

Edible Oil Barriers for Treatment of Perchlorate Contaminated Groundwater

Final Report



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14. ABSTRACT Solutions-IES conducted laboratory studies and a pilot-scale field test to evaluate the cost and performance of edible oil emulsions for remediation of perchlorate plumes at DoD installations. The demonstration was conducted at a site in Maryland with a mixed perchlorate and 1,1,1-TCA groundwater plume. The PRB performance was evaluated by monitoring the distribution of the oil emulsion in the aquifer, the impact of the oil injection on aquifer permeability and groundwater flow paths, and the changes in contaminant concentrations and biodegradation indicator parameters. Laboratory microcosms showed rapid and complete removal of perchlorate with slower degradation of 1,1,1-TCA to measurable daughter products. Results from the pilot-scale PRB showed substantial reductions in perchlorate and 1,1,1-TCA. Perchlorate concentrations in all of the injection wells were non-detect (<4 µg/L) within 5 days of injection. Eighteen months post-injection perchlorate removal rates remained greater than 90% in the downgradient monitor wells compared to pre-injection levels. Over the course of the pilot test, 1,1,1-TCA was reduced by 94 to 98% twenty feet downgradient of the barrier. Geochemical data confirm anaerobic conditions favorable for biodegradation of these compounds have been established in the treatment area. The PRB continues to perform as designed 2 years post-injection.					
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LIST OF ABBREVIATIONS USED IN THIS DOCUMENT

1. AFB – Air Force Base
2. AFCEE – Air Force Center for Environmental Excellence
3. AP – Ammonium Perchlorate
4. BOD – Biochemical Oxygen Demand
5. BTEX – Benzene, Toluene, Ethylbenzene and Xylenes
6. CA – Chloroethane
7. CADHS – California Department of Health Services
8. CAH – Chlorinated Aliphatic Hydrocarbons
9. CF – Chloroform
10. CPT – Cone Penetrometer Test
11. CT – Carbon Tetrachloride
12. 1,1-DCA – 1,1-Dichloroethane
13. 1,2-DCA – 1,2-Dichloroethane
14. *cis*-DCE – *cis*-1,2-Dichloroethene
15. *trans*-DCE – *trans*-1,2-Dichloroethene
16. DNAPL – Dense Non-Aqueous Phase Liquid
17. DO – Dissolved Oxygen
18. DoD – Department of Defense
19. DOC – Dissolved Organic Carbon
20. EISOPQAM – Environmental Investigation Standard Operating Procedure and Quality Assurance Manual
21. EOS[®] - Edible Oil Substrate
22. ESTCP – Environmental Security Technology Certification Program
23. GRAS – Generally Recognized As Safe
24. HASP – Health and Safety Plan
25. HLB – Hydrophilic/Lipophilic Balance
26. HRC[®] – Hydrogen Release Compound[®]
27. IDW – Investigation-Derived Waste

28. MCL – Maximum Contamination Limits
29. MLS – Multi-Level Sampling well
30. MSDS – Material Safety Data Sheet
31. NAPL – Non-Aqueous Phase Liquid
32. NPV – Net Present Value
33. OC – On Center
34. O&M – Operation and Maintenance
35. ORP – Oxidation-Reduction Potential
36. PCE – Tetrachloroethene (Tetrachloroethylene)
37. PI – Principal Investigator
38. PID – Photoionization Detector
39. PPE – Personal Protective Equipment
40. PRB – Permeable Reactive Barrier
41. PVC – Polyvinyl Chloride
42. RTDF – Remediation Technologies Development Forum
43. SEFA – Sucrose Esters of Fatty Acids
44. SERDP – Strategic Environmental Research and Development Program
45. TC – Total Carbon
46. 1,1,1-TCA – 1,1,1-Trichloroethane
47. 1,1,2-TCA – 1,1,2-Trichloroethane
48. TCE – Trichloroethene (Trichloroethylene)
49. THM - Trihalomethane
50. TIC – Total Inorganic Carbon
51. TOC – Total Organic Carbon
52. TSI – Terra Systems Inc.
53. UST – Underground Storage Tank
54. VC – Vinyl Chloride
55. VOC – Volatile Organic Compound

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EXECUTIVE SUMMARY

This final technical report documents the demonstration of emulsified edible oils for remediation of perchlorate in groundwater. The demonstration was conducted at a confidential site in Maryland with a mixed perchlorate and 1,1,1-TCA groundwater plume. The primary objective of this project was to evaluate the cost and performance of an emulsified oil permeable reactive barrier (PRB) to control the migration of perchlorate plumes at DoD installations. The performance of the PRB was evaluated by monitoring the distribution of the oil emulsion in the aquifer, the impact of the oil injection on the aquifer permeability and groundwater flow paths, and the changes in contaminant concentrations and biodegradation indicator parameters both upgradient and downgradient of the PRB. Data obtained during the pilot test were used to demonstrate the cost-effectiveness of emulsified edible oils for remediation of perchlorate and chlorinated ethanes in groundwater through enhanced biodegradation.

The primary advantages of emulsified oils for groundwater remediation are:

- No aboveground remediation equipment
- Rapid conversion of aquifer to reducing conditions
- Low operation and maintenance costs
- Long-lasting (est. 5 years) *in situ* treatment
- Cost-effective

The cost-effective use of emulsified oils may be limited by the potential impacts on groundwater geochemistry, the absence of the appropriate microorganisms, and the depth to groundwater. However, proper design can account for many of these issues.

Demonstration Design

The demonstration was conducted at a site in Maryland with a mixed perchlorate and 1,1,1-TCA groundwater plume. The shallow aquifer at the site consists of silty sand and gravel to a depth of approximately 15 feet below ground surface (bgs) and has been impacted by a former lagoon that received ammonium perchlorate and waste solvent. The water table is approximately 5 feet bgs with a groundwater velocity of approximately 100 feet/year. The demonstration activities included both laboratory studies using site soils and a field pilot test involving injection of emulsified oil substrate (EOS[®]) to form a PRB.

A laboratory microcosm study was conducted to evaluate the effectiveness of EOS[®] for remediating perchlorate and 1,1,1-TCA, and a column study was performed to assess EOS[®] distribution in site sediments. The microcosm study demonstrated that EOS[®] addition was effective in stimulating anaerobic biodegradation of perchlorate and 1,1,1-TCA in site sediments and that bioaugmentation was not required to achieve complete dechlorination of 1,1,1-TCA and

other chlorinated compounds to non-toxic end products. These column study results indicated that EOS[®] could be effectively distributed in aquifer material from the Maryland site.

The field demonstration consisted of a one-time injection of EOS[®] and chase water to create a 50-ft long PRB. In October 2003, approximately 110 gallons of EOS[®] and 2,070 gallons of water were injected into the subsurface. Monitoring activities were conducted over an 18-month period to evaluate performance of the PRB. The PRB was located approximately 50 feet upgradient of an existing interceptor trench. Groundwater is extracted from the interceptor trench, treated via an air stripper, and re-injected via an upgradient infiltration gallery.

Summary of Results

EOS[®] injection resulted in substantial reductions in perchlorate and 1,1,1-TCA concentrations within and downgradient of the PRB. Perchlorate concentrations in all of the injection wells were non-detect (<4 µg/L) within 5 days of injection. Eighteen months post-injection perchlorate removal rates remained greater than 90% in the downgradient monitor wells compared to pre-injection levels. Over the course of the pilot test, 1,1,1-TCA was reduced by 94 to 98% twenty feet downgradient of the barrier with the average chlorine number reduced from 3.0 to 1.5 indicating that biodegradation to less chlorinated daughter products is occurring.

Geochemical data collected at the site confirm that anaerobic conditions favorable for biodegradation of these compounds have been established in the treatment area. In general, nitrate and sulfate concentrations decreased with time in the injection and downgradient wells indicating nitrate and sulfate reduction, while iron and manganese concentrations increased with time indicating iron and manganese reducing conditions. Methane concentrations increased in the injection wells suggesting methanogenic conditions within the PRB. No significant changes were observed in the upgradient monitor wells. During the pilot test, increased fouling of the air stripper was observed requiring increased maintenance. The increased fouling may have resulted from increased levels of dissolved iron and manganese or from increased biofouling as a result of enhanced microbial activity in the groundwater and/or elevated BOD in the air stripper influent.

Elevated concentrations of total organic carbon (TOC) within and immediately downgradient of the injection wells indicate good distribution of EOS[®] throughout the target zone forming a PRB. Although permeability reductions were observed in the injection wells, tracer test data indicate that groundwater flow through the barrier does not appear to have been affected by the measured changes in hydraulic conductivity. Based on data collected during the pilot test, the longevity of the EOS[®] barrier was estimated to be between approximately 2.5 and 3.5 years. This pilot-scale barrier was only designed to last approximately 3 years; and, therefore, appears to be performing as designed. Additional monitoring will be conducted at the site to assess the long-term performance of the PRB.

Comparison of Results with Primary Objectives

All of the primary performance criteria for this project were met. The primary qualitative performance criteria included reduced risk, faster remediation, no maintenance, and ease of use. Faster remediation was achieved through immediate reductions in perchlorate to non-detectable levels and reduction in 1,1,1-TCA by >90%. No maintenance was required during the 18-month demonstration period, and the PRB was easily installed with injection completed by two field personnel in two days.

The primary quantitative performance criteria were also met. The 90% target perchlorate reduction was exceeded with non-detectable levels observed down gradient of the PRB. Perchlorate was completely degraded with no production of hazardous by-products. CAH parent molecules were degraded, but residual daughter products are still detectable. Anaerobic conditions were quickly achieved as indicated by changes in bio geochemical parameters and the desired biodegradation of the contaminants. Minimal IDW was generated during installation of the PRB. EOS[®] was effectively distributed to create a PRB with no evidence of flow bypassing.

Cost Analysis

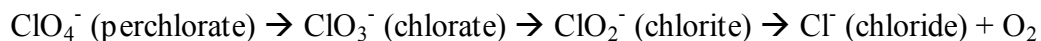
This demonstration was performed in conjunction with a second demonstration evaluating the use of emulsified oils for remediation of chlorinated solvent impacted groundwater at the Charleston Naval Weapons Station (NWS) in South Carolina. A detailed cost comparison will be provided in the Cost and Performance Report and will incorporate cost data from both demonstration sites. For the purposes of this report, we compared the cost of installing a full-scale emulsified oil PRB at the Maryland site to adding ion exchange for perchlorate treatment to an existing pump-and-treat system located at the site. The installation costs of a full-scale emulsified oil PRB at the Maryland site are estimated to be approximately \$38,000 which is equivalent to \$19/square foot of barrier or \$0.02/gallon treated. The estimated costs for ion exchange are \$50,000 capital cost with \$17,000 annual O&M. The 30-year life cycle costs for installing an emulsified oil PRB are estimated to be \$161,400 compared to \$383,600 for adding an ion exchange unit to the existing pump-and-treat system.

1.0 Introduction

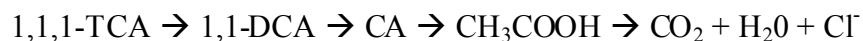
This final technical report documents the demonstration of emulsified edible oil barriers for groundwater remediation at a confidential perchlorate site in Maryland. The general purpose of the demonstration was to evaluate the efficacy of emulsified oils for treating perchlorate contaminated groundwater. A second demonstration was performed as part of this project to evaluate the use of emulsified oils for remediation of chlorinated solvent impacted groundwater at the Charleston Naval Weapons Station (NWS) in South Carolina. The work at the Charleston NWS is still ongoing and will be reported separately. In addition, a technical protocol document is being written under this demonstration project which describes in detail the use of emulsified oils for enhanced anaerobic bioremediation of perchlorate and chlorinated solvents.

1.1 Background

Groundwater contamination by perchlorate (ClO_4^-) has become a major environmental issue for the US Department of Defense (DoD). In many cases, perchlorate has entered groundwater through the release and/or disposal of ammonium perchlorate (AP), a strong oxidant that is used extensively in solid rocket fuel, munitions, and pyrotechnics. Perchlorate is highly soluble in water and poorly sorbs to mineral surfaces. A variety of studies have shown that microorganisms from a wide variety of aquifers can anaerobically biodegrade perchlorate when supplied with appropriate organic substrates and related amendments. The specific biochemical pathways necessary for perchlorate reduction are not well known, but there is good evidence that the pathway proceeds via the following sequence (Logan et al., 2000):



Similarly, chlorinated solvents in groundwater are also a frequently encountered problem at DoD facilities. 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. Chlorinated solvents amenable to *in situ* anaerobic bioremediation include tetrachloroethene (PCE), trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-DCE), vinyl chloride (VC), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,2-dichloroethane (1,2-DCA), carbon tetrachloride (CT), and chloroform (CF). For example, in the following reaction, 1,1,1-TCA can be biodegraded to intermediate compounds including 1,1-DCA and chloroethane (CA), which then can abiotically transform to acetic acid (CH_3COOH). The result of complete degradation by this pathway is the formation of carbon dioxide and water.



In the same manner, chlorinated ethenes, such as PCE and TCE, can be biologically degraded into non-toxic end products. The typical breakdown pathway for these compounds is illustrated below.



To enhance *in situ* biodegradation, the perchlorate and chlorinated solvents must be brought into contact with a biodegradable organic substrate. This substrate serves as a carbon source for cell growth and as an electron donor for energy generation. The most common method for adding the organic substrate is to dissolve it in water and flush the substrate through the contaminated zone using a series of injection and production wells.

Several groups, including ESTCP and the RTDF, have completed large-scale pilot studies of enhanced anaerobic bioremediation of chlorinated solvents. In these projects, readily biodegradable, soluble substrates have been flushed through the contaminated zone (sometimes with a bioaugmentation culture) to stimulate anaerobic biodegradation. While several of these projects have been successful, they have also shown that effectively delivering a soluble, readily biodegradable substrate to the contaminated interval can be difficult and expensive. Application of soluble, readily biodegradable substrates is subject to other cautions, as well.

- When an easily biodegradable, dissolved substrate is injected into a formation, the contaminants surrounding the injection point will be removed by both flushing and enhanced biodegradation. Over time, this results in a 'clean' zone surrounding the injection point. To be effective, the substrate has to pass through this clean zone to reach the contaminants. If the substrate is fermented to methane in this zone, it will be wasted and will not enhance contaminant degradation. Excessive biological growth may also cause clogging of the injection zone, potentially reducing injection rates.
- Continuously feeding a soluble, easily biodegradable substrate can be expensive. There is a significant capital cost for the required tanks, pumps, mixers, injection and pumping wells, and related process controls. In addition, operation and maintenance costs are high because of problems associated with clogging of mechanical equipment, injection wells and infiltration galleries.

This project was conducted to assess an innovative, low-cost approach for distributing and immobilizing biodegradable organic substrates in contaminated aquifers to promote biodegradation of perchlorate. At the demonstration site, chlorinated solvents were also present, commingled with the perchlorate. The transformation of each type of contaminant was monitored throughout the project, but the primary demonstration focused on perchlorate. Instead of using a rapidly exhausted soluble product as the primary substrate (e.g., molasses or lactate), the approach involves the one-time injection of low solubility, moderately biodegradable, edible oil-in-water emulsion to provide the primary source of organic carbon. The emulsion is distributed throughout the treatment zone using either conventional wells or temporary direct-push points. A portion of the oil becomes trapped within the soil pores leaving a residual oil

phase to support long-term anaerobic biodegradation of target contaminants. This approach provides good contact between the oil and the contaminants and substantially reduces initial capital and long-term operation and maintenance (O&M) costs.

1.2 Objectives of the Demonstration

The primary objective of this project was to evaluate the cost and performance of a permeable reactive barrier (PRB) composed of emulsified oil to control the migration of perchlorate plumes at DoD installations. The technology was validated for perchlorate in groundwater through a demonstration at a site in northeast Maryland. The site selected also contained elevated concentrations of 1,1,1-TCA and low concentrations of PCE/TCE in the aquifer with the perchlorate. Consequently, the effectiveness of emulsified oil for promoting the degradation of chlorinated ethanes and ethenes was also evaluated. The demonstration involved installing a pilot-scale emulsified oil substrate (EOS[®]) PRB and monitoring the PRB performance over an 18-month period. The objectives of the monitoring activities were to evaluate the distribution of the oil emulsion in the aquifer, the impact of the oil injection on the aquifer permeability and groundwater flow paths, and the changes in contaminant concentrations and biodegradation indicator parameters both upgradient and downgradient of the PRB. Data obtained during the pilot test was used to demonstrate the cost-effectiveness of the approach for distributing emulsified edible oil in the subsurface to remediate perchlorate and chlorinated ethanes in groundwater through enhanced biodegradation.

1.3 Regulatory Drivers

There is currently no federal maximum contaminant level (MCL) for perchlorate in drinking water. In February 2005, the USEPA established an official reference dose (RfD) of 0.0007 mg/kg/day of perchlorate, which is a scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans. Some states have adopted advisory levels for perchlorate in drinking water, but no states have established official promulgated perchlorate standards or cleanup levels. As an example, California and Arizona have established health-based goals of 6 ppb and 14 ppb, respectively. (ITRC, 2005).

Chlorinated solvents in groundwater are regulated on a federal level by the National Primary Drinking Water Regulations, which establish maximum contaminant levels (MCLs) for drinking water to protect human health. MCLs have been established for 1,1,1-TCA, PCE, TCE, and their daughter products. In addition, many individual states have developed their own standards for contaminants in groundwater. Innovative technologies are needed to remediate groundwater contaminated by perchlorate and chlorinated solvents to concentrations below the Federal or State standards.

The Maryland Department of the Environment Generic Numeric Cleanup Standards for Groundwater for the primary constituents at the Maryland project site are summarized in Table 1-1. Maryland does not have an established cleanup standard for perchlorate at this time.

Table 1-1
Maryland Department of the Environment
Generic Numeric Cleanup Standards for Groundwater
Type I and II Aquifers

Compound	Concentration (µg/L)
Tetrachloroethene (PCE)	5
Trichloroethene (TCE)	5
<i>cis</i> - 1,2- Dichloroethene (<i>cis</i> -DCE)	70
<i>trans</i> - 1,2- Dichloroethene (<i>trans</i> -DCE)	100
Vinyl chloride	2
1,1,1-Trichloroethane (TCA)	200
1,1-Dichloroethane (1,1-DCA)	80
1,2-Dichloroethane (1,2-DCA)	5
1,1-Dichloroethene (1,1-DCE)	7
Chloroethane (CE)	3.6
Chloroform	100
Bromoform	100
Perchlorate	No Standard

1.4 Stakeholder/End-User Issues

Pump-and-treat is the standard approach for controlling the migration of groundwater contaminants. In this process, groundwater is pumped out of the ground, treated in aboveground reactors and discharged back into the ground or to surface water. This basic process is very well understood and reasonably reliable. However, it is also very expensive to implement. Initial capital costs are high and long-term operation and maintenance costs can be prohibitive. For chlorinated ethanes and ethenes, many pump-and-treat systems have been in operation for over 10 years with little improvement in groundwater quality and no end in sight for high O&M costs.

As a consequence, a variety of other approaches are being pursued to reduce costs. One approach that has gained a great deal of interest is the use of zero valent iron (Fe⁰) barriers for controlling groundwater contaminant migration. These barriers are installed by excavating a trench below the water table and backfilling the trench with metallic or zero valent iron (Fe⁰). Long term monitoring at multiple sites has shown that these barriers can be effective for controlling the migration of a variety of contaminants including chlorinated solvents, heavy metals, and radionuclides. However, construction costs for Fe⁰ barriers can be very high because of the cost associated with excavation below the water table. For example, construction costs for

both pilot and full-scale Fe⁰ barriers range from \$30 to \$490 per square foot of total barrier with a median of about \$150 per ft² (ESTCP, 1999). Iron barriers are believed to have much lower O&M costs. Even given these high construction costs, many site managers are installing Fe⁰ barriers because of their low operation and maintenance costs.

Emulsified oil barriers are expected to have much lower capital and O&M costs than competing technologies. Edible oil barriers have tremendous cost and operational advantages over other competing technologies including pump-and-treat, zero valent iron barriers, and anaerobic bioremediation using soluble substrates. Construction costs for emulsified oil barriers are also quite low in comparison to Fe⁰ barriers. A cost comparison is provided in Section 5. Once installed, the emulsified oil barriers operate in a passive mode with little or no operation and maintenance.

Perchlorate is readily soluble in water, is not air strippable, and is not a candidate for conventional pump-and-treat technologies (O'Neill et al., 2000). The relatively recent awareness of the magnitude of perchlorate contamination in the environment, especially at military and military-support facilities, has spurred new interest in perchlorate remediation. For this reason, at this time, there is little experience with technologies for treating this contaminant in groundwater and no reservoir of prior cost information for comparison.

If the edible oil barrier technology can be adequately developed, this approach has the potential to significantly reduce the cost and improve the effectiveness of aquifer remediation for perchlorate as well as chlorinated solvents, nitrate, acid mine drainage, chromate, and oxidized radionuclides (TcO₄⁻, UO₂⁺²). These are major environmental problems for the DOD and the public as a whole.

2.0 Technology Description

2.1 Technology Development and Application

Our team has developed a novel, low-cost process for delivering a low solubility, slowly degradable substrate to the subsurface to enhance the anaerobic biodegradation of perchlorate and chlorinated solvents. The process of injecting emulsified oil into a contaminated aquifer for contacting the dissolved contaminants is similar, but the actual metabolic mechanisms that are enhanced to stimulate *in situ* biodegradation of perchlorate and chlorinated ethanes differ.

Several factors may limit *in situ* degradation of perchlorate. These include: 1) presence or absence of perchlorate reducing microorganisms (PRMs) or, if present, insufficient biomass of these bacteria; 2) insufficient oxidizable substrate; and 3) inhibition by high dissolved oxygen concentrations (Logan *et al.*, 2000). Perchlorate reducing microorganisms have been found widely distributed in nature, but their abundance varies by site-specific conditions. It has been shown that prolonged exposure to perchlorate can acclimate an existing microbial population to actively degrade perchlorate.

