deep GW* plume (25,000 ft^3)	50	25	10 ft/PRB x 2 PRBs	10 HSA*** wells 10-ft OC	2 parallel 50-ft long barriers
4	Wide, shallow GW* plume (40,000 ft^3)	200	10	10 ft/PRB x 2 PRBs	40 DPT** injection wells 10-ft OC	2 parallel 200-ft long barriers
5	Wide, deep GW* plume (100,000 ft^3)	200	25	10 ft/PRB x 2 PRBs	40 HSA*** wells 10-ft OC	2 parallel 200-ft long barriers

Table 5. Treatment design scenarios used for sensitivity analysis (continued)**.**

Scenario	Name	Length (ft)	Vertical Interval (ft)	Treatment Zone Width (ft)	Well Installation/ Injection Method/Rate	Notes
Source Area Treatment Cell Configurations						
6	Small source area; shallow contamination (25,000 ft^3)	50	10	50	100 DPT** injection wells 5-ft OC	0.06 acre
7	Small source area; deep contamination (62,500 ft^3)	50	25	50	25 HSA*** wells 10-ft OC	0.06 acre
8	Large source area (0.5 Acre); shallow contamination 200,000 ft^3)	200	10	100	200 DPT** injection wells 10-ft OC	0.5 acre
9	Large source area (0.5 Acre); deep contamination (500,000 ft^3)	200	25	100	100 HSA*** wells 10-ft OC	0.5 acre

Length = face of PRB or edge of treatment cell perpendicular to groundwater flow
Vertical interval = vertical width of aquifer layer where contamination is found
Treatment zone width = determined for PRB configurations from the width of one PRB times the number of PRBs constructed. Represents total width of the treatment zone that groundwater must flow through.
*GW = groundwater
**DPT = direct-push technology. Substrate injected via 1-inch diameter temporary injection wells manifolded together; injection rate = 0.25 to 0.3 gpm for substrate and chase water to create desired radius of influence around each injection point.
***HSA = hollow-stem auger drilling. Substrate injected via 2-inch diameter deep injection wells, installed by hollow-stem auger and manifolded together during injection; injection rate = 1.0 gpm for substrate and chase water to create desired radius of influence around each injection point.

Concentrations of perchlorate, chlorinated ethene or ethane contaminants, sulfate and nitrate concentrations do not significantly affect treatment costs other than as they require adjustment to the width or number of barriers to achieve the desired contact time. The scenarios for the PRB configurations was set at 60 days contact time, except Scenario 2, which was set at 90 days. To achieve the desired contact time, Design Tool created additional PRBs placed behind and parallel to the original barrier. Thus, when using 5-ft OC spacing where the radius of influence around each injection point is only 5 ft, four or five PRBs are shown to be required resulting in treatment zone widths of 20 ft (i.e., 4 barriers x 5 ft wide per barrier) or 25 ft (i.e., 5 barriers x 5 ft wide per barrier) in Scenarios 1 and 2, respectively. When moving to 10-ft OC to create a 10 ft radius of influence, only two parallel PRBs are required (Scenarios 3, 4, and 5) and the treatment zone width is 20 ft (i.e., 2 barriers x 10 ft wide per barrier).

In the source area treatment cell configurations, contact time is not as large an issue, especially in the relatively tight conditions prevailing in South Carolina that were used in these models. Scenarios 6 through 9 were created to compare costs for treating a small shallow and small deep source area compared to larger (0.5 acre) shallow and deep conditions.

Table 6 shows the output of Design Tool for the nine scenarios described above. The initial fixed cost for these scenarios was between $65,000 and $69,000. The fixed costs include project management, design, permitting, preparation of a work plan to guide the installation and

monitoring activities, and some additional time for mobilization and installation of injection equipment. No costs for baseline site characterization are included; it is presumed that this has been completed before design begins.

Table 6. Cost comparison of various treatment design scenarios.

Scenario	Installation & Injection Cost	Treatment Zone Volume (ft^3)	Unit Cost (per ft^3)	PRB Dimension (ft^2)	Unit Cost (per ft^2)	NPV
Permeable Reactive Barrier Configurations						
1	$111,413	10,000	$11.14	2000	$55.70	$232,783
2	$122,576	12,500	$9.81	2500	$49.03	$249,268
3	$115,865	25,000	$4.63	2500	$46.35	$244,994
4	$166,371	40,000	$4.16	4000	$41.59	$344,719
5	$249,640	100,000	$2.50	10,000	$24.96	$454,334
Source Area Treatment Cell Configurations						
6	$156,657	25,000	$6.26	NA	NA	$443,,413
7	$154,662	62,500	$2.47	NA	NA	$442,234
8	$362,306	200,000	$1.81	NA	NA	$787,314
9	$545,833	500,000	$1.09	NA	NA	$1,068,839

NPV = Net Present Value for 7 year project.