As the oil emulsion substrate slowly biodegrades over time, it provides a slow continuous source of dissolved organic carbon (DOC; i.e., fermentation products) to support anaerobic biodegradation of the target contaminants. Degradation of the oil results in removal of oxygen and production of hydrogen. This reaction is illustrated below.



Perchlorate reducing microorganisms use the substrate directly as a carbon and energy source; the generation of hydrogen is not required for this reaction to occur. By contrast, the degradation of 1,1,1-TCA and TCE requires the fermentation of the oil to generate hydrogen that can be used by the specific population of bacteria capable of carrying out this transformation. As shown above, a mole of soybean oil can be fermented and produce 156 moles of hydrogen, which is equivalent to 82 moles of hydrogen per pound of soybean oil. By comparison, as shown below, a mole of lactate would be expected to produce only 6 moles of hydrogen (or 30 moles of hydrogen per pound of lactate).



In addition to evaluating the use of emulsified oils for stimulating biodegradation of the target compounds, our team has also developed a novel, low-cost process for delivering this substrate to the treatment zone. The distribution of the oil throughout the target zone is enhanced by the use of emulsifying agents that serve to reduce the viscosity of the substrate and improve its handling characteristics. To date, we have shown that the emulsified oil approach can provide a very cost-effective method for providing dissolved organic carbon to support the long-term anaerobic biodegradation of chlorinated aliphatic hydrocarbon solvents in contaminated aquifers (Borden et al., 2001; Lee et al., 2001; Lee et al., 2003).

Implementation of the emulsified oils involves preparation of the emulsion and injection of the emulsion into the treatment zone. Emulsified oil can be injected into “hot spots”, throughout the plume, or as a permeable reactive barrier using conventional wells or direct-push injection points. All materials used in the process are Generally Recognized As Safe (GRAS), food-grade materials (21 CFR 184.1400). 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, and the geologic and hydrogeologic conditions.

2.2 Previous Testing of the Technology

The current field demonstration project was funded by ESTCP. Concurrently, SERDP is supporting fundamental research examining the effects of the oil distribution technique on aquifer permeability and the rate of oil biotransformation. AFCEE and private industries have supported pilot and full-scale field evaluations of the oil injection process for the degradation of chlorinated aliphatic hydrocarbons. This work has provided much valuable information on both the theoretical and practical aspects of oil and oil emulsion injection and distribution in the

subsurface, as well as the effectiveness of the process for stimulating anaerobic reductive dechlorination in groundwater.

The research and application of bioremediation techniques for the transformation of perchlorate is relatively recent. Work performed in soil at Longhorn Army Ammunition Plant in Texas identified chicken manure, cow manure, and ethanol as suitable carbon sources for the enhancement of *in situ* bioremediation of perchlorate (Nzengung *et al.*, 2002). In bench-scale studies, Jackson *et al* (2002) tested electrokinetic injection of lactic acid and glycine into soils to stimulate perchlorate degradation. Three different bioreactors, a microbial mat, an algae, and a phytoremediation uptake system, were tested by O'Neill *et al* (2000) with the conclusion that the microbial mat bioreactor could achieve very fast half-lives for the degradation of perchlorate from water. Hatzinger *et al* (2000) evaluated a fluidized bed bioreactor for treating groundwater in a laboratory pilot study with good success that was carried into the field at a site in California. Thus, the potential for the degradation of perchlorate by supplying organic substrate has been demonstrated.

Edible oils have been used at multiple DoD facilities. Some of the sites where either NAPL edible oil or emulsified oils have been used are summarized in Table 2-1.

**Table 2-1
Summary of Department of Defense Edible Oil Process Applications**

Site Name	Location	Scale	Date	Injection Summary
Air Force Facilities				
Hangar K	Cape Canaveral Air Force Station, FL	Pilot Expanded	June 1999 July 2000	Single Well Push-Pull Test Straight Injection/Water Push
SS015	Travis AFB, CA	Pilot Expanded	April 2000 December 2000, April 2002	Straight Injection/Water Push Straight Oil/Water Push and Emulsions. Injection Points and Direct Injection
Site FF-87	Former Newark AFB, OH	Full Expanded	September 2001 September 2003	Injection Points with Emulsion
Site LF-08	Whiteman AFB	Pilot	July 2002	Direct Injection with Emulsion
AOC 2	NAS Fort Worth JRB, TX	Pilot	August 2003	Injection Points with Emulsion
FTA-2	Tinker AFB, OK	Pilot	October 2003	Injection Points with Emulsion
LF-05	Hickam AFB, HI	Pilot	April 2003	Injection Points with Emulsion into DNAPL Zone
DP98	Elmendorf AFB, AK	Pilot	July 2005	Injection Points with Mixed Substrate of Lactate and Emulsion
WP-21	Dover AFB, DE	Pilot	April 2000	Injection Points with Emulsion
WP-21	Dover AFB, DE	Pilot	April 2000	Soybean Oil/Water Push into Injection Points
WP-21	Dover AFB, DE	Expanded	August 2003	Injection Points with Emulsion
Site 14	Edwards AFB, CA	Pilot	September 2000	Injection Points with Emulsion
SS-17	Altus AFB, OK	Pilot	December 2001	Injection Points with Emulsion
OU-1	Altus AFB, OK	Pilot	December 2001	Injection Points with Emulsion
SWMU 10	Arnold AFB, TN	Pilot	December 2003	Straight Injection into DNAPL Zone

Site Name	Location	Scale	Date	Injection Summary
SWMU 10	Arnold AFB, TN	Pilot	December 2003	Injection Points with Emulsion
	Beale AFB, CA		2004	Emulsion Injection
	Ellsworth AFB, SD		2004 and 2005	Emulsion Injection
	Kelly AFB, TX		2005	Emulsion Injection
	McCoy AFB, FL		2005	Emulsion Injection
	Moody AFB, GA		2005	Emulsion Injection
	Seymour Johnson AFB, NC		2005	Emulsion Injection
Navy Facilities				
Site N-6	NSA Mid-South, TN	Pilot	August 2000	Straight Injection/Water Push
NIROP	NIROP Fridley	Pilot	November 2001	Injection Points with Emulsion
SWMU 17	Charleston NWS, SC	Pilot	May 2004	Recirculation of Emulsion
Site 13	NAB Little Creek, VA		2004	Injection Points with Emulsion
	White Oak NSWC, MD		2004	Emulsion Injection
OU-4 and SA-17	Orlando NTC, FL	Pilot	2005 (planned)	Emulsion Injection
Army Facilities				
Waste Accumulation Pad	Tarheel Army Missile Plant, NC	Pilot	July-Aug. 2004	Recirculation of emulsion through source area
Other DoD Facilities				
	Confidential Site, MD	Pilot	Oct 2003	Injection Points with Emulsion (PRB configuration)
DDMT	DDMT, TN	Pilot		
ANGB	ANGB, VT	Pilot		
Site 2	ANGB, VT	Pilot	June 2002	Injection Wells with Emulsion
OU-2	DDHU, UT	Pilot	July 1999	Single Well Push-Pull
OU01	DDHU, UT	Pilot	April 2000	Injection Points with Emulsion
BRAC-51	DDHU, UT	Full-Scale	July 2002	Excavation Back fill with Neat Oil
IC-42	McClellan AFB, CA (AFRPA)	Pilot		Injection Wells with Emulsion
SWMU-97	Dugway Proving Grounds (USACE)	Pilot	November 2004	Injection Wells with Emulsion
OU-2	DDHU, UT	Pilot		Single Well Push-Pull
OU-4	DDHU, UT	Pilot		Injection Points with Emulsion

Two different procedures have been used to inject and distribute the oil: (1) direct injection of the oil as a non-aqueous phase liquid (NAPL); and (2) preparation of an oil-in-water emulsion using a food-grade emulsifier followed by injection into the aquifer. With either method, a water chase is often used to distribute the oil throughout the aquifer. In general, injection of the oil as a

NAPL has not been very successful because: (a) the differences in density between oil and water make it difficult to effectively distribute the oil over significant vertical intervals; (b) capillary forces immobilize the oil within ~1 ft. of the injection point; and (c) it is more difficult to work with a fluid that is not miscible with water. In contrast, injection of the oil as an emulsion has been much more successful. The emulsions are fully miscible with water, so they are easier to handle; and the emulsion specific gravity is close to that of water, so density effects are not a significant issue. Use of food-grade emulsifiers reduces the oil:water interfacial tension resulting in much more effective distribution of the oil throughout the treatment zone.

2.3 Factors Affecting Cost and Performance

The primary costs associated with installation of emulsified oil substrate barriers include injection point installation, substrate, and substrate injection. These costs are affected by the mass of contaminants in the aquifer, the subsurface lithology, the depth to groundwater, and the vertical extent of contamination. The performance of an emulsified oil PRB for remediating perchlorate and chlorinated solvents is primarily related to the ability to distribute the substrate throughout the treatment zone, the biodegradation of the substrate after it is injected, the presence of microorganisms capable of complete biodegradation, and the rate of biodegradation of the target contaminants that can be achieved *in situ*.

2.3.1 Costs

The amount of emulsified oil required at a specific site depends on the amount of oil needed for biodegradation (e. g., contaminant concentrations, competing electron acceptors) and the oil retention by sediment. Compared to competing technologies, such as iron PRBs or Hydrogen Release Compound (HRC[®]), the material costs are lower. The injection costs for installing an emulsified oil barrier are influenced by the number of injection points, injection point spacing, the time needed to complete the injections, and how the injections are completed (i.e., direct-push points or wells). All of these factors are primarily related to the subsurface lithology and the depth to groundwater. Emulsified oils can be injected through direct-push points, temporary injection wells, or conventional monitor wells. The subsurface lithology (i.e., heterogeneity) also influences the ability to distribute emulsified oil throughout the aquifer which affects the number and spacing of the injection points.

2.3.2 Emulsified Oil Distribution

In order to be effective as a barrier, emulsified oil must be distributed vertically and horizontally throughout the treatment zone and must not result in an excessive decrease in the permeability of the aquifer. If the emulsified oil is not thoroughly distributed, contaminated groundwater could short-circuit the barrier and remain untreated. If injection of emulsified oil substantially decreases the permeability of the aquifer, the contaminated groundwater may flow around the barrier instead of through the barrier.

2.3.3 Emulsified Oil Biodegradation

If the edible oil emulsion is biodegraded too rapidly, then the barrier does not last as long as designed and re-injection could be necessary to reduce contaminant concentrations to

the desired levels. This could be a problem at some sites. However, at the sites we have examined to date, this has not been a significant problem.

2.3.4 Absence of Appropriate Microorganisms

Available information suggests that perchlorate-degrading microorganisms are fairly common. However, there is a possibility that these organisms may not be present at all sites. For chlorinated solvents, the indigenous microbial population is not capable of complete reductive dechlorination of chlorinated aliphatic hydrocarbons at all sites. At these sites, intermediate degradation products of chlorinated solvent reduction may accumulate.

One of the first tasks in this project was to construct microcosms to determine if microorganisms were present that can degrade perchlorate and chlorinated solvents using edible oil as a substrate and to determine if the oil biodegrades too rapidly in this aquifer material.

2.4 Advantages and Limitations of the Technology

2.4.1 Advantages of Emulsified Oils

The primary advantages of emulsified oils are:

- No aboveground remediation equipment
- Rapid conversion of aquifer to reducing conditions
- Low operation and maintenance costs
- Long-lasting (est. 5 years) *in situ* treatment
- Cost-effective

2.4.2 Limitations of Emulsified Oils

The cost-effective use of emulsified oils may be limited by the potential impacts on groundwater geochemistry, the absence of the appropriate microorganisms, and the depth to groundwater. Each of these potential limitations is further discussed below.

2.4.2.1 Adverse Impacts on Groundwater Geochemistry and Biology

At many contaminated sites, the aquifer is an important water supply. At these sites, the release of high concentrations of organic carbon, methane, or sulfide could have adverse impacts on the water supply and associated treatment costs.

The successful application of edible oil substrate into the aquifer will result in several changes to groundwater geochemistry and biology. Some are short-lived and others may be more long-lasting. Initially, the objective of our process is to increase the amount of biodegradable organic carbon or Biochemical Oxygen Demand (BOD) of the groundwater. The immobilized oils break down producing short-chain fatty acids. Perchlorate-degrading microorganisms directly utilize the oil and its breakdown products for carbon, energy and growth. Concurrently,

other indigenous microbial populations ferment these fatty acids producing H₂ and CO₂. In turn, the dehalorespiring microbial population uses the hydrogen to carry out reductive dechlorination. Other microbial populations are also stimulated by the change in aquifer conditions from oxidative to reductive. Methanogens, sulfate-reducers, and nitrate-reducers compete for the electron donor that is supplied by the method.

Emulsified oils typically contains a faint soybean oil odor. The biological formation of fatty acids from the breakdown of the oil may impart secondary taste and odor to the groundwater. Most of these fatty acids are expected to biodegrade within 25 to 50 ft of the injection. Typically, if a water supply well is located a short distance downgradient, we would not recommend the use of emulsified oils. At the Maryland site, there are no drinking water sources downgradient of the barrier. However, the existing extraction trench that feeds the on-site air stripper system is located ~50 ft downgradient of the test barrier. The air stripper influent and effluent were monitored during the pilot test to evaluate potential impacts to the system from the emulsified oil injection.

Injection of emulsified oils is designed to stimulate the degradation of the targeted chlorinated contaminants (e.g., perchlorate, 1,1,1-TCA, TCE, DCE, VC) to non-toxic end-products. To accomplish this, excess organic carbon donor substrate is added to groundwater to intentionally make it anaerobic and create a strongly reducing environment. Perchlorate reducing microorganisms are expected to readily utilize the substrate to support the complete biodegradation of perchlorate. Daughter products of perchlorate degradation do not typically accumulate. For this reason the ability to remove perchlorate and reach an assumed regulatory target of 4 µg/L will be an important performance metric. By contrast, biodegradation of chlorinated ethanes and ethenes typically results in the temporary accumulation of some daughter products. The presence of the existing air-stripper downgradient of this zone offers a backup for treatment of intermediates such as DCA, CA, DCE, VC, ethene and ethane that may migrate out of the treatment zone and move downgradient. All these intermediate products of biodegradation are air-strippable. The ability to achieve the regulatory standard for one or more of the commingled chlorinated ethanes and ethenes is a secondary performance objective for this test.

Methane production as a result of increased methanogenesis is also an outcome expected from the introduction of high concentrations of degradable organic substrate into the aquifer. Methane is not expected to impart any hazardous, flammable or adverse impacts on the aquifer, the overlying vadose zone, nearby buildings, or the downgradient air-stripper system.

Anaerobic conditions can also result in increased concentrations of dissolved iron and manganese or mobilization of other materials in the subsurface that may

already be present. While the groundwater downgradient of the emulsified oil treatment may be of reduced quality as a drinking water supply due to tastes and odors, it is not expected to pose significant human or environmental health risks. However, increased operation and maintenance costs for the existing air stripper system due to fouling from biomass, iron, or other non-hazardous precipitates are a possibility at the Maryland site.

2.4.2.2 Hydraulic Limitations

In low permeability environments, it may be difficult to distribute emulsified oil throughout the treatment zone. This difficulty may be further amplified when groundwater velocity is low resulting in higher emulsion concentrations in the immediate vicinity of the injection wells and limited distribution. Low permeability and low groundwater velocity may limit the effectiveness of the injection and increase the project costs.

Injection of emulsified oil could result in a reduction in aquifer permeability due to clogging of the soil pores with oil droplets, biomass, or methane gas bubbles. At the Maryland site, these permeability effects are expected to be confined to the immediate vicinity of the emulsified oil barrier and are not expected to adversely impact the performance of the air stripper system.

2.4.2.3 Microorganisms

In order for enhanced *in situ* biodegradation to successfully degrade perchlorate and chlorinated solvents completely to their non-toxic end products, the appropriate microorganisms must be present. Available information suggests that perchlorate-degrading microorganisms are fairly common (Logan et al., 2000). However, they may not be present at all sites. Similarly, microbial reductive dechlorination is thought to be fairly ubiquitous in anaerobic, chloroethene-contaminated aquifers, but the extent of dechlorination is highly variable from site to site (Bradley, 2000). Certain dehalorespirers are able to grow using chloroethanes as sole terminal electron acceptors. However, microorganisms capable of complete reduction of 1,1,1-TCA to non-toxic end products may not be present at the proposed field site.

Assuming that the appropriate microorganisms are present, the rate of *in situ* biodegradation is another key factor. The time it takes for contaminants to pass through the oil emulsion treatment zone must be sufficient for the stimulated microbial population to carry out the desired biotransformations. If the rate of biodegradation is too slow, untreated parent contaminant molecules may pass through un-degraded or only partially degraded. In the latter case, daughter products may pass out of the zone without reaching the desired metabolic end products. In either case, regulatory goals may not be met.

Despite the efforts to enhance or create conditions that will support growth of these microorganisms, some sites do lack the required microbes. One of the first tasks in the project was to construct microcosms to determine if microorganisms were present that can degrade perchlorate and chlorinated solvents using edible oil as a substrate.

2.4.2.4 Excessive Depth to Groundwater

The depth at which emulsified oils can be applied is based on available drilling technologies. To date, the maximum depth we have treated is 65 ft bgs.

Application at greater depths will increase the drilling cost resulting in greater overall project costs. At the northeast Maryland site, this is not an issue because the maximum depth of the shallow saturated zone in the area designated for the pilot test is approximately 15 ft below ground surface (bgs).

2.4.3 Comparison of Emulsified Oil to Other Technologies

Perchlorate contamination is a relatively new issue that is gaining attention at military and military-support facilities. Some remediation technologies that are currently being used include ion exchange, ex situ bioremediation, and in situ bioremediation. Ion exchange is a physical treatment process in which perchlorate is exchanged with another anion. The spent resin needs to be either disposed of or regenerated. Regeneration creates brine, which requires further treatment. Ex situ bioremediation relies on biological processes to degrade perchlorate in aboveground reactors (e.g., continuous-flow stirred tank reactors, packed bed reactors, and fluidized bed reactors) with additional treatment to separate the bio solids. Both ion exchange and ex situ bioremediation require groundwater extraction and aboveground treatment equipment with associated long-term operation and maintenance costs. However, there is little readily available performance or cost information for comparison. Advantages of in situ bioremediation include lower capital and O&M costs, minimal impact on site infrastructure, and no secondary waste stream to treat.

Several technologies have been used for remediation of chlorinated solvents in groundwater, but these are not applicable to perchlorate. Such traditional approaches have included pump-and-treat with air stripping and air sparging, both of which rely on physical dissociation of the contaminants from the aqueous phase to the gaseous phase for removal. Pump-and-treat with activated carbon adsorption also removes contaminants without destroying them. Pump-and-treat and air sparging methods both require aboveground treatment equipment, associated operation and maintenance costs, and higher capital costs which make these options more expensive than in situ bioremediation.

In situ bioremediation can be enhanced using a variety of substrates including soluble substrates (e.g. lactate, molasses), slow-release substrates (e.g., HRC[®], vegetable oil, emulsified oils), and solid substrates (e.g., mulch, chitin). These substrates can be

applied in various configurations to remediate source areas, contain plumes (biobarriers), and provide plume-wide treatment. Materials successfully employed as barriers promoting anaerobic reductive dechlorination include zero valent iron, chitin, compost, and bark mulch. Iron PRBs have higher life cycle costs compared to emulsified oil, primarily because of higher capital and installation costs (see Section 1.4). Furthermore, iron PRBs do not work for perchlorate. Natural materials such as chitin, compost and bark mulch are relatively inexpensive to acquire, but may suffer from inconsistency of composition and are limited to installation in shallower aquifers. The prominent technologies that compete with emulsified oil are materials that can be injected into the aquifer to stimulate anaerobic conditions and in situ anaerobic biodegradation. These include soluble substrates (lactate, molasses) and HRC[®] and HRC[®]-X (which are polymeric lactate-based materials marketed by Regenesi Bioremediation Products, Inc. as a slow-release carbon source for stimulating reductive dechlorination of chlorinated solvents and more recently, perchlorate).

Approaches using soluble substrates, slow-release, and solid substrates to treat chlorinated solvents and perchlorate are all based on the same microbial processes. As a consequence, none of these approaches is inherently more or less effective in degrading perchlorate, PCE, TCE, or 1,1,1-TCA. The only real difference is in the short- and long-term costs of delivering substrate to the bacteria. Emulsified oils are relatively inexpensive, innocuous, food-grade substrates. When properly prepared and injected emulsified oils are immobile and slowly biodegraded in most aquifers. A single, low-cost injection can provide sufficient carbon to drive anaerobic biodegradation for several years. This is expected to significantly lower O&M costs compared to aqueous-phase injection of soluble carbon sources (e.g., lactate and carbohydrates) and will allow addition of slow-release substrates at locations where placement of solid-phase carbon in trenches is not feasible (e.g., large depths, fractured rock).

3.0 Demonstration Design

3.1 Performance Objectives

The overall objective of this demonstration project was to evaluate the cost and performance of an edible oil emulsion PRB for remediating perchlorate and chlorinated solvents in groundwater. The performance of the barrier was evaluated by monitoring changes in contaminant mass, the distribution of emulsified oil substrate (EOS[®]) in the subsurface, and the impact of the emulsion injection on aquifer permeability and groundwater flow. The performance objectives are summarized in Table 3-1 and are discussed in more detail in Section 4.

**Table 3-1
Performance Objectives**

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)
Qualitative	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 five years.	Not Determined ¹
	4. Ease of Use	Installation of PRB using readily available equipment.	Yes
	5. Compatible with MNA 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.	Not Determined ²
Quantitative	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 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

Type of Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance (Objective Met?)
	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 Maryland standards.	Yes

Notes:

1. System operated without maintenance for 1.5 years. Monitoring will continue to determine the required re-injection frequency.
2. Extraction trench was located 50 feet downgradient of the barrier. Increased concentrations of dissolved iron and manganese entering the trench did increase maintenance costs for the air stripper.

3.2 Selecting the Test Site

The following selection criteria represent the ideal demonstration test site:

- Site hydrogeology and contaminant distribution are reasonably well-defined.
- Groundwater velocity is >50 ft/year.
- Contaminants are present at moderate to high concentrations.
- Pilot test location is NOT upgradient of a critical receptor.
- Sufficient working area is available.

A good understanding of the site hydrogeology/contaminant distribution is desirable to aid in design of the PRB. Moderate to high contaminant concentrations need to be present to allow detection of changes in contaminant concentrations and degradation products. The groundwater velocity needs to be sufficient to detect changes over time as groundwater migrates through the barrier within the timeframe of the demonstration project. To protect human health and the environment and to aid in gaining regulatory approval, it is important that the pilot test location is NOT upgradient, in close proximity to a critical receptor. Finally, sufficient working space is required to allow installation of the PRB and associated monitor wells without interfering with ongoing site operations.

3.3 Test Site Description

Based on an evaluation of the site selection criteria, a site in northeast Maryland was selected as the test site for this demonstration. The project was performed within a commingled perchlorate and chlorinated solvent plume downgradient of a closed surface impoundment. Figure 3-1 shows the site location and the pilot test area. The following sub-sections briefly describe the site history and characteristics.

3.3.1 Test Site History and Description

The following information is summarized from *Pre-Remediation Investigation, Incinerator Feed Surface Impoundment* (Groundwater Technology, Inc., 1990) and *Perchlorate Investigation* (ARCADIS Geraghty & Miller, 1999):

The facility has been used for industrial purposes, such as fireworks manufacturing, munitions production, pesticide production, and research and manufacturing of solid propellant rockets. Ammonium perchlorate was used to manufacture and test rocket engines at the facility. A surface impoundment was operated at the site from 1976 through 1988 for the storage of an aqueous solution of ammonium perchlorate and waste solvent. The impoundment was 30 ft by 30 ft by 6 ft deep and included a rubber liner. Total organic halogens were discovered in groundwater at the site in 1983. Subsequently, the impoundment was emptied and the failed rubber liner was replaced with a plastic liner material. The impoundment was used until 1988 when it was permanently closed.

VOCs were first discovered in groundwater from two production wells at the facility in 1984. Various investigation activities were conducted to assess the extent of TCE and 1,1,1-TCA in groundwater in the vicinity of the former impoundment. In 1998, the presence of the perchlorate ion (ClO_4^-) was discovered in groundwater in some on-site wells. A subsequent perchlorate investigation was performed by ARCADIS Geraghty & Miller in 1999.

3.3.2 Test Site Characteristics

The pilot test barrier was constructed in an open grassy area approximately 150 feet downgradient from the former impoundment. A pump-and-treat system is currently used to treat impacted groundwater in this area. Groundwater is extracted from an interceptor trench, treated via an air stripper, and re-injected via an upgradient infiltration gallery. The locations of the interceptor trench and infiltration gallery are shown on Figure 3-1. The pilot test barrier is located approximately 50 feet upgradient of the interceptor trench, as shown in the figure.

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1130.02A3.ESTC

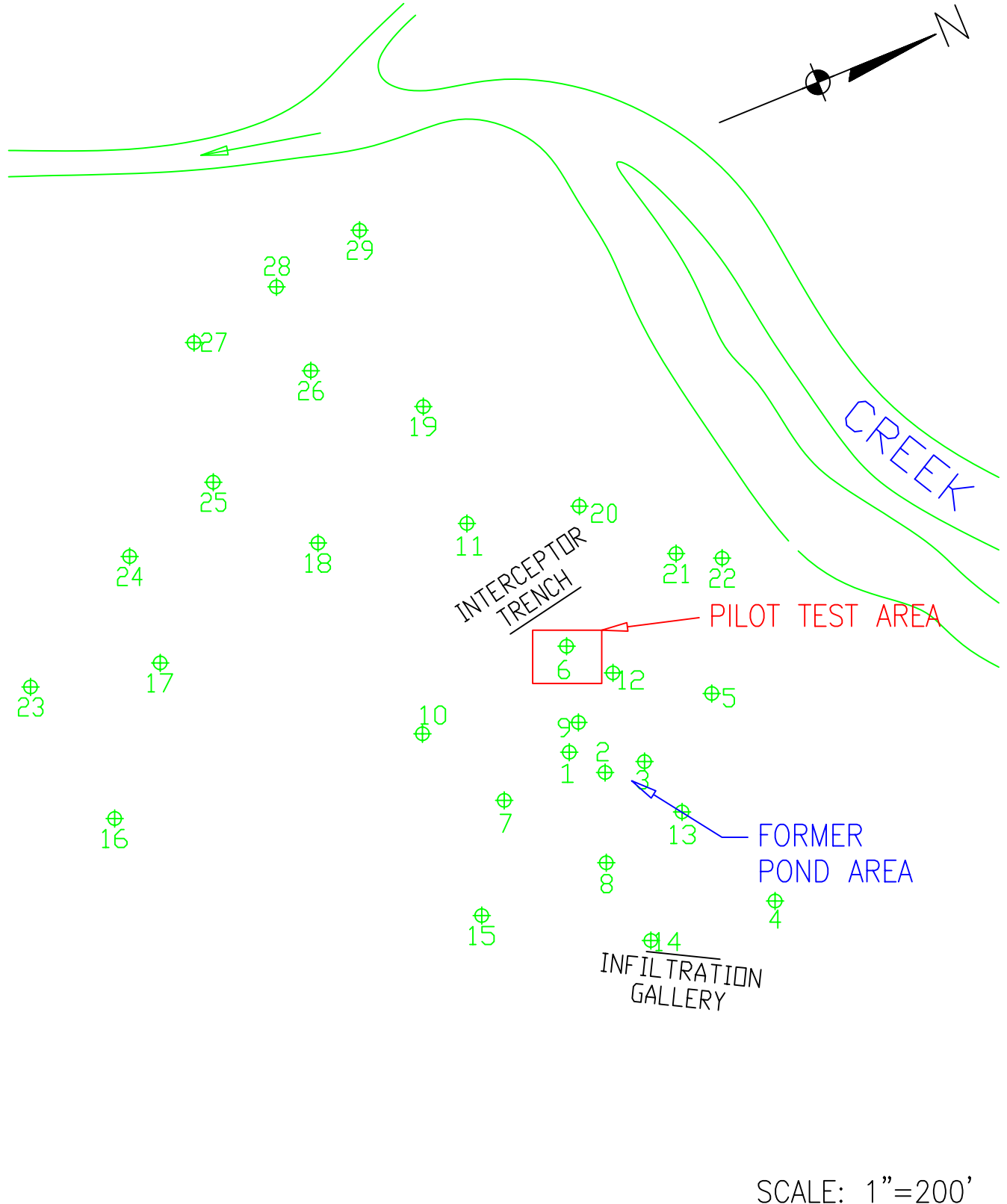
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The water table aquifer at the site is composed of silty sand and gravel to approximately 15 ft bgs and is underlain by silty clay. The primary contaminated zone appears to be this sand and gravel layer. Boring logs for existing site monitor wells in the vicinity of the pilot test barrier are provided in Appendix A, along with boring logs from the pilot test injection and monitor wells.

Groundwater flow in the pilot test area is generally to the west towards the interceptor trench. The water table varies between approximately 1 and 8 feet bgs. The groundwater flow velocity in the immediate vicinity of the proposed pilot test area was not well known prior to initiating the field test activities. Using permeability measurements from slug tests on MW-3 conducted in 1990, the groundwater velocity was estimated to be 2.5 to 5.0 ft/yr. However, based on the extraction and injection rates for the pump-and-treat system provided by site representatives, the groundwater velocity appeared to be substantially higher. Aquifer testing conducted as part of the pre-demonstration activities (see Section 3.4.1) indicated that the groundwater velocity was approximately 80 ft/yr. 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. This value was used in evaluating the performance of the PRB.

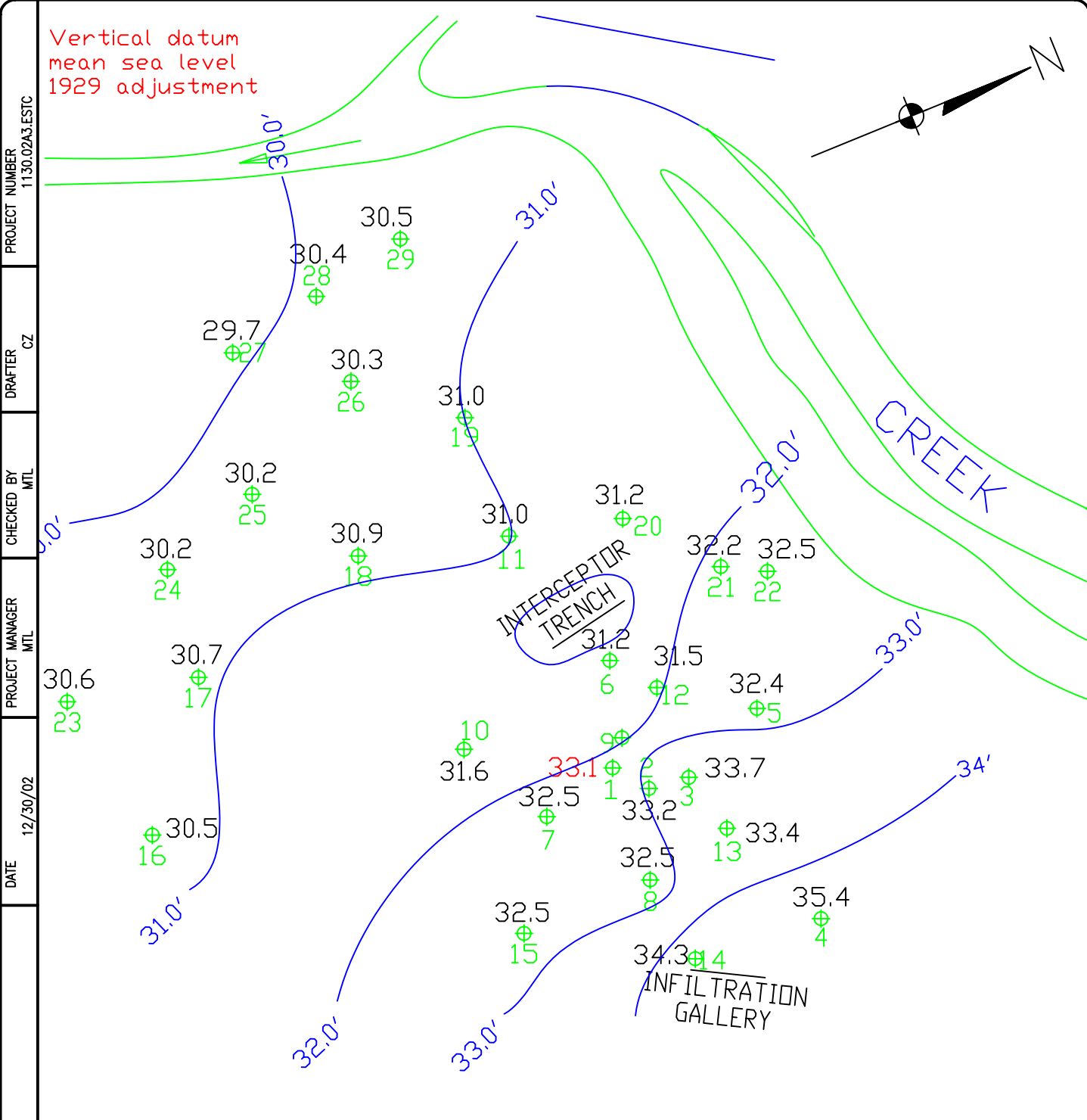
Figures 3-2, 3-3, and 3-4 show the site-wide groundwater elevation, 1,1,1-TCA concentration, and TCE concentration maps, respectively, in the vicinity of the proposed pilot test area. More detailed site characterization data were collected as part of the pre-demonstration testing activities.

3.4 Pre-Demonstration Testing and Analysis

Prior to installation of the EOS[®] barrier, Solutions-IES performed a detailed site characterization in the immediate vicinity of the pilot test area to more precisely define the distribution of contaminants, local stratigraphy, and permeability. As part of the characterization activities, Solutions-IES also collected soil and groundwater for laboratory microcosm and column studies. Data obtained from the site characterization were used to provide baseline data against which the performance of the EOS[®] technology was compared and were used in conjunction with the results of the laboratory studies to finalize the design plans for installation of the test barrier. The pilot test injection and monitor wells were installed during the pre-demonstration testing activities. Figure 3-5 shows the layout of the pilot test area.

3.4.1 Aquifer Testing

Limited hydraulic conductivity data were available for the demonstration site. To gain injection design information and baseline aquifer permeability data, Solutions-IES conducted hydraulic conductivity tests and an injection test. Previous permeability measurements from slug tests on existing well MW-3 conducted in 1990 indicated the groundwater velocity was 2.5 to 5.0 ft/yr. However, based on the extraction and injection rates for the pump-and-treat system provided by site representatives, the groundwater



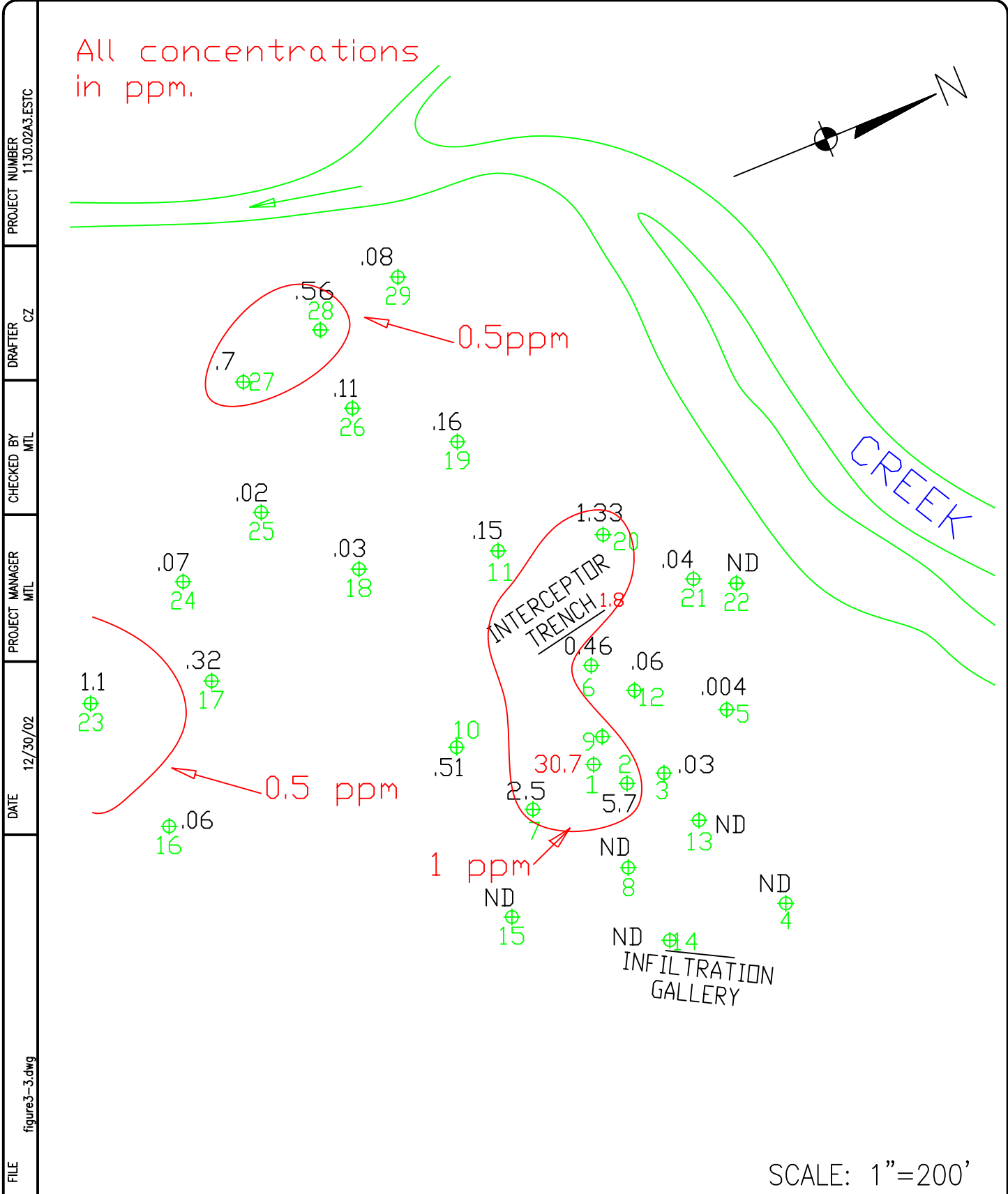
Quarterly average air stripper feed rate = 6.5 gpm. Average shallow aquifer depth = 6.26 ft.
 Approximate shallow groundwater gradient (dh/dl) = 4ft/1000ft = 0.004 ft/ft
 Calculated shallow groundwater velocity = (k/n dh/dl) = 2.2 feet/year. (n=.25=effective porosity)
 Aquifer transmissivity, T = kd, = 2.3 sqft/day = 17.3 gal/day/ft
 Shallow aquifer hydraulic conductivity (k) = 0.37ft/day (1.3x10⁻⁶m/s), (GTI slug test 3/15/90)

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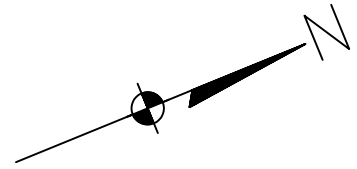


GROUNDWATER POTENTIOMETRIC SURFACE
 DECEMBER 6 & 7, 2001
 PERCHLORATE SITE
 MARYLAND

FIGURE:
 3-2



All concentrations
in ppb.



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1130.02A3.ES1C

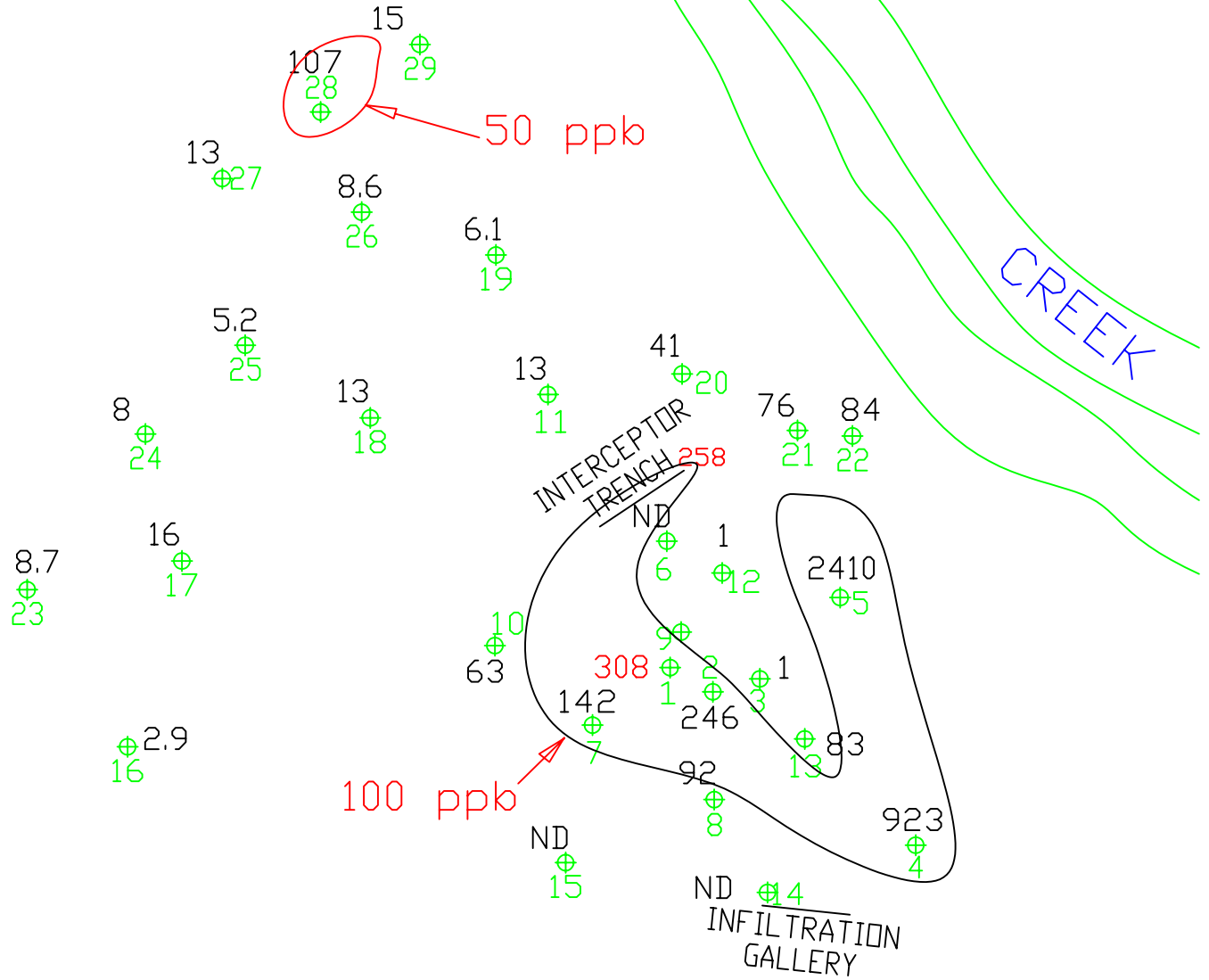
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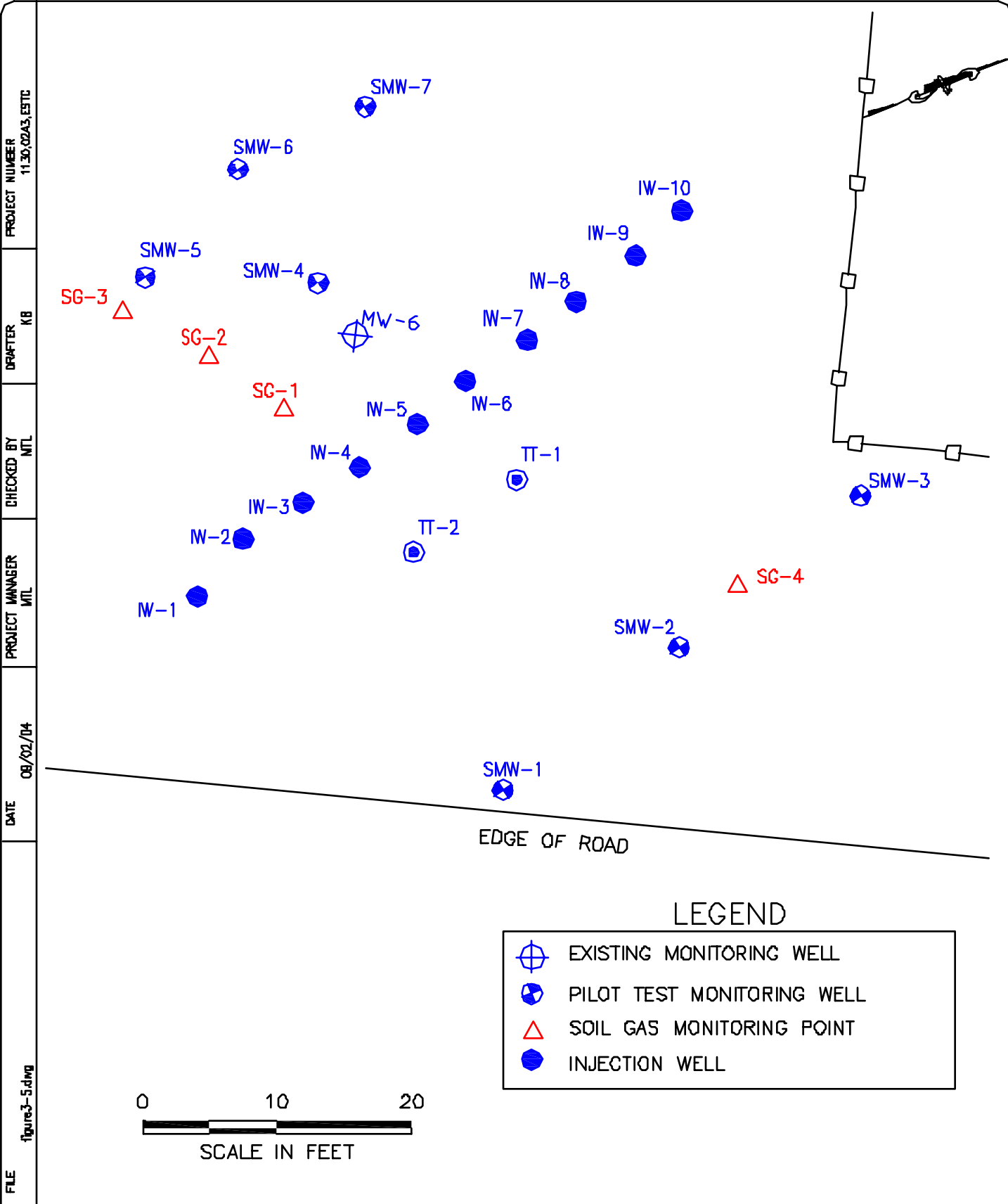
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velocity appeared to be substantially higher. Prior to proceeding with the pilot test well installation activities, Solutions-IES conducted slug tests on several existing monitor wells at the site. These slug tests indicated an average hydraulic conductivity of approximately 22 ft/day. Assuming a hydraulic gradient of 0.003 ft/ft and a porosity of 0.3, the average groundwater flow velocity was estimated to be 80 ft/yr. This velocity met the desired test site selection criteria of >50 ft/yr. Therefore, Solutions-IES decided to proceed with the demonstration at this site.