Injection costs assume manifolding and simultaneously injecting up to 10 wells (or a maximum of 50% of total number of wells) for 9 hours of injection per day at a labor cost of $1490/day. Mass and volume scaling factors of 0.5 were utilized as described in the Design Tool (Borden et al., 2008a; Weispfenning and Borden, 2008).

An average cost of $2.45/lb delivered for the emulsion concentrate was used in the nine scenarios to match the cost used in the pilot tests. The substrate costs are per pound of oil and assume the concentrated emulsion is 60% soybean oil. Well rehabilitation costs for future injection events were assumed to be 25% of the initial well installation cost. Thus, the NPV calculations are based on 4% interest rate over the course of a 7-year project life and include projections for performance monitoring based on the size of the treatment area.

In general, unit costs to install either a PRB or source area treatment cell under the prescribed site conditions are relatively insensitive to site conditions. For treatment zone volumes over 50,000 ft^3, unit costs are generally less than $3/$ft^3$. The cost to construct PRBs ranging from 2500 to 10,000 ft^2 was $50 to $25/$ft^2$, generally decreasing in unit cost as the size increased. Krug et al. (2009) compared costs of several in situ approaches for treating perchlorate. The capital cost for installation of a "passive injection biobarrier" that was 400 ft long by 30 ft deep (i.e., 12,000 ft^2) was $320,000 or $27/$ft^2$ of barrier. The width of the barrier was not specified, but assuming injections on 20-ft centers yielding a width of 20 ft, this would comprise 240,000 ft^3 at a cost of $1.16/$ft^3$.

Using the nine scenarios presented in Table 6, the nine EOS® scenarios provided in the Cost & Performance Section of the Final Report on the Charleston NWS Pilot Study (ESTCP, 2009), the unit costs calculated from the Maryland PRB, the two injection scenarios at the Charleston NWS pilot test, and the estimate from Krug et al. (2009), unit costs were related to the treatment zone

volume (Figure 9) (r^2 = .909). The average cost for installing an emulsified oil in situ bioremediation design based on these 22 scenarios was \$4.99±4.34/ft^3 (\$135±117/yd^3). For a small site, the total costs are lower while unit costs are higher due to the proportionately large contribution of up-front fixed costs.

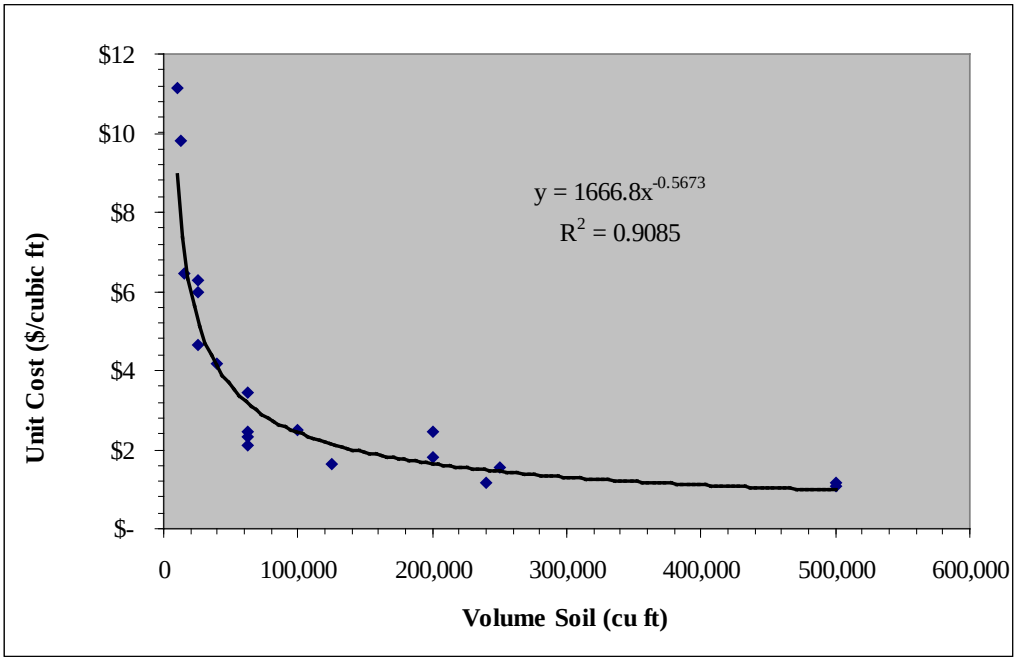

Figure 9. Unit cost to construct versus volume of treatment zone for PRB and source area treatment cell using emulsified oil substrate.

6.4 COST COMPARISON—EMULSIFIED OIL SUBSTRATE VERSUS OTHER TECHNOLOGIES

The following sections discuss other applicable technologies and provide a comparison of costs for the emulsified oil technology with other in situ bioremediation (ISB) approaches, organic trench biowall; in situ chemical oxidation (ISCO), and in situ low temperature thermal treatment (ISLTT). McDade et al. (2005) conducted a detailed evaluation of remediation costs for several technologies. They conducted a review of peer-reviewed literature, conference proceedings, state and federal government agency reports, Internet databases, and technical surveys to acquire cost and performance data at 36 full-scale and pilot-scale sites. Eleven sites used enhanced ISB with unspecified substrate although some sites may have included vegetable oil applications. Thirteen of these sites used ISCO and six employed ISLTT. None of the costs presented included monitoring. Krug et al. (2009) evaluated two additional in situ bioremediation applications using organic substrates: an actively recirculating biobarrier with soluble substrate and a semipassive biobarrier with recirculation of fresh substrate at extended intervals.

Costs developed by Krug et al. (2009) for a passive trench biowall were also compared with costs for permeable organic biowalls calculated by Henry et al. (2009). A comparison of the estimated cost/yd^3 for technologies including the unit cost estimates calculated from both pilot studies are summarized in Table 7.

Table 7. Comparison of unit costs to implement different in situ treatment technologies.

Data Source	Comments	Number Sites/Scenarios	Cost Range per yd^3	Average
In Situ Bioremediation – Unspecified Substrates				
A		11 sites	$2 - $225	$79±$73
B		2 sites	$48 each	
In situ Bioremediation – Emulsified Oil Substrate				
C	Source area grid	9 scenarios	$32 - $174	$123±$124
D		4 scenarios	$29 - $169	
E		Charleston NWS Pilot Test	$325 - $468	
D	Permeable reactive barrier	5 scenarios	$68- $301	$161±$103
B		1 site	$31	
E		Maryland Pilot Test	$226	
Trench Permeable Reactive Barrier				
F	Mulch biowall	1 site	$85	$61±$35
B	Passive trench biowall	1 site	$36	
In Situ Chemical Oxidation				
A		13 sites	$24 - $518	$146±$132
In Situ Low Temperature Thermal Treatment				
A		6 sites	$32 - $300	$114±$100

Data Sources:
A. McDade et al., 2005
B. Krug et al., 2009
C. ESTCP, 2009
D. Table 6 (this report)
E. Table 3 (this report)
F. Henry et al., 2009

The capital costs to install various in situ substrate-based bioremediation technologies range from $2 to $468/$yd^3$. Of the in situ bioremediation approaches, those using soluble substrates may be the least expensive to install, and the cost of substrate is lower compared to emulsified oil. Trench biowalls were the least expensive. Although least expensive, trench biowalls are somewhat limited to shallower applications.

The long-term cost savings afforded by the emulsified oil approach tends to place it ahead of the others for cost-effectiveness. This is measured by calculating the NPV of the technology for the prescribed treatment period. In the Final Report for the Charleston NWS site, an NPV of 7 years was selected for comparison of design scenarios (ESTCP, 2009). This assumed an initial injection in Year One, one subsequent injection in Year Four to rejuvenate the treatment zone, seven years of monitoring and termination after 7 years, with future costs based on a 4% annual discount rate. The same conditions were applied to the nine scenarios presented in Table 5 and the passive injection biobarrier described by Krug et al. (2009). The size of the treatment zone was compared with the NPV for these scenarios (Figure 10) and a strong correlation was shown (r^2=.89, n=19).