Additional hydraulic conductivity tests (slug tests and/or specific capacity tests) were conducted following installation of the pilot test injection and monitor wells to establish baseline conditions prior to injection of EOS[®]. The results of the hydraulic conductivity tests are summarized in Table 3-2, and the well installation activities are discussed in the following subsection. The average hydraulic conductivity in the injection wells was approximately 40 ft/day, and the average for the monitor wells was 29 ft/day.

TABLE 3-2
Summary of Pre-Injection Hydraulic Conductivity Tests
Maryland Perchlorate Site

Well ID	Test Date	Test Before or After Injection	Type of Test	Hydraulic Conductivity	
				cm/sec	ft/day
Upgradient Monitoring Wells					
TT-1	4/14/2003	Pre-Injection	Slug In	3.46E-04	0.98
	4/14/2003	Pre-Injection	Slug In	4.27E-04	1.21
	4/23/2003	Pre-Injection	Spec Capacity	1.90E-04	0.54
	TT-1 Pre-Injection Average			3.21E-04	0.91
Injection Wells					
IW-1	6/24/2003	Pre-Injection	Spec Capacity	1.76E-02	49.89
IW-2	6/24/2003	Pre-Injection	Spec Capacity	1.09E-02	30.90
IW-3	6/24/2003	Pre-Injection	Spec Capacity	1.90E-02	53.86
IW-4	6/24/2003	Pre-Injection	Spec Capacity	1.47E-02	41.67
IW-5	6/24/2003	Pre-Injection	Spec Capacity	1.11E-02	31.46
IW-6	6/24/2003	Pre-Injection	Spec Capacity	4.18E-03	11.85
IW-7	6/24/2003	Pre-Injection	Spec Capacity	1.13E-02	32.03
IW-8	6/24/2003	Pre-Injection	Spec Capacity	1.79E-02	50.74
IW-9	6/24/2003	Pre-Injection	Spec Capacity	1.79E-02	50.74
IW-10	6/24/2003	Pre-Injection	Spec Capacity	1.69E-02	47.90
Injection Wells Pre-Injection Average				1.41E-02	40.10
Downgradient Monitoring Wells					
SMW-6	4/14/2003	Pre-Injection	Slug In	3.29E-03	9.32
	4/14/2003	Pre-Injection	Slug In	1.80E-03	5.09
	4/23/2004	Pre-Injection	Spec Capacity	3.05E-03	8.65
	SMW-6 Pre-Injection Average			2.71E-03	7.69
MW-6	4/14/2003	Pre-Injection	Slug In	1.30E-02	36.91
	4/14/2003	Pre-Injection	Slug Out	1.90E-02	53.73
	4/14/2003	Pre-Injection	Slug In	1.90E-02	53.73
	4/14/2003	Pre-Injection	Slug Out	1.90E-02	53.73
MW-6 Pre-Injection Average				1.75E-02	49.53
Downgradient Monitoring Wells Pre-Injection Average				1.11E-02	31.59

An injection test was also performed to assist with planning the EOS[®] injection activities. The primary purpose of the injection test was to obtain an estimate of potential flow rates that could be used during the EOS[®] injection to allow us to estimate the time required to complete the injection activities. The injection test was conducted on SMW-6 using treated water from the air stripper effluent. During the injection test, flow rates around 1 gpm were maintained with pressures less than 10 psi.

3.4.2 Well Installation

After confirming that the groundwater flow velocity at the site was sufficient for the demonstration, Solutions-IES installed the pilot test injection wells, monitor wells, and soil gas monitoring points. The well layout is shown on Figure 3-5. The pilot test wells included the following:

- Ten injection wells installed approximately 5 feet on center in a line generally perpendicular to groundwater flow.
- Three upgradient monitor wells approximately 25 feet upgradient of the barrier (SMW-1, -2, and -3)
- Five downgradient monitor wells:
 - One existing well (MW-6) approximately 7.5 feet downgradient.
 - One monitor well (SMW-4) approximately 12.5 feet downgradient of the barrier.
 - Three monitor wells (SMW-5, -6, and -7) approximately 20 feet downgradient. (These well locations actually varied between 19 and 21 feet downgradient, but are referred to as 20 feet downgradient in this report for simplicity).
- Four soil gas monitoring points (SG-1 through SG-4)
- Two tracer test wells (TT-1 and TT-2). Originally, we planned to install only one well for use in the bromide tracer tests. However, after installing TT-1, we discovered that this well was completed in a low permeability area and injection tests yielded very low flow rates. Therefore, a second well (TT-2) was installed and was used for the tracer tests.

The pilot test injection and monitor wells were installed using a Geoprobe to total depths of approximately 15 feet bgs. The wells were constructed of 1-inch Schedule 40 PVC well materials with 10 feet of 0.020-inch slotted screen and casing to the surface. The sand pack extended from the total depth of each well to 2 feet above the screened interval. A bentonite seal was placed above the sand pack with Portland cement-bentonite grout to the surface. Each well was completed within a flush-mounted manhole cover.

Existing well MW-6 was used as a downgradient monitor well for the pilot test. According to the boring log prepared by Groundwater Technology, Inc., MW-6 is a 4”

PVC well screened from 3 to 14.5 feet bgs. The well was drilled using a hollow-stem auger rig. A copy of the boring log is provided in Appendix A.

The soil gas monitoring points were installed using a hand auger. The points were completed with 1-inch Schedule 40 PVC well materials to a total depth of 2.5 feet bgs with 1 foot of 0.020-inch slotted screen and casing to the surface. Pea gravel was placed around the screen with a bentonite seal to the surface.

3.4.3 Soil Sampling

Six pre-injection soil samples were collected during installation of the initial pilot test wells, IW-1, IW-10, SMW-6, and TT-1. The samples were analyzed for TOC, VOCs, and perchlorate. The sample depths and results are shown on Table 3-3. VOCs were not detected in any of the soil samples. Perchlorate was detected in 4 of the 6 samples at concentrations ranging from 660 to 2,100 µg/kg. TOC concentrations in the soil samples varied from <1.0 to 920 mg/kg.

TABLE 3-3
Pre-Injection Soil Sample Results
Maryland Perchlorate Site

Sample Location	Sample Depth (feet bgs)	Sample Date	VOCs (µg/kg)	Total Organic Carbon (mg/kg)	Perchlorate (µg/kg)
TT-1	8-12	4/22/2003	ND	440	<500
TT-1	12-14	4/22/2003	ND	<1.0	930
IW-10	6-8	4/23/2003	ND	200	<500
IW-10	12-14	4/23/2003	ND	920	660
IW-1	12-14	4/23/2003	ND	<1.0	2100
SMW-6	14-15	4/22/2003	NS	NS	760

Notes:

ND denotes not detected.

NS denotes not sampled.

3.4.4 Groundwater Sampling

Groundwater samples were collected from IW-1, SMW-6, and TT-1 immediately after installation of these wells in April 2004 to confirm concentrations in the pilot test area for use in design of the pilot test. Subsequent groundwater samples were collected following installation of all of the wells in September 2003 to establish baseline conditions prior to EOS[®] injection. This baseline sampling event consisted of the following:

- Field measurements from all injection wells and pilot test monitor wells for:
 - Water level
 - DO
 - pH
 - Conductivity
 - Temperature
 - ORP
- Groundwater samples from all upgradient and downgradient pilot test monitor wells and five injection wells (IW-1, IW-3, IW-5, IW-7, and IW-10) for analysis of:
 - VOCs
 - Perchlorate
 - Total organic carbon and total inorganic carbon
 - Methane, ethane, and ethene
 - Nitrate, nitrite, sulfate, phosphate
 - Chloride
 - Bromide
- Groundwater samples from monitor wells SMW-2, SMW-4, SMW-6, and MW-6 and injection wells IW-3 and IW-7 for analysis of:
 - Volatile fatty acids
 - Dissolved iron
 - Manganese
 - Arsenic

The results of the pre-demonstration groundwater sampling activities are summarized in Table 3-4 for the key constituents at the site and in Table 3-5 for the biogeochemical parameters.

TABLE 3-4
Average Pre-Injection Concentrations
Primary Constituents of Concern

Constituent	Average Concentration (µg/L)	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)
Perchlorate	8,600	3,100	20,000
1,1,1-TCA	11,000	5,700	17,000
1,1-DCA	30	7	62
Chloroethane	ND	<5	<20
1,1-DCE	602	270	1,200
PCE	53	25	110
TCE	94	28	210
cis-1,2-DCE	8	5.5	10

Constituent	Average Concentration (µg/L)	Minimum Concentration (µg/L)	Maximum Concentration (µg/L)
trans-1,2-DCE	ND	<5	<20
Vinyl chloride	ND	<5	<20
Ethane	1.10	0.16	4.28
Ethene	0.43	0.04	1.94

TABLE 3-5
Average Pre-Injection Concentrations
Biogeochemical Parameters

Constituent	Average Concentration	Minimum Concentration	Maximum Concentration
Total Organic Carbon (mg/L)	1.2	<1.0	1.4
Total Inorganic Carbon (mg/L)	22.8	20.5	27.9
Nitrate (mg/L)	9.5	<0.5	13.9
Sulfate (mg/L)	27.7	18.3	34.4
Dissolved Oxygen (mg/L)	2.73	1.27	5.83
ORP (mV)	132	102	154
pH (standard units)	5.9	5.4	6.2
Dissolved Iron (mg/L)	<0.5	<0.5	<0.5
Arsenic (mg/L)	<0.010	<0.010	<0.010
Manganese (mg/L)	0.23	0.05	0.60
Chloride (mg/L)	14.2	6.6	18
Methane (µg/L)	0.5	<0.2	0.8

3.4.5 Tracer Test

Following installation of the pilot test injection and monitor wells, a pre-injection bromide tracer test was conducted to monitor the movement of groundwater in the pilot test area. The purpose of the tracer test was to establish baseline flow conditions. A duplicate tracer test was later conducted approximately 9 months after EOS[®] injection to assess the possible effects of permeability changes on flow conditions in the pilot test area.

The tracer test consisted of injecting 1,000 gallons of a 500 mg/L bromide solution into tracer test well TT-2. The pre-injection tracer test was initiated on July 23 and 24, 2003. Groundwater samples were collected for bromide analysis before initiation of the tracer test (July 21-22, 2003), immediately after injection of the tracer (July 24, 2003), and then monthly for two months (August 26, 2003, September 29-30, 2003). A similar post-

injection tracer test was conducted in July 2004. The bromide tracer test data are discussed in Section 4.3.3.

3.4.6 Laboratory Studies

Laboratory studies were conducted under the direction of Dr. Robert C. Borden, P.E., in the Department of Civil, Construction, and Chemical Engineering at North Carolina State University to aid in the design of the field pilot test. The laboratory work consisted of microcosm studies and column tests, as described below.

3.4.6.1 Microcosm Studies

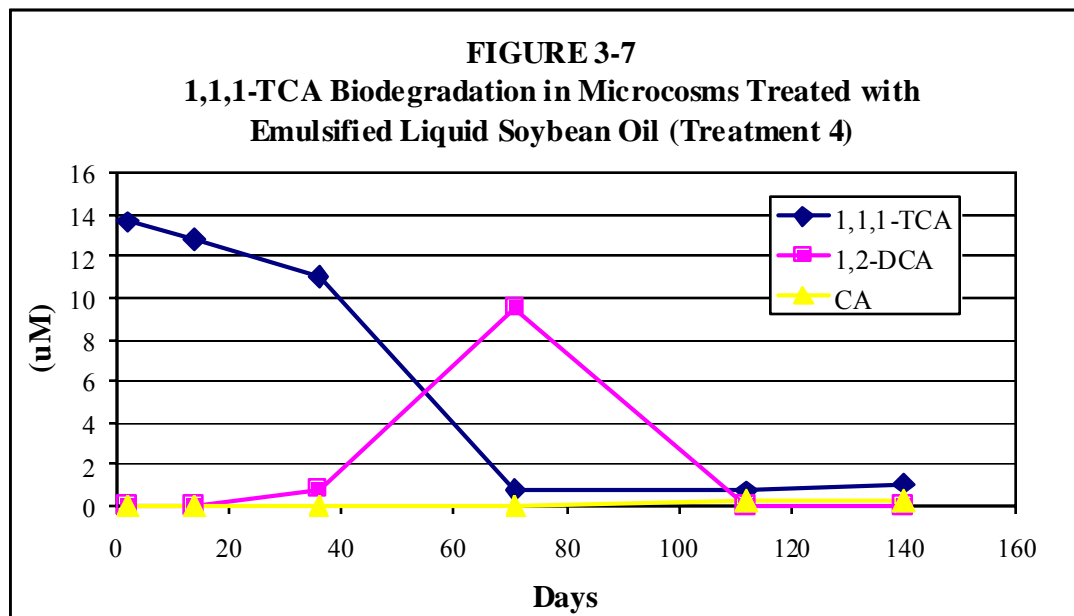
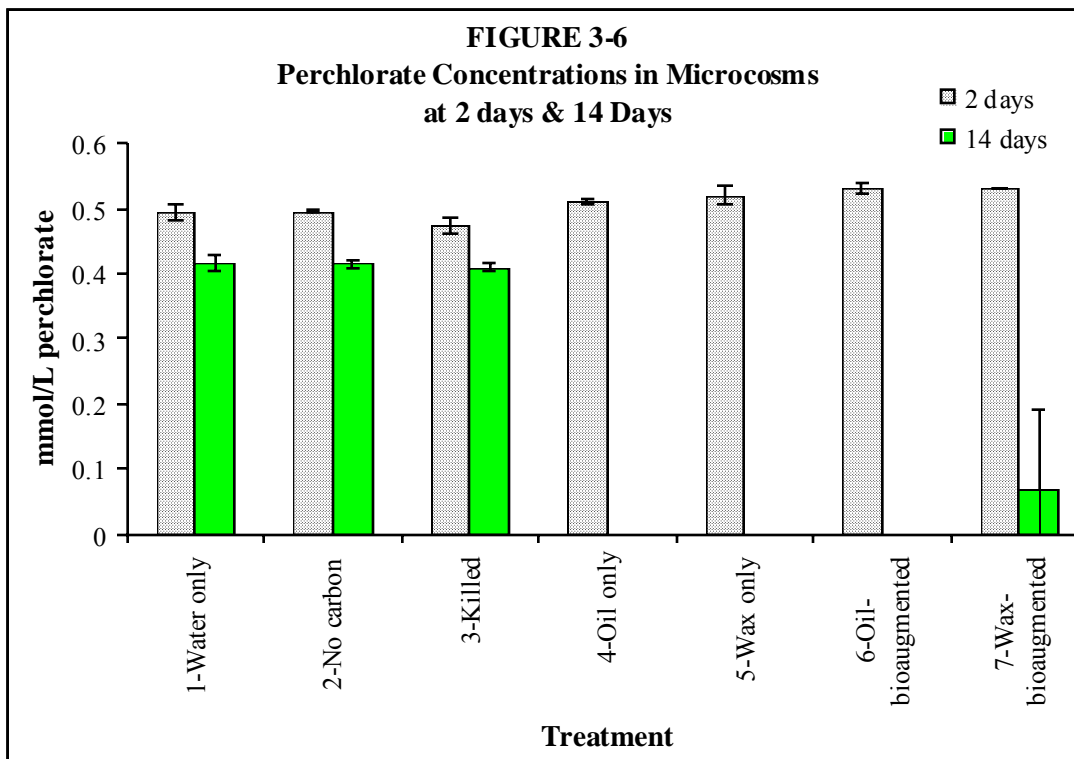
Laboratory microcosm studies were conducted prior to barrier installation to: (1) identify an appropriate oil that will support complete biodegradation of perchlorate in the groundwater with minimal methane production; (2) identify an appropriate oil that will support complete biodegradation of 1,1,1-TCA in the groundwater with minimal methane production, and (3) determine whether bioaugmentation is needed to achieve complete conversion of 1,1,1-TCA to non-toxic end products. The microcosms were constructed using aquifer sediment and groundwater obtained from the field test site. Details of the experimental set-ups and results are provided in the laboratory report in Appendix B, and a brief summary is provided below.

The laboratory microcosms were created in triplicate using site aquifer sediments and groundwater to evaluate the ability of edible oil substrate to support contaminant biodegradation. Treatments included:

- #1 – No sediment, no added carbon
- #2 – Live control, no added carbon
- #3 – Killed control, EOS[®], NaOH
- #4 – EOS[®]
- #5 – Hydrogenated soybean wax
- #6 – EOS[®] with bioaugmentation culture
- #7 – Hydrogenated soybean wax with bioaugmentation culture

Perchlorate degradation was rapid and complete in all microcosms treated with EOS[®]. In all three replicates in treatment #4, perchlorate concentrations decreased from approximately 50 mg/L to less than 0.008 mg/L within 14 days (Figure 3-6). 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. There was no correlation between extent of 1,1-DCA degradation and addition of a bioaugmentation culture. 1,1-DCA was completely degraded in some incubations that did not receive the bioaugmentation culture and persisted in some incubations that were bioaugmented. Figure 3-7 shows results from one microcosm where 1,1,1-TCA degraded from 13.7 μ M (1,820

$\mu\text{g/L}$) to less than $0.5 \mu\text{M}$ ($\sim 50 \mu\text{g/L}$). Near stoichiometric amounts of 1,1-DCA were produced followed by a decrease in 1,1-DCA to below $1 \mu\text{g/L}$. Trace levels of chloroethane (CA) were produced and then declined suggesting further conversion of CA to non-toxic end products.