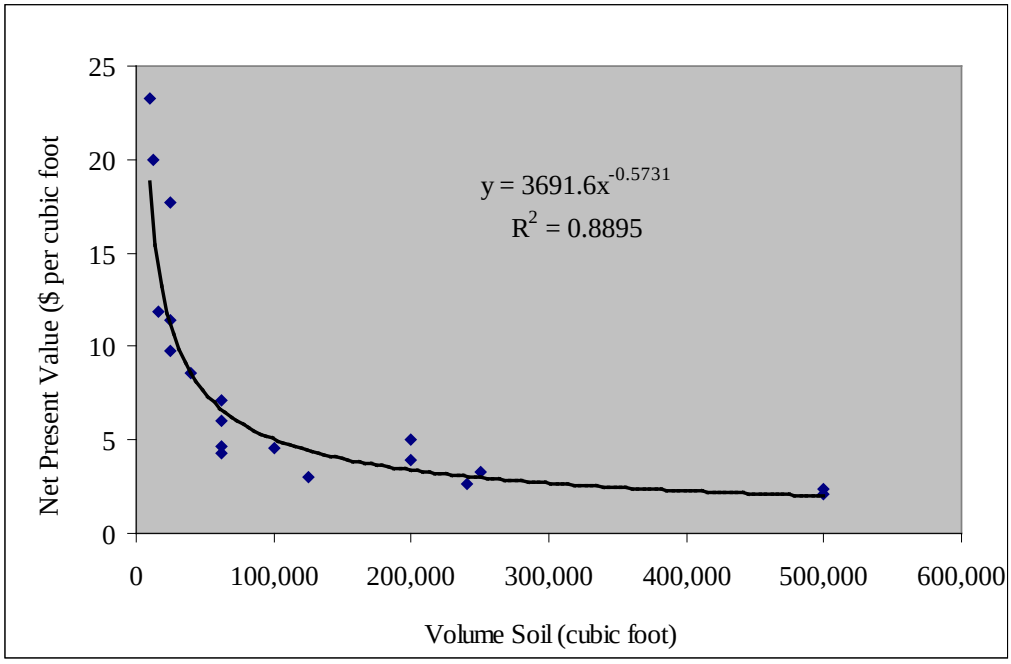

Figure 10. Net present value for 7-year in situ bioremediation projects compared to volume of treatment interval.

Krug et al. (2009) also compared the NPV for similar size projects using active biobarrier, semi-passive biobarrier, passive injection biobarrier, and passive trench biowall. If the remediation was limited to 7 years, the passive injection barrier was approximately 38% less expensive than the most costly option, which was active treatment. However, if the project lasted 30 years, the NPV for the active approach was still the highest, followed by the passive injection biobarrier, and the semi-passive biobarrier. The NPV of the three approaches varied by less than 16%. Zero valent iron (ZVI) PRBs, ISCO, and ISLTT are generally more expensive to implement, but there is substantial overlap and site specificity that can influence the overall cost.

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7.0 IMPORTANT DESIGN CONSIDERATIONS

Emulsified edible oil is an effective, long-lasting, natural time-release, organic substrate that can quickly produce groundwater conditions conducive to anaerobic biodegradation of perchlorate and many CVOCs. Initial capital costs for in situ treatment using emulsified oil substrate are comparable to other in situ anaerobic bioremediation approaches. Long-term costs are potentially much lower. Emulsified oil substrate is relatively easy to apply in a variety of layouts and, with proper design, can meet regulatory goals for the site. The limitations to the technology are similar to other in situ bioremediation strategies. Important design considerations identified during the two field demonstrations are noted below:

- **Water Injection Rate.** Aquifer permeability affects both the rate that substrate can be injected and the rate that groundwater can be extracted. High permeability generally speeds injection and reduces time on site. However, high permeabilities may reduce longevity of substrate in the ground. Conversely, low permeabilities increase the difficulty and time to inject and may increase labor and equipment cost.
- **Groundwater pH.** Dhb and Dhc are sensitive to low pH, but perchlorate-reducing bacteria are not as sensitive. In situ anaerobic bioremediation processes can, but do not always, result in a decline in aquifer pH due to production of volatile fatty acids, H_2CO_3 (carbonic acid), and HCl during reductive dechlorination. However, the injection of emulsified oil does not always cause aquifer pH to decrease. At present, there is no widely accepted approach for predicting when or if the aquifer pH will decline following substrate injection. Current practice is simply to monitor groundwater pH and take appropriate action, such as adding buffer, when required.
- **Capability of the Microbial Community.** Microorganisms capable of rapid and complete reductive dechlorination of chlorinated solvents are not present at every site whereas bacteria capable of biodegrading perchlorate are considered unbiquitous in the environment. Molecular biology tools can be used during the assessment phase to identify Dhb and Dhc populations as well as perchlorate-reducing bacteria. In addition to population density, these tests can also provide indications of enzymatic capability to biodegrade the contaminants of concern. Using this information, the need for and cost of bioaugmentation can be factored into the design and budget.
- **Contact Time**. For biodegradation to occur, there must be adequate contact time between contaminants, substrate, and microorganisms for metabolic processes to occur. In some cases, a PRB contact time of 2 to 3 months may be required to effectively degrade chlorinated solvents to nontoxic end products. When groundwater velocities are low, a single narrow EOS® barrier should provide effective treatment. However, when groundwater velocities are high, the width of the treatment zone parallel to groundwater flow may need to be increased to provide a high level of treatment. This can be accomplished by increasing the injection well spacing, the amount of substrate injected, or by installing more than one barrier.

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APPENDIX A

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