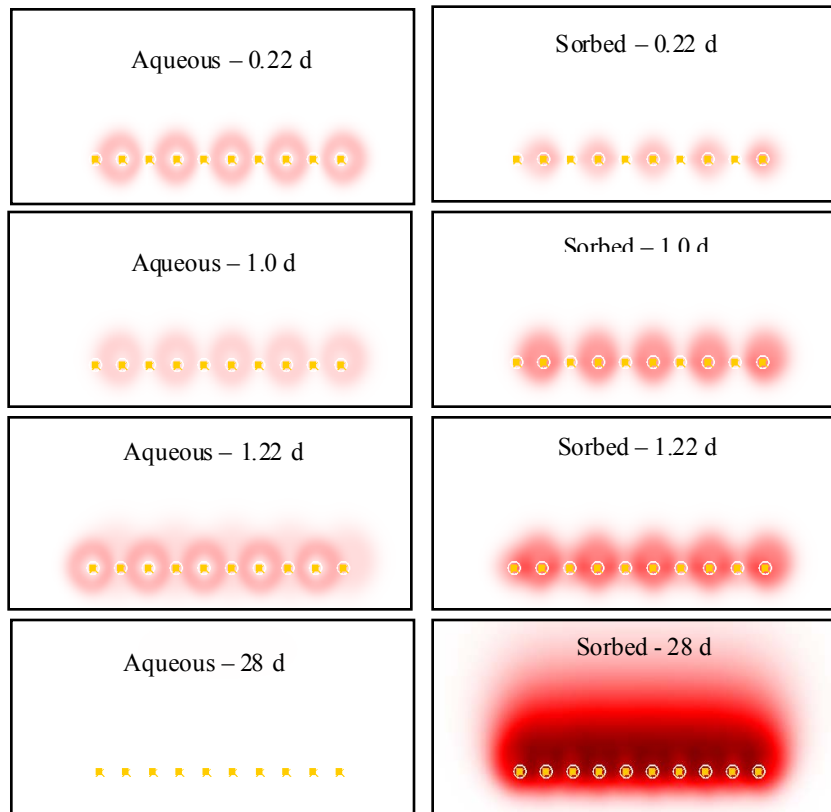


Overall, the microcosm results demonstrated that EOS[®] addition was effective in stimulating an aerobic biodegradation of perchlorate and 1,1,1-TCA in site sediments and that bioaugmentation was not required to achieve complete dechlorination of 1,1,1-TCA and other chlorinated compounds to non-toxic end products.

3.4.6.2 Column Tests

Small diameter column experiments (2.5 cm dia. x 80 cm long) were also conducted using aquifer material from the Maryland site 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. Measurements of volatile solids in the effluent over time indicated that 97% of the volatile solids were retained in the column. The oil distribution was measured over the length of the column, and the oil was found to be distributed throughout the entire column with higher concentrations near the inlet. These results indicated that EOS[®] could be effectively distributed in aquifer material from the Maryland site. Data from the column studies were used to develop model parameters to simulate the distribution of EOS[®] at the site in preparation for the field pilot study. Figure 3-8 shows the EOS[®] distribution predicted by the model. Details of the column tests can be found in the laboratory report in Appendix B.

FIGURE 3-8
Model Simulated EOS[®] Distribution in Sediment



3.5 Testing and Evaluation Plan

3.5.1 Demonstration Installation and Start-Up

The field pilot test consisted of a one-time injection of emulsified oil substrate (EOS[®]) and chase water to create an *in situ* PRB. Most of the demonstration set-up (injection well, monitor well, and soil gas monitoring point installation; baseline monitoring; etc.) was conducted as part of the site characterization activities. No injection permits were required by the Maryland Department of the Environment (MDE) for this pilot test.

The pilot barrier was created by injecting a soybean oil-in-water emulsion (EOS[®]) into the contaminated zone through ten injection wells. Dispersion of the soybean oil away from the injection points and into the formation was enhanced by a two-step process:

- (1) Injection of the soybean oil-in-water emulsion as the primary substrate; and
- (2) Injection of a second volume of water to encourage further displacement of the emulsion away from the injection wells.

Solutions-IES mobilized to the site to perform the emulsion injection in October 2003. The physical setup for the injection was minimal. The temporary equipment required for the injection included the following: a solution mixing/holding tank, a gasoline powered transfer pump, injection hoses, flow meters, pressure gauges, and valves. Utility requirements were limited to a source of water for diluting the concentrated emulsion and for use as chase water. A diagram of the injection process is shown in Figure 3-9, and photographs taken during the injection activities are provided below.



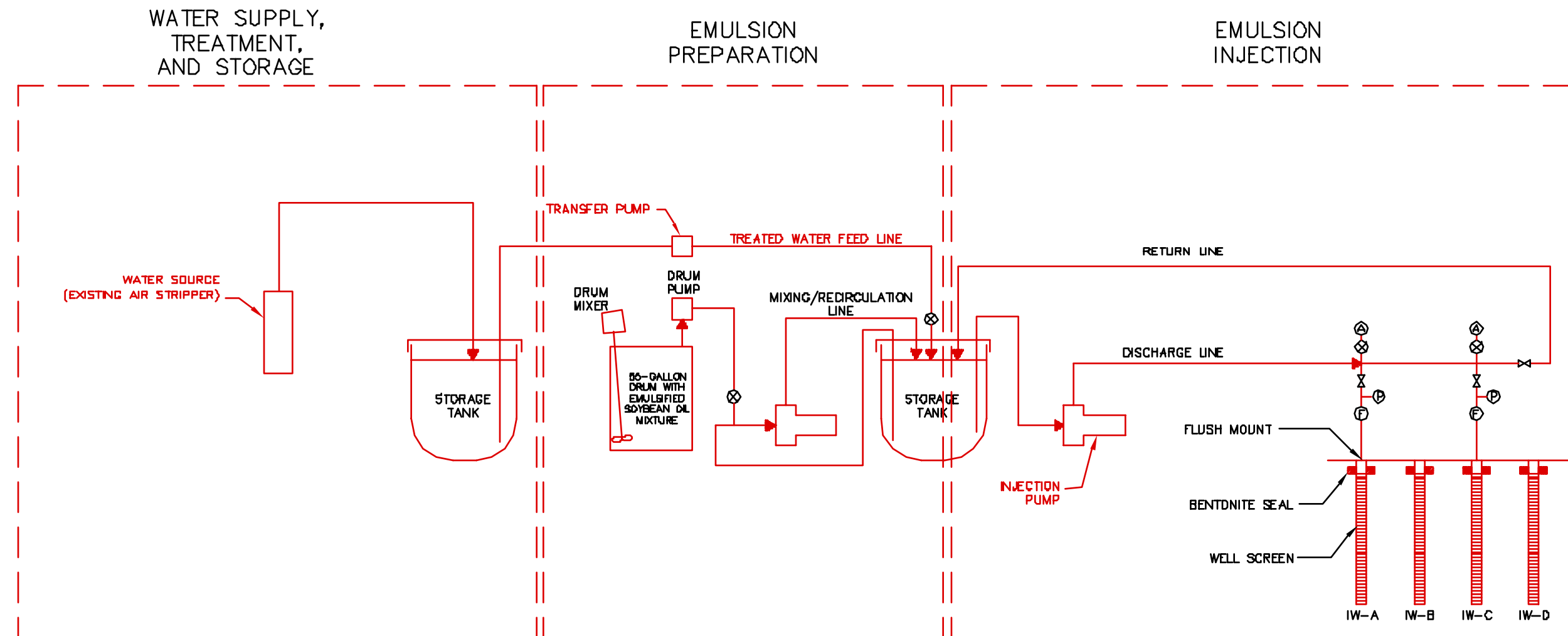
PHOTOGRAPH 1
Mixing of dilute EOS[®] for injection.



PHOTOGRAPH 2
Injecting EOS[®] at the Maryland site.

LEGEND

PRESSURE GAGE	⊕
FLOW METER	⊖
VALVE - GATE	×
VALVE - BALL	⊗
QUICK-CONNECT UNION	— —
AIR RELEASE VALVE	⊕



3.5.1.1 Water Supply

A convenient source of water was required to prepare and disperse the emulsion. This water was obtained from an air stripper located approximately 150 feet south of the PRB. The air stripper treats groundwater from the extraction trench located 50 feet downgradient of the pilot test injection wells. The air stripper effluent is re-injected into the subsurface through an infiltration gallery located approximately 425 feet upgradient of the pilot test area. The effluent from the air stripper was diverted into a temporary holding tank for use during injection.

A sample of the air stripper effluent was collected prior to initiation the injection activities on September 29, 2003. The analytical results for key parameters are summarized in Table 3-6. Perchlorate was detected at a concentration of 3,100 µg/L. No chlorinated solvents were detected at concentrations above the laboratory method detection limits.

TABLE 3-6
Air Stripper Effluent Data
September 29, 2003
Maryland Perchlorate Site

Constituent	Concentration
Perchlorate (µg/L)	3,100
1,1,1-TCA (µg/L)	<0.5
1,1-DCE (µg/L)	<0.5
PCE (µg/L)	<0.5
TCE (µg/L)	<0.5
Total Organic Carbon (mg/L)	<1.0
Total Inorganic Carbon (mg/L)	3.57
Bromide (mg/L)	<0.5
Nitrate (mg/L)	10.9
Nitrite (mg/L)	<0.5
Sulfate (mg/L)	25.0
Phosphate (mg/L)	<0.5
Chloride (mg/L)	12.5
ORP (mV)	132.0
pH (standard units)	6.91
Temperature (°C)	18.3
Conductivity (µS/cm)	166.5

3.5.1.2 Substrate Preparation and Emplacement

The emulsified oil was obtained as a pre-blended concentrated emulsion, EOS[®], from EOS Remediation, Inc. of Raleigh, NC. The EOS[®] concentrate consisted of approximately 60% soybean oil, 24% water, 2% yeast extract, 10% emulsifier, 1% lactic acid, and 3% sodium lactate. A Product Sheet and Material Safety Data Sheet (MSDS) for EOS[®] are provided in Appendix C. The EOS[®] concentrate was delivered to the site in two 55-gallon drums. Prior to injection, the EOS[®] was diluted by mixing 1 part EOS[®] with 4 parts water. The emulsion was mixed in batches on site in temporary holding tanks.

After mixing, the emulsion was injected under low pressure into the injection points followed by chase water to distribute the emulsion throughout the aquifer. Half of the wells (every other injection well) were injected simultaneously using a manifold system to reduce the time required to complete the injection. The process was then repeated for the remaining injection wells. Approximately 55 gallons of emulsion and 165 gallons of chase water were injected into each well. Individual flow meters and pressure gauges were located at each wellhead to monitor the injection volumes and pressures. Table 3-7 summarizes the measured amounts of emulsion and water that were added to each injection well. Injection pressures were maintained below 5 psi to prevent hydraulic fracturing of the formation.

TABLE 3-7
Substrate and Chase Water Injection Volumes
Maryland Perchlorate Site

Well ID	Diluted EOS Injected (gallons)	Chase Water Injected (gallons)
IW-1	44.5	175.5
IW-2	55.0	165.5
IW-3	55.0	165.0
IW-4	54.2	157.3
IW-5	55.0	165.0
IW-6	41.0	157.3
IW-7	51.7	157.3
IW-8	66.0	170.0
IW-9	55.0	165.0
IW-10	55.0	170.0
Total	532	1,648
Total Volume of Emulsion and Water = 2,180 gallons		

Note:
EOS concentrate was diluted 1:4 with water.

3.5.2 Period of Operation

Table 3-8 provides the dates and duration of each phase of the demonstration. The Technology Demonstration Plan was finalized in April 2003 and pre-demonstration field work was initiated. The injection and monitor wells were installed April 22-23, 2003 and June 23-24, 2003. The pre-injection tracer test was initiated on July 23, 2003 with subsequent monthly sampling for three months. Injection of the emulsion and chase water was performed between October 7 and 9, 2003, and the first performance monitoring event was conducted October 13-14, 2003. Routine performance monitoring was conducted for 18 months with the last event completed April 21, 2005. The Cost and Performance Report and Application Protocol for this demonstration are being prepared in conjunction with a similar on going demonstration being conducted under this project (CU-0221) evaluating the use of emulsified oils for chlorinated solvent remediation at the Charleston NWS.

**TABLE 3-8
 Demonstration Project Schedule
 Maryland Perchlorate Site**

TASK	2002				2003				2004				2005				2006																					
	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5		
Contract Award	█																																					
Test Site Identification		█	█	█	█	█																																
Technology Demonstration Plan							█	█	█	█																												
Pre-Demonstration Testing/Well Installation										█	█																											
Pre-Injection Tracer Test											█	█	█	█																								
Laboratory Column Studies											█	█	█	█	█																							
Laboratory Microcosm Studies												█	█	█	█	█																						
Emulsion Injection																																						
Performance Monitoring																																						
6-Month Post-Injection Geoprobe Sampling Event																																						
Post-Injection Tracer Test																																						
Final Report																																						
Application Protocol																																						
Cost/Performance Analysis																																						

3.5.3 Amount/Treatment Rate of Materials to be Treated

During the demonstration period, the average groundwater flow rate was 400 feet/year and the effective porosity was 0.18 in the immediate pilot test area. Using these data, the barrier treated approximately 740 gallons/day or approximately 405,000 gallons during the 18-month demonstration period. Perchlorate concentrations upgradient of the barrier ranged from 2,700 µg/L to 72,000 µg/L with an average of 11,700 µg/L. Upgradient 1,1,1-TCA concentrations ranged from 2,000 µg/L to 19,000 µg/L with an average of 9,100 µg/L.

3.5.4 Residuals Handling

The groundwater was treated *in situ*; therefore, only minimal investigation-derived waste (IDW) was generated during the demonstration. Soil cuttings from well installation and soil sampling activities were containerized in 55-gallon drums. Purge water and decontamination fluids from the monitor wells were collected in drums as they were generated. The site's project representative arranged for disposal of all IDW.

3.5.5 Operating Parameters for the Technology

The installation of the barrier constitutes an *in situ* remediation approach for cleanup of the aquifer. Once the EOS[®] was introduced into the subsurface, there was no aboveground equipment to operate or maintain. Consequently, there are no mechanical operating parameters for the technology.

Groundwater monitoring and hydraulic conductivity testing were used to monitor the performance of the barrier and to evaluate the impact of the soybean oil emulsion injection on the permeability of the aquifer. Groundwater monitoring was conducted as described in Section 3.5.7. Hydraulic conductivity measurements were performed using either standard slug-in and slug-out tests or specific capacity tests. *In situ* hydraulic conductivity was measured throughout the pilot test program. Measurements were collected prior to injection of the emulsion, four months after injection, and eighteen months after injection.

A post-injection tracer study was conducted nine months after the emulsion injection to evaluate the impact of the emulsion injection on the groundwater flow in the vicinity of the barrier. Procedures for preparation and distribution of the inorganic tracer were identical to the first tracer test (Section 3.5.1).

3.5.6 Experimental Design

The results of the site characterization activities, laboratory microcosm studies, and laboratory column tests were used to aid in the design of the EOS[®] barrier. The primary design components were:

- Screen interval of the injection wells;
- Spacing of the injections wells;
- Amount of substrate; and

- Total injection volume (substrate and chase water).

The screen interval of the injection wells was determined based on the site lithology. Existing boring logs and observations during the well installation activities indicated between approximately 5 and 15 feet bgs. Therefore, this was the vertical interval targeted for injection and the injection wells were screened across this zone.

The pilot test barrier was designed as a 50-foot long barrier perpendicular to groundwater flow. Due to uncertainties regarding the permeability of the aquifer, a conservative injection well spacing of 5 feet was utilized.

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. The oil required for biodegradation was determined by first calculating the oil demand based on concentrations of background electron acceptors (dissolved oxygen, nitrate, sulfate), concentrations of contaminants to be treated (primarily perchlorate and 1,1,1-TCA), the expected levels of organic carbon to be released from the barrier (typically 50 to 100 mg/L TOC), and estimated concentrations of reduced compounds produced (dissolved iron, manganese, methane). The oil requirement was then calculated by multiplying the groundwater flux through the barrier by the design life and the oil demand, as shown in the following equations.

$$\text{Oil required} = Q \text{ (L/yr)} * T \text{ (yr)} * \text{Oil Demand (mg/L)}$$

Where, Q = Water flux
 T = Design life

The water flux, Q, is calculated as follows:

$$Q = y * z * n_e * K * i$$

Where, y = Design width perpendicular to groundwater flow (ft)
 z = Effective height (ft)
 n_e = Effective porosity
 K = Hydraulic conductivity (ft/yr)
 i = Hydraulic gradient (ft/ft)

A design spreadsheet was used to perform these calculations. Data for the Maryland site were entered into the spreadsheet, and it was determined that 2 drums of EOS[®] were required for biodegradation based on a 3-year design life. Typically, design lives of 5 to 10 years are used. However, a shorter design life was chosen for this demonstration so we could observe oil depletion/reduced treatment efficiency within the timeframe of the project. A copy of the spreadsheet is provided in Appendix D.

We also evaluated the oil requirement based on oil retention by sediment. In order to form a permeable reactive barrier using emulsified oils, the sediments within the barrier need to be coated with oil. The oil retention by the sediment can be determined using the following equation:

$$\text{Oil required} = x * y * z * \rho_B * O_R$$

Where,

- x = Treatment zone length parallel to groundwater flow (ft)
- y = Design width perpendicular to groundwater flow (ft)
- z = Effective height (ft)
- ρ_B = Sediment bulk density (lb/ft³)
- O_R = Effective oil retention (lb oil/lb sediment)

The field pilot test barrier was designed to be 50 feet wide perpendicular to groundwater flow (y). The effective height of the barrier was estimated to be between 5 and 10 feet (z). Although we were injecting into a 10-foot zone, the site lithology indicated 5 feet of higher permeability material where most of the injected material would likely be distributed. The length of the barrier parallel to groundwater flow was determined based on the desired contact time. The barrier was designed to provide a contact time of 30 days. Based on groundwater velocity data for the site, a design length of 5 feet (x) was used. The sediment bulk density was estimated to be 120 lb/ft³, and the effective oil retention was determined to be between 0.001 and 0.002 from the laboratory column tests. Using these numbers, the oil required for retention by the sediment was calculated to be between 150 to 600 lbs, which is equivalent to between 1 and 3 drums of EOS[®] (EOS[®] is approximately 60% oil).

Solutions-IES also calculated to the total volume of water and emulsion that needed to be injected to create the desired PRBB. In order to spread the emulsion across the desired treatment zone, one pore volume of the design treatment zone must be injected. The total injection volume can be calculated using the following equation:

$$V = x * y * z * n_e$$

Where,

- V = Total volume of water and emulsion
- x = Treatment zone length parallel to groundwater flow (ft)
- y = Design width perpendicular to groundwater flow (ft)
- z = Effective height (ft)
- n_e = Effective porosity

Based on the calculations above, Solutions-IES decided to inject two 55-gallon drums of EOS[®] and 2,200 gallons total volume (water and emulsion) to create the PRB.

During injection, pressures and flow rates were recorded and adjusted to optimize the injection process. Following injection, a combination of soil, groundwater, and hydraulic conductivity testing was performed to evaluate the distribution of EOS[®] and performance of the barrier. Details of the sampling activities are provided in the next subsection.

3.5.7 Sampling Plan

Sampling activities primarily consisted of soil sampling to evaluate the radius of influence after injection, groundwater sampling to monitor the EOS[®] performance and distribution, soil gas sampling to monitor the accumulation of VOC vapors in the soil, and aquifer testing to evaluate permeability effects. Prior to the injection activities, samples were also collected from the water supply that was used in the injection process. The sampling activities were conducted in accordance with the Quality Assurance Project Plan, which was provided in the Technology Demonstration Plan. The analytical/testing methods that were used are discussed in Section 3.7.

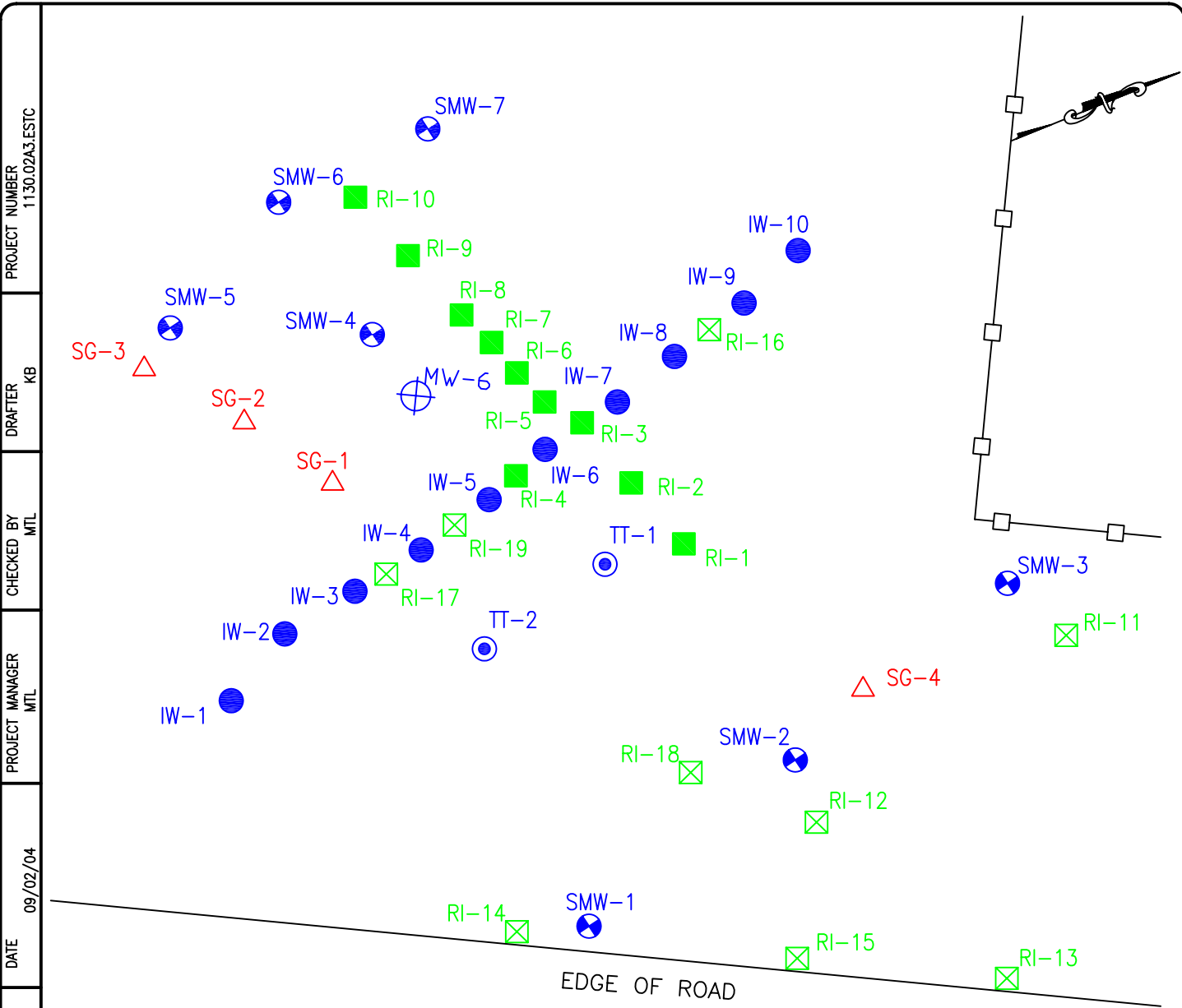
3.5.7.1 Radius of Influence and Soil Sampling

During and after injection of the emulsion at the pilot test site, the radius of influence away from the injection wells was evaluated. The radius of influence was evaluated in three ways: (1) by noting any visual changes such as coloration or miliness due to the emulsion in nearby monitor wells; (2) by analyzing groundwater samples from the monitor well network for TOC (Section 3.6.7.2); and (3) by collecting soil samples adjacent to the barrier.

During the injection, groundwater samples were collected from nearby wells to assess the spread of the emulsion in the subsurface. The first injection phase consisted of injecting into wells IW-1, IW-3, IW-5, IW-7, and IW-9 and collecting groundwater samples from IW-6 for visual observation and TOC analysis. In the second phase, IW-2, IW-4, IW-6, IW-8, and IW-10 were injected and monitoring was conducted at SMW-4. The results are discussed in Section 4.3.2.

Soil sampling was conducted approximately six months after injection of the oil emulsion (April 2004) using a Geoprobe to evaluate the distribution of EOS[®] in the subsurface. Soil samples were collected at the following 11 locations (see Figure 3-10):

- Downgradient – 2.5 ft, 5 ft, 7.5 ft, 10 ft, 15 ft, and 20 ft (6 locations)
- Upgradient – 5 and 10 feet (2 locations)
- One location halfway between injection wells IW-5 and IW-6
- One location halfway between injection wells IW-6 and IW-7
- One background location



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LEGEND

	EXISTING MONITORING WELL
	PILOT TEST MONITORING WELL
	SOIL GAS MONITORING POINT
	INJECTION WELL
	GEOPROBE SOIL SAMPLE-APRIL 2004
	GEOPROBE SOIL SAMPLE-SEPT 2004

An additional Geoprobe soil sampling event was conducted in September 2004 primarily to obtain additional background data and to collect a couple additional soil samples from within the barrier to expand the data set. The soil samples were collected at the following 8 locations (see Figure 3-10):

- One location halfway between injection wells IW-4 and IW-5
- One location halfway between injection wells IW-8 and IW-9
- Six background locations

In general, the borings were completed to a total depth of approximately 15 feet bgs. Up to four soil samples were collected from each boring depending on recovery and field observations. The samples consisted of the following:

- One shallow composite sample (5 to 10 feet)
- One deep composite sample (10 to 15 feet)
- Up to two discrete grab samples collected from locations where there were visible signs of emulsion or other impact (e.g., black coloration)

All of the soil samples were analyzed for TOC to evaluate the distribution of oil emulsion in the aquifer.

3.5.7.2 Groundwater Sampling

Baseline groundwater sampling was conducted as part of the site characterization activities and prior to injection (April 23, 2003 and September 29-30, 2003). Performance monitoring was initiated after the oil emulsion was injected to form the barrier and included the collection of samples immediately after injection (October 13-14, 2003) and then approximately 1 month (November 13, 2003), 2 months (December 16, 2003), 4 months (February 18-19, 2004), 11 months (September 21 and 22, 2004), and 18 months (April 21, 2005) after substrate emplacement.

During each performance monitoring event the field measurements and samples were collected:

- Field measurements from all injection wells and pilot test monitor wells for:
 - Water level
 - DO
 - pH
 - Conductivity
 - Temperature
 - ORP

- Groundwater samples from all up gradient and down gradient pilot test monitor wells and five injection wells (IW-1, IW-3, IW-5, IW-7, and IW-10) for analysis of:
 - VOCs
 - Perchlorate
 - Total organic carbon and total inorganic carbon
 - Methane, ethane, and ethene
 - Nitrate, nitrite, sulfate, phosphate
 - Chloride
 - Bromide
- Groundwater samples from monitor wells SMW-2, SMW-4, SMW-6, and MW-6 and injection wells IW-3 and IW-7 for analysis of:
 - Volatile fatty acids
 - Dissolved iron
 - Manganese
 - Arsenic
- Samples from the influent and effluent of the nearby air stripper for:
 - pH
 - Conductivity
 - Temperature
 - ORP
 - VOCs
 - Perchlorate
 - Total organic carbon and total inorganic carbon
 - Methane, ethane, and ethene
 - Nitrate, nitrite, sulfate, phosphate
 - Chloride
 - Bromide

In general, purging and sampling protocols followed the procedures outlined in *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual* (EISOPQAM; EPA, 1997). Prior to the collection of groundwater samples, water level measurements were collected for each monitoring and injection well using a water level interface probe. Each well to be sampled was then purged to remove stagnant water from the well and to allow its replacement by groundwater from the adjacent formation, which is more representative of actual aquifer conditions. Because of the shallow depth to water, the wells were sampled using a peristaltic pump and low-flow purging and sampling methods. An adequate purge was achieved when the pH, specific conductance, and temperature of the groundwater had stabilized. The goals for stabilization were as follows:

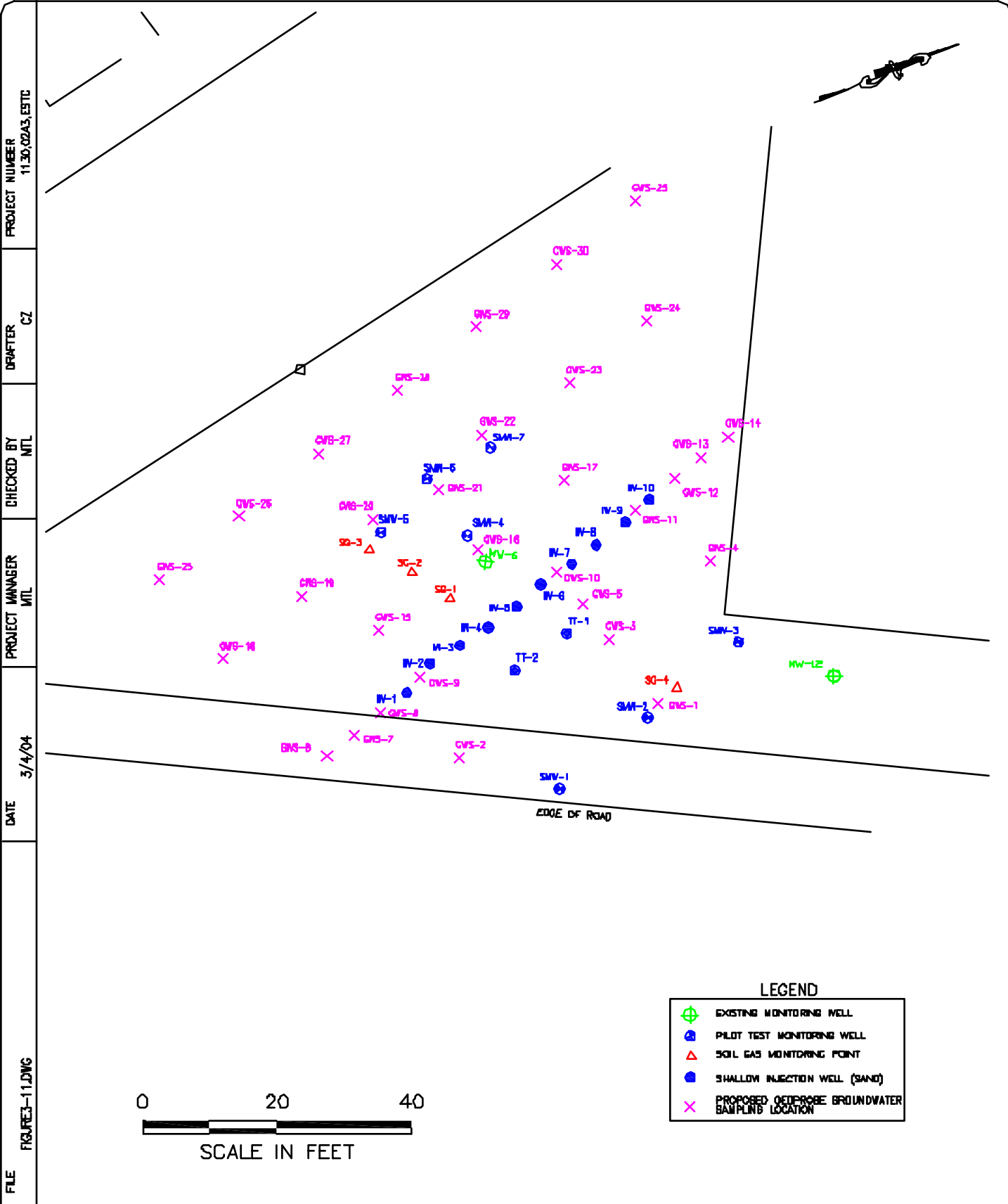
- pH- Measurements remain constant within 0.1 Standard Unit (SU).
- Specific Conductance – Measurements vary by no more than 10 percent.

- Temperature – Measurements remain constant for at least three successive readings.

After an adequate purge was achieved, field measurements were recorded and groundwater samples were collected for analysis. The samples were collected in laboratory prepared sample containers appropriate for the analytical method being used. The sample containers were immediately sealed, labeled, and placed on ice in an insulated cooler for subsequent delivery to the analytical laboratory. Chain-of-custody forms accompanied all samples sent to the laboratory. The sequence of sample collection for analysis was as follows:

- 1) Field parameters:
 - a. Dissolved Oxygen (DO);
 - b. Oxidation-Reduction Potential (ORP);
 - c. pH
 - d. Temperature
 - e. Specific Conductance
- 2) Laboratory parameters:
 - a. Volatile Organic Compounds (CAHs and trihalomethanes)
 - b. Ethene (C₂H₄), Ethane (C₂H₆), and Methane (CH₄);
 - c. Perchlorate
 - d. Total Organic Carbon (TOC), Total Inorganic Carbon (TIC);
 - e. Nitrate, Nitrite, Sulfate, Phosphate; and
 - f. Bromide, Chloride.

In addition to the routine performance monitoring events, a set of groundwater samples was collected from the pilot test plot using a Geoprobe Screen-Point Sampler[®] approximately 6 months after injection (April 19-23 2004). Samples were collected from 30 locations (see Figure 3-11). At four locations, samples were collected from two depths: 1 within the 5 to 10-foot interval and 1 within the 10 to 15-foot interval. At each depth in these four borings, specific capacity measurements were also collected. At the remaining locations, one sample was collected from within the 10 to 15-foot interval. All samples were field measured for pH, temperature, conductivity and ORP and laboratory analyzed for perchlorate, TOC, chloride, nitrite, bromide, nitrate, phosphate, sulfate. The results of these analyses were used to map areas in the vicinity of the barrier with confirmed impact by the placement of oil emulsion in the barrier.



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3.5.7.3 Soil Gas Sampling

The soil-gas monitoring points adjacent to the PRB and the headspace of the pilot test monitoring and injection wells were tested in the field for the accumulation of vapors. Measurements of methane, carbon dioxide, oxygen, percent lower explosive limit (LEL), hydrogen sulfide, and carbon monoxide were collected using a four-gas analyzer, landfill gas meter, OVA and/or other appropriate monitoring equipment.

3.5.7.4 Permeability Testing

Hydraulic conductivity testing was performed before and after injection to evaluate permeability changes. As mentioned in Section 3.5.1, slug-in and slug-out tests or specific capacity tests were performed on selected injection and monitor wells during the demonstration project. Pre-injection testing was conducted on April 14 and 23, 2003 and June 24, 2003, and post-injection testing was conducted four months after injection (February 19, 2004) and 18 months post-injection (April 20, 2005). Data obtained from the slug-in and slug-out tests was reduced using standard Bouwer-Rice methodology; data obtained from specific capacity tests was reduced as described in Cho et al. (2000).

3.5.7.5 Water Supply Sampling

Water from the air stripper effluent was utilized in the injection process. Prior to use, a sample of the effluent was collected to characterize the water. The sample was field tested for pH, temperature, conductivity, and ORP and was analyzed for perchlorate, VOCs, nitrate, nitrite, sulfate, phosphate, chloride, bromide, TOC, and TIC. The sample was collected directly into the appropriate laboratory prepared containers.

3.5.8 Demobilization

Immediately after injection of the EOS[®] in October 2003, all temporary equipment used in the injection process was removed from the site. Since EOS[®] process is an *in situ* treatment technology, there was no associated aboveground equipment or structures requiring removal at the end of the demonstration. Residual oil emulsion remains *in situ* to continue enhancement of subsurface degradation activity. The presence of residual substrate continues to provide long-term reducing power, capable of slow, continuous degradation of the groundwater contaminants. Other equipment utilized during this demonstration was limited to the pilot test injection wells and monitor wells. These wells were left in place for potential future use.

3.6 Selection of Analytical/Testing Methods

Analytical methods used in this demonstration are listed in Table 3-9.

3.7 Selection of Analytical/Testing Laboratory

The laboratories where the analyses were performed are identified in Table 3-9. The majority of the analyses were performed by Prism Laboratories in Charlotte, NC. Perchlorate analyses were conducted by Babcock Labs in Riverside, CA; dissolved gases were performed by VaporTech Services, Inc. of Valencia, PA; IC analyses were conducted at NCSU's Environmental Engineering Lab in Raleigh, NC; and volatile fatty acid analyses were performed by Microbial Insights, Inc. of Rockford, Tennessee.

**Table 3-9
Analytical Methods and Laboratories**

Analyte	Analytical Method	Laboratory
Perchlorate	EPA Method 314.0	Babcock Labs Riverside, CA
CAHs	EPA Method 6230 (GC, only)	Prism Laboratories Charlotte, NC
Methane, ethane, ethene	Gas chromatography	VaporTech Valencia, PA
Chloride, bromide, sulfate	Ion Chromatography	NCSU Env. Eng. Lab, Raleigh, NC
Nitrate, nitrite	Ion Chromatography	NCSU Env. Eng. Lab, Raleigh, NC
Phosphate	Ion Chromatography	NCSU Env. Eng. Lab, Raleigh, NC
Total Organic Carbon, Total Inorganic Carbon	EPA Method 415.1	Prism Laboratories Charlotte, NC
Volatile fatty acids	Modified EPA Method 8015	Microbial Insights Rockford, TN
Manganese, arsenic	EPA Method 3010A (sample prep) EPA Method 6010B (analysis)	Prism Laboratories Charlotte, NC
Dissolved iron	Filtration and EPA Method 3010A (sample prep) EPA Method 6010B (analysis)	Prism Laboratories Charlotte, NC

4.0 Performance Assessment

4.1 Performance Criteria

The performance criteria for this technology demonstration project are presented in Table 4-1.

**Table 4-1
Performance Criteria**

Performance Criteria	Description	Primary or Secondary
Generate reducing conditions	Convert aquifer to anaerobic conditions. Increase amount of biodegradable organic carbon near barrier. Reduce concentrations of competing electron acceptors (NO ₃ , SO ₄)	Primary
Minimal Adverse Impacts	Chemical quality of groundwater at substantial distances (> 100 ft) downgradient from the barrier is not severely impacted (TOC near background levels, moderate to low methane concentrations).	Primary
Compatible with MNA	Any degradation products released by barrier (e.g., DCA, chloroethane) are more easily biodegraded under ambient geochemical conditions than parent compounds (1,1,1-TCA).	Primary
Biodegrade perchlorate	Reduce perchlorate concentrations by 90%. Evaluate the reductions (by calculations, microbial analyses, and downgradient soil and groundwater testing) to determine that they are a result of biodegradation rather than physical/chemical removal mechanisms.	Primary
Convert TCA to less chlorinated compounds	Over 50% of the chlorinated ethanes (molar concentration) will be converted to non-chlorinated end products during passage through treatment zone with over 75% reduction in the mole fraction of 1,1,1-TCA.	Secondary
Reduce contaminant mass flux	Reduce total mass flux of perchlorate by over 75%.	Primary
Meet regulatory standards	There is currently no Maryland groundwater standard for perchlorate, but the secondary goal will be to try to achieve a 4 µg/L goal. Achievement of this goal will be a function of the contaminant concentrations entering the barrier, hydraulic residence time in barrier, and rate of contaminant biotransformation. If concentrations are high, it may not be feasible to achieve this goal with a single barrier and multiple barriers may be required.	Secondary
Hazardous Materials	All ingredients of EOS [®] are non-hazardous. If incomplete degradation of chlorinated ethanes occurs, elevated concentrations of daughter products may be formed. Nuisance changes including odor, color and taste may also occur, but are non-hazardous.	Secondary
Process Waste	Process is an <i>in situ</i> remediation technology; therefore, waste will be limited to soil cuttings from well installation and groundwater from well development and purging. IDW could potentially contain elevated concentrations of perchlorate and CAHs. Representative samples will be tested and disposed of according to MD regulations. Leftover (unused) substrate will be disposed of via sanitary sewer.	Secondary
Factors Affecting	Technology performance is affected by the following operating conditions: 1) Ability to distribute EOS [®] throughout the vertical impacted zone (affected	Primary

Performance Criteria	Description	Primary or Secondary
Technology Performance	<p>by heterogeneities in the subsurface lithology).</p> <p>2) Presence of appropriate microorganisms.</p> <p>3) Changes in aquifer permeability after EOS[®] injection that could impact flow through the barrier.</p> <p>4) Presence of aquifer conditions (pH, DO, ORP, etc.) favorable to anaerobic reductive dechlorination.</p>	
Reliability	<p>1) There should be no breakdown of equipment since there are no aboveground appurtenances remaining after the PRB is installed.</p> <p>2) The reliability of the injection process is dependent on the knowledge of the subsurface lithology.</p>	Secondary
Ease of Use	<p>1) The installation of injection and monitor wells requires a drilling team and one geologist.</p> <p>2) The installation of the PRB requires two personnel, such as a project professional and a technician. These personnel must be familiar with the objectives of the project, be trained with the mixing equipment, and maintain a mechanical aptitude for field adjustments.</p> <p>3) During installation, continuous monitoring is desired because the material is injected under pressure.</p> <p>4) OSHA's health & safety training is required because the site contains high concentrations of chlorinated solvents as well as other mechanical and physical risks.</p>	Primary
Versatility	<p>The technology can be used in three configurations:</p> <p>1) Source areas can be treated by injecting EOS[®] directly into 'hot spots' to accelerate cleanup. As a contaminant is slowly released from low permeability zones, the contaminant comes in contact with edible oil and is degraded.</p> <p>2) Where a contaminant plume must be prevented from crossing a boundary, overlapping treatment zones can be created to prevent downgradient migration of the plume.</p> <p>3) Where natural attenuation is not completely effective in controlling the migration of chlorinated solvents, edible oils can be distributed throughout the plume to supplement the naturally occurring organic carbon.</p> <p>The technology can potentially be used for a variety of contaminants (e.g., perchlorate, nitrate, heavy metals, radionuclides) and geologic environments (sedimentary and fractured rock, deep water tables, etc.)</p>	Secondary
Maintenance	<p>No operation and maintenance will be required during ESTCP demonstration. Mass flux calculations indicate that less than 20% of injected carbon is consumed per year.</p>	Primary
Scale-Up Constraints	<p>The potential issues of concern associated with scaling up the technology for full implementation include:</p> <p>1) Variability of concentrations of target contaminants throughout the plume. DNAPL concentrations of some CAHs have the potential to inhibit biological activity.</p> <p>2) Accessibility to areas of the plume to be treated. Depending on the configuration, aboveground structures may interfere with the ability to inject or locate injection points.</p> <p>3) Lithology varies though out the plume.</p>	Secondary

Performance Criteria	Description	Primary or Secondary
	These issues of concern will be addressed in the demonstration by: 1) Limiting the area of the test to a small portion of the plume. 2) Conducting additional site characterization in the immediate vicinity of the pilot test to characterize site conditions.	

4.2 Performance Confirmation Methods

The effectiveness of the demonstration was evaluated through the use of groundwater sampling, soil sampling, hydraulic conductivity testing, and tracer tests. These tools were used to evaluate 1) the ability of the technology to promote degradation of perchlorate and 1,1,1-TCA, 2) the distribution of EOS[®] in the aquifer, and 3) the impacts of the EOS[®] injection on the hydraulic conductivity of the aquifer and groundwater flow in the vicinity of the barrier, as further discussed below. Table 4-2 summarizes the expected performance, performance confirmation methods, and actual performance.

**Table 4-2
Expected Performance and Performance Confirmation Methods**

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual Performance Metric (post demo)
Primary Criteria (Qualitative Performance Objectives)			
Faster Remediation	Reduced contaminant concentrations	Monitor well data.	Yes. Perchlorate concentrations were immediately reduced to non-detectable levels. 1,1,1-TCA was reduced by >90%.
Maintenance	No maintenance after injection	Experience from demonstration operations	Yes. System operated for 1.5 years without maintenance. Additional monitoring is planned to determine required re-injection frequency.
Ease of Use	Injection process is relatively simple. No O&M required after injection.	Experience from demonstration operations	Yes. Injection was completed by two field personnel in 2 days with minimal set-up. No O&M was required after injection.
Primary Performance Criteria (Quantitative Performance Objectives)			
Target Contaminant -- % Reduction	Expect concentrations of perchlorate in the pilot test area to range around 5.0 mg/L; expect up to	Groundwater samples collected from several locations at different distances upgradient,	Yes. Perchlorate was reduced to <4 µg/L downgradient of the PRB, based on data

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual Performance Metric (post demo)
-- Regulatory Standard	90% reduction of perchlorate concentration in groundwater from upgradient of the PRB to downgradient, resulting in concentrations <0.5 mg/L; there is no MD regulatory standard for perchlorate, but target will be proposed national standard of 4 µg/L (>99.9 % removal). Achieving 4 µg/L is a secondary performance criterion.	downgradient, and within the PRB were analyzed for perchlorate. Changes in concentration were calculated both on a concentration and molar basis for comparison.	from SMW-6 along the centerline of the barrier.
Hazardous Materials -- Generated	Biodegradation of perchlorate is not expected to result in production of hazardous by-products. Degradation of CAHs may result in accumulation of daughter products.	Analysis of groundwater samples for degradation products.	Yes. Perchlorate was completely degraded with no production of hazardous by-products. CAH parent molecules were degraded, but residual daughter products are still detectable.
Process Waste -- Generated	Minimal IDW from drilling injection and monitor wells. Potential unused substrate.	Observation	Yes. Minimal IDW was generated during installation of the PRB.
Factors Affecting Performance -- Distribution	-- Distribution will be determined in final design of PRB based on site characterization results.	-- Actual distribution was evaluated by 1) noting any visual changes such as coloration or milkiness due to the emulsion in monitor wells; (2) analyzing groundwater samples from the monitor well network for TOC; and (3) collecting soil samples adjacent to the barrier.	-- EOS [®] was effectively distributed to create a PRB with no evidence of flow bypassing.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual Performance Metric (post demo)
-- Microbial population	-- Laboratory microcosms will be used to determine if bioaugmentation is necessary.	-- Groundwater samples were analyzed for CAH degradation products to evaluate whether complete conversion to non-toxic end products is occurring.	-- Bioaugmentation was not needed. Complete degradation of perchlorate was observed and CAH degradation end products were detected.
-- Changes in aquifer permeability	-- Some reduction in aquifer permeability may occur after substrate injection; however, groundwater should continue to flow through the PRB.	-- Hydraulic conductivity and/or specific capacity tests were performed before and after injection to evaluate potential changes. Bromide tracer tests were also performed to evaluate flow through the barrier.	-- Changes in hydraulic conductivity were observed. There was no evidence of flow bypassing, but along the edges of the barrier there was some evidence of flow around the PRB.
-- Favorable aquifer conditions	-- Injection of EOS [®] should convert aquifer to anaerobic conditions favorable for reductive dechlorination.	-- Groundwater samples from wells upgradient, within, and downgradient of the barrier were analyzed for DO, ORP, nitrate, sulfate, dissolved iron, and methane as secondary indicators of performance.	-- Anaerobic conditions were quickly achieved as indicated by changes in biogeochemical parameters and the desired biodegradation of the contaminants.
Secondary Performance Criteria (Qualitative Performance Objectives)			
Contaminant Mobility	Reduced contaminant mobility due to sorption and degradation.	Monitor well data.	Perchlorate was quickly degraded.
Safety -- Hazards -- Protective Clothing	Injection substrates are food-grade materials. Potential exposure to contaminants could occur during drilling and sampling. Injection is performed under pressure. Level D PPE should be worn.	Experience from demonstration operation.	No safety issues related to use of emulsified oil.
Versatility -- Other Applications	Yes – Technology can be applied as source area treatment, throughout	Experience.	Yes.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual Performance Metric (post demo)
	plume, or as PRB. Technology is also effective for other contaminants, such as perchlorate, nitrate, and chromium.		
Scale-up Constraints			
-- Contaminant Concentration	-- Toxicity levels to bacteria.	--Literature values and project experience suggest starting concentrations should not be toxic to bacteria.	--Shown to support degradation of up to 72 mg/L perchlorate and 25 mg/L 1,1,1-TCA.
-- Lithology	--Varying lithology could affect distribution.	Changes in hydraulic conductivity and specific capacity before and after injections will be monitored frequently.	--Injection wells completed with 10 feet of screen, but likely a 5-foot higher permeability zone. Heterogeneity should be considered in design.
-- Accessibility	-- Areas of plume covered by buildings or other structures may be inaccessible for injection.		--Not applicable for this demonstration.

The primary objective of this demonstration was to evaluate the use of EOS[®] for promoting biodegradation of perchlorate. This was evaluated by measuring changes in concentrations of perchlorate and chloride over time in wells upgradient, within, and downgradient of the PRB. A secondary objective was to demonstrate *in situ* reductive dechlorination of 1,1,1-TCA. This was evaluated by measuring changes in concentrations of 1,1,1-TCA and its daughter products over time. In the field, it can be difficult to distinguish between reduced contaminant concentrations due to dissolution or absorption versus biodegradation. To assist with the interpretation of the data, in addition to the measurement of perchlorate and CAHs in groundwater, other typical biogeochemical parameters were utilized as secondary indicators of method performance. These parameters include:

- Dissolved Oxygen (DO) –Successful transformation of the aquifer to anaerobic conditions will be evidenced by DO concentrations in the PRB impact zone of less than 0.5 mg/L.

- Oxidation-reduction potential (ORP) –Successful transformation of the aquifer to anaerobic conditions will be evidenced by ORP measurements less than 50 mV and preferably less than -100 mV.
- Nitrate - Successful transformation of the aquifer to anaerobic conditions will be evidenced by reduction of nitrate as a result of its use as an electron acceptor during the initial degradation of the EOS[®] substrate.
- Sulfate (SO₄) - Successful transformation of the aquifer to anaerobic conditions will be evidenced by reduction of sulfate as a result of its use as an electron acceptor during the initial degradation of the substrate.
- Dissolved iron (Fe⁺²) –Successful transformation of the aquifer to anaerobic conditions will be evidenced by an increase in the concentration of dissolved iron as ferric iron is reduced to ferrous iron.
- Methane - The presence of methane above background conditions indicates microbial degradation (methanogenesis) is occurring and conditions are favorable for reductive dechlorination.

The ability to distribute EOS[®] throughout the contaminated aquifer zone also affects the performance of this technology. Soil and groundwater samples were used to evaluate the distribution of EOS[®] in the aquifer. Soil sampling was conducted approximately 6 months after injection of the oil emulsion (with supplemental sampling conducted approximately 11 months after injection) and involved the collection of soil cores at background locations and at various locations within, upgradient, and downgradient of the barrier. Soil samples from multiple depths in each core were sampled for TOC and to evaluate the spread of oil throughout the aquifer. Throughout the demonstration, groundwater samples were visually inspected for changes due to the emulsion, such as coloration or milkiness. The groundwater samples were also analyzed for TOC.

Substantial changes in aquifer permeability following injection of the emulsion could impact groundwater flow and lead to short-circuiting of the barrier. Changes in hydraulic conductivity were measured by conducting standard slug-in/slug-out tests and/or specific capacity tests on selected test area wells prior to injection and during performance monitoring activities after injection. Slug-in/slug-out data were reduced using standard Bouwer-Rice methodology and specific capacity data were reduced according to Cho et al (2000) to calculate hydraulic conductivity values. Changes in permeability were evaluated by comparing hydraulic conductivity measurements in injection and monitor wells. The post-injection data was compared to the pre-injection data to evaluate the effect of the oil injection on aquifer permeability. In addition, a tracer test was performed by injecting a sodium bromide solution into an upgradient monitor well after injection of the emulsion and subsequently monitoring bromide concentrations in the test area wells.

4.3 Data Analysis, Interpretation and Evaluation

The following subsections discuss the data obtained during the 18-month demonstration project focusing on the three primary objectives of the demonstration: 1) the ability of the technology to promote degradation of perchlorate and 1,1,1-TCA, 2) the distribution of EOS[®] in the aquifer,

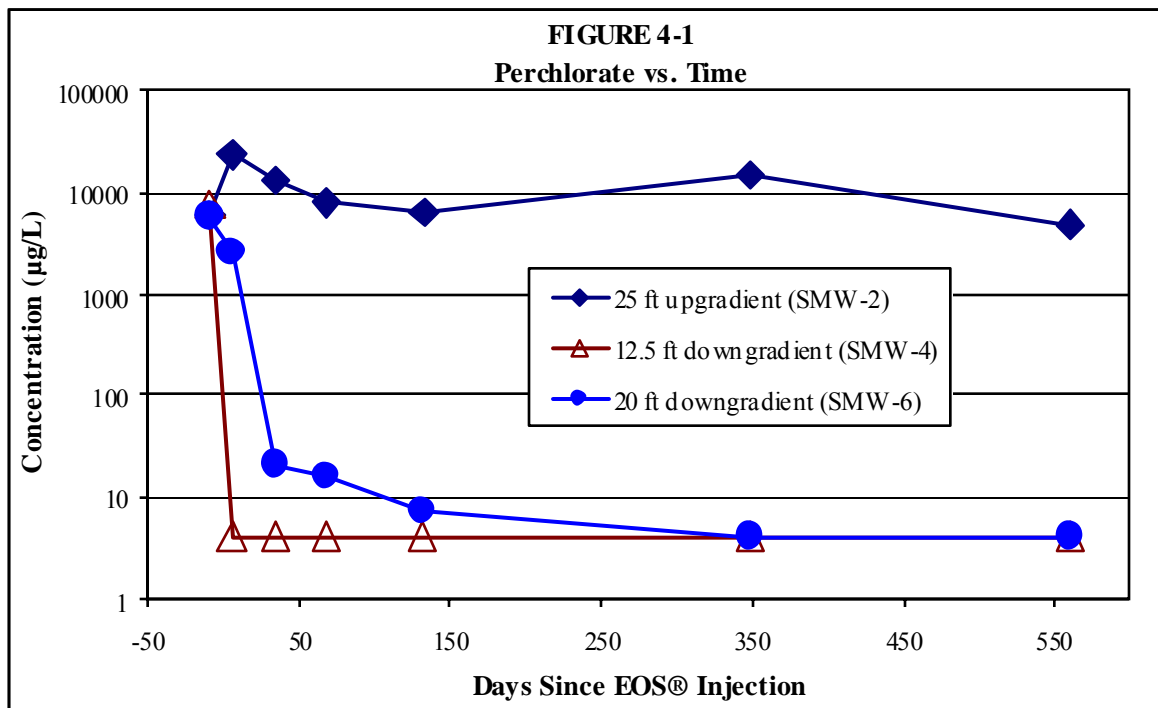
and 3) the impacts of the EOS[®] injection on the hydraulic conductivity of the aquifer and groundwater flow in the vicinity of the barrier. Secondary water quality impacts were also evaluated.

4.3.1 Effectiveness of the EOS[®] PRB

The effectiveness of the PRB was evaluated by assessing the ability of the EOS[®] injection to degrade perchlorate and 1,1,1-TCA. Changes in other contaminants (e.g., PCE and TCE) and biogeochemical parameters were also evaluated.

4.3.1.1 Perchlorate

The EOS[®] PRB was very effective at degrading perchlorate throughout the duration of the pilot study. The perchlorate data are summarized in Table 4-3 and presented graphically in Figure 4-1. Prior to injection, perchlorate concentrations ranged from 3,100 to 20,000 µg/L in the pilot test area.



Upgradient Monitor Wells

Upgradient perchlorate concentrations fluctuated during the pilot test, but no evidence of biodegradation was observed. This is illustrated on Figure 4-1, which shows the perchlorate concentrations in upgradient well SMW-2. The upgradient concentrations ranged from 2,200 µg/L to 72,000 µg/L over the 19-month monitoring period. The highest concentrations were generally detected in

TABLE 4-3
Summary of Perchlorate in Groundwater
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	Days Since Injection	Perchlorate		
			(µg/L)	(µM)	% Reduction
UPGRADIENT MONITORING WELLS					
SMW-1 (25 feet)	9/30/03	-9	16,000	161.0	
	10/14/03	5	72,000	724.3	
	11/13/03	35	11,000	110.7	
	12/16/03	68	11,000	110.7	
	2/19/04	133	11,000	110.7	
	9/21/04	348	14,000	140.8	
	4/21/05	560	6,900	69.4	
SMW-2 (25 feet)	9/30/03	-9	6,100	61.4	
	10/14/03	5	23,000	231.4	
	11/13/03	35	13,000	130.8	
	12/16/03	68	7,900	79.5	
	2/19/04	133	6,300	63.4	
	9/21/04	348	15,000	150.9	
	4/21/05	560	4,900	49.3	
SMW-3 (25 feet) (Dup-1)	9/30/03	-9	4,400	44.3	
	10/14/03	5	3,400	34.2	
	11/13/03	35	2,700	27.2	
	11/13/03	35	2,200	22.1	
	12/16/03	68	3,300	33.2	
	2/19/04	133	4,800	48.3	
	9/21/04	348	4,700	47.3	
	4/21/05	560	4,400	44.3	
Upgradient Average	9/30/03	-9	8,833	88.9	
	10/14/03	5	32,800	330.0	
	11/13/03	35	8,900	89.5	
	12/16/03	68	7,400	74.4	
	2/19/04	133	7,367	74.1	
	9/21/04	348	11,233	113.0	
	4/21/05	560	5,400	54.3	
INJECTION WELLS					
IW-1 (Dup-1)	4/23/03	-169	21,000	211.3	
	9/29/03	-10	20,000	201.2	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	300	3.0	98.5%
	12/16/03	68	570	5.7	97.2%
	2/18/04	132	2,200	22.1	89.0%
	9/21/04	348	4,200	42.3	79.0%
	4/21/05	560	3,600	36.2	82.0%
IW-3	9/29/03	-10	12,000	120.7	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/18/04	132	<4.0	<0.04	100%
	9/21/04	348	<4.0	<0.04	100%
	4/21/05	560	<4.0	<0.04	100%

TABLE 4-3
Summary of Perchlorate in Groundwater
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	Days Since Injection	Perchlorate		
			(µg/L)	(µM)	% Reduction
IW-5	9/29/03	-10	5,600	56.3	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/18/04	132	20	0.2	99.6%
	9/21/04	348	420	4.2	92.5%
	4/21/05	560	800	8.0	85.7%
IW-7 (Dup-1)	9/29/03	-10	4,300	43.3	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/18/04	132	140	1.4	96.7%
	2/18/04	132	140	1.4	96.7%
	9/21/04	348	800	8.0	81.4%
4/21/05	560	180	1.8	95.8%	
IW-10	9/29/03	-10	6,500	65.4	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/19/04	133	<4.0	<0.04	100%
	9/21/04	348	NA	NA	NA
	4/21/05	560	340	3.4	94.8%
Injection Well Average	9/29/03	-10	9,680	97.4	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	60	0.6	99.4%
	2/18/04	132	472	4.7	95.1%
	9/21/04	348	1,355	13.6	86.0%
	4/21/05	560	984	9.9	89.8%
DOWNGRADIENT MONITORING WELLS					
MW-6 (7.5 feet)	9/30/03	-9	3,100	31.2	
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	18	0.2	99.42%
	2/18/04	132	9.8	0.1	99.68%
	9/22/04	349	200	2.0	93.55%
	4/21/05	560	13	0.1	99.58%
SMW-4 (12.5 feet) (Dup-1)	9/30/03	-9	7,400	74.4	
	9/30/03	-9	7,400	74.4	
	10/14/03	5	<4.0	<0.04	100%
	10/14/03	5	<4.0	<0.04	100%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/18/04	132	<4.0	<0.04	100%
	9/22/04	349	<4.0	<0.04	100%
	4/21/05	560	<4.0	<0.04	100%
	4/21/05	560	<4.0	<0.04	100%

TABLE 4-3
Summary of Perchlorate in Groundwater
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	Days Since Injection	Perchlorate		
			(µg/L)	(µM)	% Reduction
SMW-5 (20 feet)	9/30/03	-9	13,000	130.8	
	10/14/03	5	4,700	47.3	63.8%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	170	1.7	98.7%
	2/18/04	132	83	0.8	99.4%
	9/22/04	349	450	4.5	96.5%
	4/21/05	560	40	0.4	99.7%
SMW-6 (20 feet)	4/22/03	-170	7,000	70.4	
	9/30/03	-9	5,800	58.4	
	10/14/03	5	2,500	25.2	56.9%
	11/13/03	35	21	0.2	99.8%
	12/16/03	68	16	0.2	99.9%
	2/18/04	132	7.5	0.1	99.9%
	9/22/04	349	<4.0	<0.04	100%
4/21/05	560	<4.0	<0.04	100%	
SMW-7 (20 feet)	9/30/03	-9	7,200	72.4	
	10/14/03	5	6,500	65.4	9.7%
	11/13/03	35	<4.0	<0.04	100%
	12/16/03	68	<4.0	<0.04	100%
	2/18/04	132	<4.0	<0.04	100%
	9/22/04	349	<4.0	<0.04	100%
	4/21/05	560	<4.0	<0.04	100%
Average 20 ft Downgradient	9/30/03	-9	8,667	87	
	10/14/03	5	4,567	46	47.3%
	11/13/03	35	7	0	99.9%
	12/16/03	68	62	1	99.3%
	2/18/04	132	30	0	99.7%
	9/22/04	349	150	2	98.3%
	4/21/05	560	13	0	99.8%
AIR STRIPPER					
Influent	9/29/03	-10	3,100	31	
	10/14/03	5	2,900	29	
	11/13/03	35	2,900	29	
	12/16/03	68	3,300	33	
	2/18/04	132	1,500	15	
	9/22/04	349	8,700	88	
	4/21/05	560	1,000	10	
Effluent	9/29/03	-10	3,100	31	
	10/14/03	5	3,100	31	
	11/13/03	35	2,400	24	
	12/16/03	68	3,300	33	
	2/18/04	132	1,600	16	
	9/22/04	349	8,400	85	
	4/21/05	560	1,000	10	

SMW-1 and the lowest concentrations in SMW-3 indicating that the southern end of the PRB (toward IW-1) was receiving a higher perchlorate loading.

Injection Wells

Perchlorate degradation was immediately observed within the emulsified oil PRB. Concentrations in all of the injection wells were non-detect (<4 µg/L) within 5 days of injection. Perchlorate remained at non-detectable levels in injection well IW-3 throughout the 18-month pilot test. The other injection wells showed detectable levels of perchlorate beginning as early as 2 months post-injection in IW-1 and as late as 18 months post-injection in IW-10. Based on up gradient data, IW-1 was receiving the highest perchlorate concentrations and this well still showed approximately 80 percent reductions in perchlorate compared to pre-injection levels at the end of the pilot test. Comparison of the average perchlorate concentrations in the five monitored injection wells pre- and post-injection indicates that perchlorate concentrations were reduced between 86% and 100%.

Downgradient Monitor Wells

Perchlorate degradation was also observed in the downgradient monitor wells. Concentrations in downgradient monitor wells 7.5 feet (MW-6) and 12.5 feet (SMW-4) from the barrier were non-detect (<4 µg/L) within 5 days of injection. By 1-month post-injection, perchlorate was not detected in any of downgradient monitor wells, except SMW-6. SMW-6 showed decreasing perchlorate concentrations after emulsion injection, and non-detectable levels were reported for this well beginning with the 11-month post-injection sampling event. Once non-detectable levels were achieved, perchlorate remained at non-detectable levels for the remainder of the pilot test in monitor wells SMW-4, SMW-6, and SMW-7. Low levels of perchlorate returned to the other downgradient monitor wells, but perchlorate reductions remained greater than 90% compared to pre-injection levels. Beginning approximately 2 months after injection, perchlorate concentrations in SMW-5 increased to approximately 170 µg/L and then fluctuated between 40 and 450 µg/L with no increasing trend observed. The low levels of perchlorate observed in SMW-5 are likely due to some flow around the PRB causing non-treated groundwater to mix with the treated groundwater (see Section 4.3.3). Even with some mixing with untreated water, perchlorate concentrations in SMW-5 were reduced by between 96% and 99%.

Six months after EOS[®] injection, a Geoprobe was used to collect groundwater samples throughout the pilot test area. These data were used to map the perchlorate concentrations and evaluate the area of influence of the injection. The data are summarized in Table 4-4 and presented on Figure 4-2. As shown in the figure, perchlorate was not detected (<4 µg/L) in a wide area extending approximately 35 feet downgradient of the barrier. Samples could not be collected past 35 feet, due to the nearby location of the interceptor trench for the existing pump-and-treat system.

TABLE 4-4
Summary of Groundwater Results - April 2004 Geoprobe Sampling Event
Maryland Perchlorate Site

Sample Location	Sample Date	Perchlorate (µg/L)	TOC (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	pH (SU)	ORP (mV)	Conductivity (µS)	Temperature (°C)
GWS-1	4/19/2004	150,000	1.75	49.9/48.9	<0.5/<0.5	<0.5/<0.5	0.5/<0.5	<0.5/<0.5	31.7/31.2	5.5	-13	NM	NM
GWS-2	4/23/2004	16,000	1.36	18.2	<0.5	<0.5	8.2	<0.5	24.1	6.00	29.0	296	17.0
GWS-3	4/19/2004	45,000	<1.0	22.8/22.5	<0.5/<0.5	<0.5/<0.5	2.4/2.4	<0.5/<0.5	17.2/17.4	6.5	-7	NM	NM
GWS-4	4/23/2004	4,200	1.49	14	<0.5	<0.5	9.7	<0.5	22.7	6.38	-497	192	15.9
GWS-5	4/21/2004	8,000	2.32	13.7	<0.5	<0.5	6.6	<0.5	21.8	6.06	-855	258	13.6
GWS-6	4/23/2004	6,200	<1.0	18.3	<0.5	<0.5	4.7	<0.5	23.4	5.79	7.7	236	17.3
GWS-7	4/23/2004	7,000	<1.0	15.2	<0.5	<0.5	4.2	<0.5	19.4	5.72	-1.3	233	16.0
GWS-8	4/23/2004	55,000	<1.0	20.6	<0.5	<0.5	3.9	<0.5	21.9	6.04	-57.3	345	17.1
GWS-9	4/23/2004	3,400	9.88	19.5/23.4	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	9.7/12.7	6.33	-239	315	15.9
GWS-10	4/21/2004	1,200	20.3	24.3	<0.5	<0.5	<0.5	<0.5	11.1	6.74	-515	383	14.4
GWS-11	4/23/2004	24	10.9	18.9	<0.5	<0.5	<0.5	<0.5	19.5	6.45	-366	278	15.9
GWS-12	4/23/2004	2,500	3.06	14.6	<0.5	<0.5	2.5	<0.5	10.9	6.51	-365	294	15.7
GWS-13 (6-10)	4/22/2004	2,400	1.26	15.6	<0.5	<0.5	10.0	<0.5	26.1	5.85	-109	157	13.7
GWS-13 (11-15)	4/23/2004	4,400	1.66	13.9/15.5	<0.5/<0.5	<0.5/<0.5	8.0/9.1	<0.5/<0.5	19.3/21.5	6.02	-149	199	14.3
GWS-14	4/23/2004	4,800	1.35	13.0	<0.5	<0.5	7.0	<0.5	19.7	6.02	-265	240	12.5
GWS-15 (6-10)	4/22/2004	340	36.6	14.0	<0.5	<0.5	<0.5	<0.5	5.7	6.79	-225	413	15.7
GWS-15 (11-15)	4/22/2004	3,300	29.2	25.7/25.8	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	2.1/2.1	6.58	-203	409	15.5
GWS-16	4/22/2004	<4.0	24.1	16.1	<0.5	0.6	<0.5	<0.5	2.9	6.79	-172	361	14.8
GWS-17 (6-10)	4/22/2004	<4.0	42.9	14.9	<0.5	<0.5	<0.5	<0.5	<0.5	6.95	-178	384	15.0
GWS-17 (11-15)	4/22/2004	<4.0	20.1	20.7	<0.5	<0.5	<0.5	<0.5	4.6	6.96	-253	389	14.3
GWS-18	4/22/2004	2,800	<1.0	19.8	<0.5	<0.5	3.3	<0.5	32.3	5.71	-284	271	14.8
GWS-19	4/22/2004	4,400	<1.0	16.8	<0.5	<0.5	5.2	<0.5	24.4	5.98	-470	255	15.2
GWS-20	4/22/2004	63	40.2	22.2	<0.5	<0.5	<0.5	<0.5	6.9	6.91	-879	466	14.2
GWS-21	4/22/2004	<4.0	31.7	24.2	<0.5	<0.5	<0.5	<0.5	0.6	7.16	-1150	467	13.9
GWS-22	4/22/2004	<4.0	12.1	21.2	<0.5	<0.5	<0.5	<0.5	6.4	6.86	-1080	376	14.6

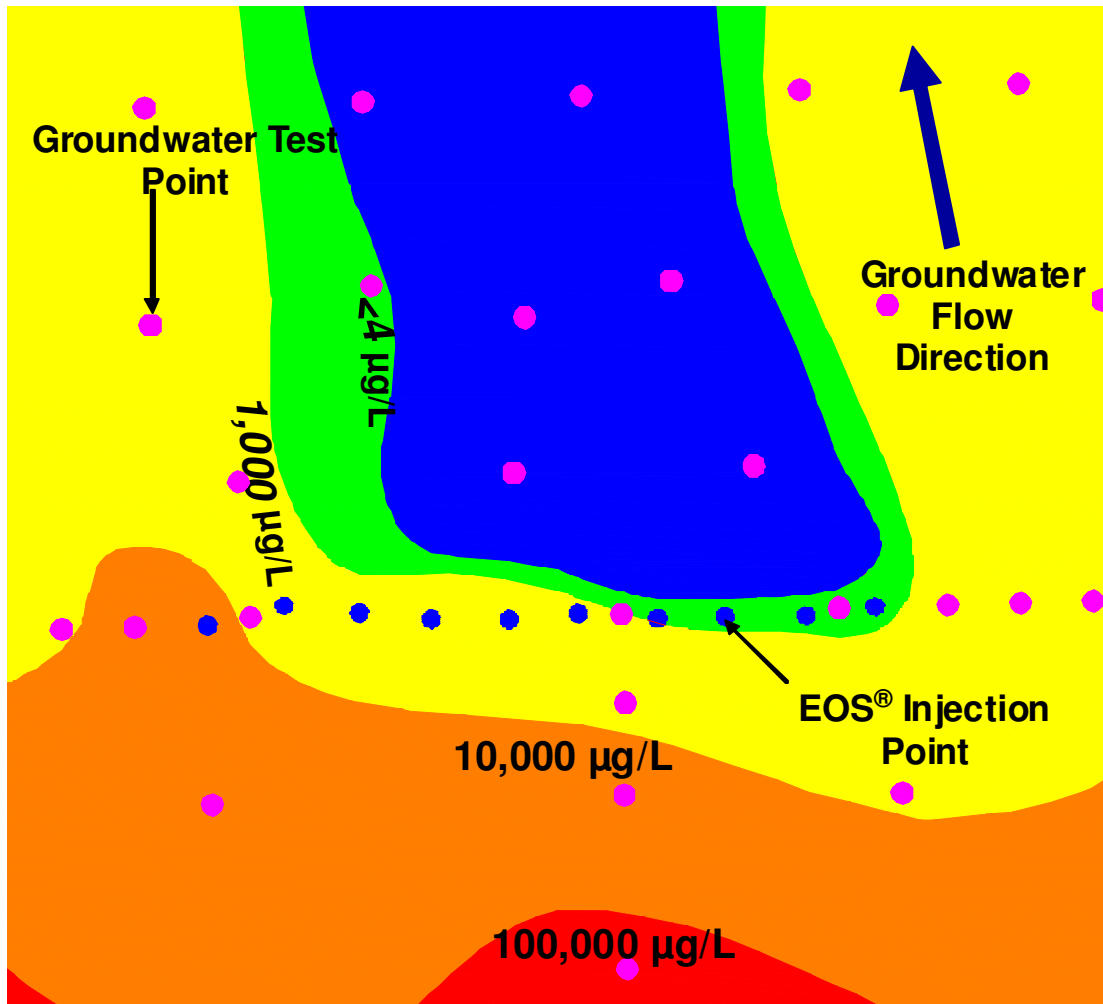
TABLE 4-4
Summary of Groundwater Results - April 2004 Geoprobe Sampling Event
Maryland Perchlorate Site

Sample Location	Sample Date	Perchlorate (µg/L)	TOC (mg/L)	Chloride (mg/L)	Nitrite (mg/L)	Bromide (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	pH (SU)	ORP (mV)	Conductivity (µS)	Temperature (°C)
GWS-23	4/22/2004	5,200	2.38	12.7	<0.5	<0.5	8.5	<0.5	17.1	5.26	-706	191.6	13.7
GWS-24	4/22/2004	9,000	1.95	13.4	<0.5	<0.5	10.6	<0.5	14.7	5.39	-1338	197.4	14.2
GWS-25	4/21/2004	3,300	<1.0	14.0	<0.5	<0.5	3.7	<0.5	18.1	5.60	-1099	182.3	12.0
GWS-26	4/21/2004	3,500	<1.0	21.1	<0.5	<0.5	6.0	<0.5	25.5	5.89	-1139	219	11.9
GWS-27	4/21/2004	<4.0	20.8	19.0/18.9	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	<0.5/<0.5	7.4/7.4	6.89	-1341	412	12.1
GWS-28	4/21/2004	<4.0	4.60	15.1	<0.5	<0.5	<0.5	<0.5	7.5	6.70	-1404	302	12.9
GWS-29 (6-10)	4/22/2004	500	2.21	9.7	<0.5	<0.5	1.5	<0.5	15.6	6.10	<-1600	160	12.0
GWS-29 (11-15)	4/22/2004	4,400	3.04	17.9	<0.5	<0.5	9.5	1.1	17.9	5.60	-1571	197.6	13.9
GWS-30	4/21/2004	1,500	1.85	17.8	<0.5	<0.5	5.9	1.3	22.9	6.09	-1442	168.2	12.9
GWS-31	4/22/2004	3,200	2.63	16.2/15.4	<0.5/<0.5	<0.5/<0.5	10.9/10.6	<0.5/<0.5	21.8/20.9	5.22	-1272	174.1	14.6

Notes:

NM denotes not measured.

FIGURE 4-2
Perchlorate Concentrations 6-Months Post-Injection



Mass Removal

To evaluate the mass of perchlorate removed by the PRB, Solutions-IES compared the average concentrations in the three wells 25 feet upgradient to the average concentrations in the three wells 20 feet downgradient over the course of the 18-month pilot test. Assuming that the barrier is 50 feet wide perpendicular to groundwater flow and 10 feet high vertically, the effective porosity is 0.18, and the groundwater velocity is 400 ft/year, the flux through the barrier was calculated to be 99 ft³/day or approximately 2,800 L/day. The mass flux calculations are summarized in Table 4-5 and indicate approximately 39 lbs of perchlorate were removed during the 18-month monitoring period.

TABLE 4-5
Perchlorate Mass Removal
Maryland Perchlorate Site

Sample Date	Days Since Injection	Average Upgradient (µg/L)	Average Downgradient (µg/L)	Change (µg/L)	Change %	Mass removed (lbs/day)	Mass removed ¹ (lbs)
10 14 03	5	32,800	4,567	28,233	86.1%	0.173	0.87
11 13 03	35	8,900	7	8,893	99.9%	0.055	1.91
12 16 03	68	7,400	62	7,338	99.2%	0.045	3.07
2 19 04	133	7,367	30	7,337	99.6%	0.045	6.00
9 21 04	348	11,233	150	11,083	98.7%	0.068	23.70
4 21 05	560	5400	13	5,387	99.8%	0.033	18.54
Total Mass of Perchlorate Removed by Emulsified Oil PRB =							39.16

Note:

1. Calculated as mass removed (lbs/day) times the number of days between each sampling event.

4.3.1.2 Chlorinated Ethanes

The analytical results for 1,1,1-TCA and its daughter products are summarized in Table 4-6 and are presented in molar form in Table 4-7. To aid in interpretation of the results, chlorine numbers (Cl#) were calculated. Monitoring the change in Cl# over time is an effective approach for evaluating the progress of reductive dechlorination processes. Groundwater containing only 1,1,1-TCA would have a Cl# = 3.0. However, if half of the 1,1,1-TCA is reduced to 1,1-DCA, the Cl# would decline to 2.5. Cl# for the biodegradation of 1,1,1-TCA is calculated as:

$$\text{Cl\#} = \frac{3 [1,1,1\text{-TCA}] + 2 [1,1\text{-DCA}] + 1 [\text{CA}]}{[1,1,1\text{-TCA}] + [1,1\text{-DCA}] + [\text{CA}]}$$

where [] indicates concentration in moles per liter. The chlorine numbers are tabulated in Table 4-8.

TABLE 4-6
Summary of CAHs, Ethane, and Ethene in Groundwater (µg/L)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µg/L)	1,1-DCA (µg/L)	1,2-DCA (µg/L)	Chloro- ethane (µg/L)	1,1-DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	<i>cis</i> - 1,2-DCE (µg/L)	<i>trans</i> - 1,2-DCE (µg/L)	Vinyl Chloride (µg/L)	Total CAHs (µg/L)	Ethane (µg/L)	Ethene (µg/L)
UPGRADIENT MONITORING WELLS														
SMW-1 (25 feet)	9/30/03	17,000	40	<20	<20	1,200	110	160	<20	<20	<20	18,510	2.41	1.02
	10/14/03	13,000	270	<20	<20	1,000	52	170	<20	<20	<20	14,492	28.73	11.36
	11/13/03	9,300	110	<20	<20	910	22	330	26	<20	<20	10,698	1.53	0.30
	12/16/03	7,400	<20	<20	<20	730	<20	290	<20	<20	<20	8,420	0.40	0.15
	2/19/04	11,000	58	50	<20	820	50	320	<20	<20	<20	12,298	0.19	0.14
	9/21/04	7,900	83	<5	<5	840	20	260	23	<5	<5	9,126	0.14	0.12
	4/21/05	3,100	95	<5	<5	500	<5	220	18	<5	<5	3,933	0.20	0.21
	SMW-2 (25 feet)	9/30/03	17,000	39	<20	<20	1,000	82	52	<20	<20	<20	18,173	4.28
10/14/03		19,000	190	<20	<20	910	69	130	<20	<20	<20	20,299	4.60	1.68
11/13/03		6,600	500	<20	<20	920	<20	73	<20	<20	<20	8,093	3.91	1.13
12/16/03		8,500	<20	<20	<20	700	82	250	<20	<20	<20	9,532	0.79	0.20
2/19/04		9,000	59	42	<20	690	58	200	<20	<20	<20	10,049	0.63	0.19
7/20/04		7,900	41	<5	<5	670	39	200	12	<5	<5	8,862	0.54	0.27
9/21/04		9,500	26	<5	<5	560	40	180	16	<5	<5	10,322	0.26	0.18
4/21/05		4,200	61	<5	<5	400	<5	160	13	<5	<5	4,834	0.05	0.05
SMW-3 (25 feet) (Dup-1)	9/30/03	14,000	<20	<20	<20	520	52	80	<20	<20	<20	14,652	1.50	0.54
	10/14/03	8,000	190	<20	<20	270	22	60	<20	<20	<20	8,542	0.51	0.21
	11/13/03	4,900	<20	<20	<20	260	30	64	<20	<20	<20	5,254	2.51	0.83
	11/13/03	5,900	<20	<20	<20	300	30	82	<20	<20	<20	6,312	NA	NA
	12/16/03	11,000	<20	<20	<20	470	85	160	<20	<20	<20	11,715	0.22	0.10
	2/19/04	2,500	<20	75	<20	730	84	150	<20	<20	<20	3,539	0.04	0.04
	9/21/04	2,000	<5	<5	<5	88	7.7	23	<5	<5	<5	2,119	0.04	0.03
	4/21/05	6,800	26	<5	<5	420	13	210	17	<5	<5	7,486	0.10	0.11
INJECTION WELLS														
IW-1 (Dup-1)	4/23/03	17,000	65	<50	<50	610	90	170	<50	<50	<50	17,935	NA	NA
	9/29/03	5,800	62	<5	<5	430	26	210	10	<5	<5	6,538	0.35	0.11
	10/14/03	580	71	<5	<5	140	<5	16	9.1	<5	<5	817	1.17	0.41
	11/13/03	4,100	130	<5	<5	310	16	250	26	<5	<5	4,832	0.16	0.19
	12/16/03	270	1,400	<5	<5	160	<5	25	110	<5	<5	1,966	0.22	0.20
	12/16/03	340	1,600	<20	<20	150	<20	<20	130	<20	<20	2,221	NA	NA
	2/18/04	1,100	1,200	18	340	160	<5	37	75	<5	<5	2,931	0.15	0.13
	9/21/04	3,900	310	<5	380	460	11	110	85	<5	10	5,266	0.02	0.75
	4/21/05	470	140	<5	140	110	<5	84	38	<5	<5	983	1.18	8.39

TABLE 4-6
Summary of CAHs, Ethane, and Ethene in Groundwater (µg/L)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µg/L)	1,1-DCA (µg/L)	1,2-DCA (µg/L)	Chloro- ethane (µg/L)	1,1-DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	<i>cis</i> - 1,2-DCE (µg/L)	<i>trans</i> - 1,2-DCE (µg/L)	Vinyl Chloride (µg/L)	Total CAHs (µg/L)	Ethane (µg/L)	Ethene (µg/L)
IW-3	9/29/03	9,300	50	<5	<5	560	42	150	5.5	<5	<5	10,108	0.94	0.34
	10/14/03	1,200	140	<5	<5	180	<5	16	<5	<5	<5	1,537	1.94	0.73
	11/13/03	11,000	240	<5	<5	770	29	230	24	<5	<5	12,293	0.25	0.17
	12/16/03	160	1,400	<5	<5	170	<5	<5	110	<5	<5	1,841	0.45	0.37
	2/18/04	1,800	2,900	23	2200	370	10	11	130	<5	<5	7,445	0.13	0.12
	9/21/04	830	1,500	<5	1000	540	6.3	17	200	<5	11	4,105	0.05	0.08
	4/21/05	940	450	<5	600	180	<5	36	68	<5	73	2,348	0.05	15.08
IW-5	9/29/03	10,000	16	<5	<5	510	49	80	<5	<5	<5	10,655	0.34	0.12
	10/14/03	1,100	70	<5	<5	220	<5	9.3	<5	<5	<5	1,400	2.09	0.69
	11/13/03	7,000	15	<5	<5	460	23	92	8.6	<5	<5	7,599	0.25	0.12
	12/16/03	3,600	290	<5	<5	190	36	78	8.7	<5	<5	4,203	1.50	0.41
	2/18/04	3,300	1600	25	<5	180	24	48	43	<5	<5	5,221	0.13	0.10
	7/19/04	1,800	750	<5	240	250	7.2	25	66	<5	<5	3,139	0.07	0.06
	9/21/04	2,300	660	<5	980	320	8.2	40	110	<5	<5	4,419	0.05	0.03
4/21/05	1,200	230	<5	400	190	<5	57	45	<5	<5	2,123	0.04	3.09	
IW-7 (Dup-1)	9/29/03	6,000	16	<5	<5	280	26	28	<5	<5	<5	6,350	0.43	0.08
	10/14/03	1,200	31	<5	<5	96	<5	8.5	<5	<5	<5	1,336	0.80	0.15
	11/13/03	3,900	22	<5	<5	230	27	44	<5	<5	<5	4,223	0.19	0.12
	12/16/03	1,500	<5	<5	<5	53	<5	14	<5	<5	<5	1,568	0.24	0.16
	2/18/04	4,000	1400	24	<5	140	21	31	31	<5	<5	5,647	0.08	0.07
	2/18/04	4,500	1400	56	<20	170	35	32	36	<20	<20	6,229	NA	NA
	9/21/04	3,200	740	<50	500	270	<50	<50	67	<50	<50	4,777	0.03	0.06
4/21/05	890	<50	<50	300	32 J	<50	<50	<50	<50	<50	1,191	0.10	2.85	
IW-10	9/29/03	10,000	14	<5	<5	480	45	41	<5	<5	<5	10,580	0.18	0.08
	10/14/03	4,000	42	<5	<5	300	<5	23	<5	<5	<5	4,366	1.79	0.24
	11/13/03	4,600	260	<5	<5	250	51	67	<5	<5	<5	5,229	0.11	0.11
	12/16/03	1,500	2,400	<5	<5	180	20	34	52	<5	<5	4,187	0.20	0.08
	2/19/04	5,300	4,500	19	<5	400	29	40	110	<5	<5	10,398	0.04	0.05
	9/21/04	3,200	1,400	<5	730	340	16	23	94	<5	<5	5,804	0.03	0.03
	4/21/05	3,500	430	<5	550	480	<5	110	71	<5	<5	5,142	0.03	0.04

TABLE 4-6
Summary of CAHs, Ethane, and Ethene in Groundwater (µg/L)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µg/L)	1,1-DCA (µg/L)	1,2-DCA (µg/L)	Chloro- ethane (µg/L)	1,1-DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	<i>cis</i> - 1,2-DCE (µg/L)	<i>trans</i> - 1,2-DCE (µg/L)	Vinyl Chloride (µg/L)	Total CAHs (µg/L)	Ethane (µg/L)	Ethene (µg/L)
DOWNGRADIENT MONITORING WELLS														
MW-6 (7.5 feet)	9/30/03	5,700	6.6	<5	<5	270	25	36	<5	<5	<5	6,038	0.16	0.04
	10/14/03	5,300	9.3	<5	<5	220	18	39	<5	<5	<5	5,586	0.15	0.03
	11/13/03	1,800	7.1	<5	<5	150	6.3	25	<5	<5	<5	1,989	0.12	0.08
	12/16/03	270	120	<5	<5	7.7	<5	<5	<5	<5	<5	399	0.10	0.03
	2/18/04	240	1600	<5	1000	150	<5	<5	67	<5	<5	3,058	0.12	0.06
	9/22/04	960	610	<50	1200	320	<50	<50	120	<50	<50	3,211	0.14	0.11
	4/21/05	1,000	220	<50	530	59	<50	<50	<50	<50	<50	1,810	0.09	10.20
	SMW-4 (12.5 feet)	9/30/03	14,000	27	<20	<20	720	66	73	<20	<20	<20	14,886	0.83
9/30/03		14,000	22	<20	<20	750	71	82	<20	<20	<20	14,925	NA	NA
10/14/03		5,300	24	<20	<20	270	21	60	<20	<20	<20	5,676	1.34	0.55
10/14/03		5,200	24	<20	<20	280	20	64	<20	<20	<20	5,589	NA	NA
11/13/03		12,000	45	<20	<20	730	46	140	<20	<20	<20	12,961	0.53	0.30
12/16/03		760	4,000	<20	<20	260	34	<20	140	<20	<20	174	0.12	0.09
2/18/04		140	2,800	<20	1600	320	<20	<20	140	<20	<20	140	0.13	0.07
7/19/04		2,000	580	<5	300	250	13	36	64	<5	<5	113	0.01	0.02
9/22/04		3,700	820	<5	380	260	16	38	70	<5	<5	124	0.06	0.07
4/21/05		300	400	<5	680	40	<5	13	21	<5	<5	1,455	0.11	23.99
(Dup-1)	4/21/05	310	420	<5	700	37	<5	12	20	<5	<5	1,500	NA	NA
SMW-5 (20 feet)	9/30/03	14,000	46	<20	<20	790	65	150	<20	<20	<20	15,051	1.50	0.51
	10/14/03	10,000	46	<20	<20	510	35	140	<20	<20	<20	10,731	0.35	0.12
	11/13/03	11,000	92	<20	<20	1,000	34	240	<20	<20	<20	12,366	0.83	0.41
	12/16/03	760	6,200	<20	<20	590	<20	<20	250	<20	<20	7,801	0.18	0.11
	2/18/04	340	390	<20	8,700	620	<20	<20	200	<20	<20	10,251	0.22	0.09
	9/22/04	720	1,400	<50	1,500	420	<50	<50	130	<50	370	4,541	0.19	0.16
	4/21/05	220	270	<50	1,100	<50	<50	<50	<50	<50	<50	1,591	3.66	43.68

TABLE 4-6
Summary of CAHs, Ethane, and Ethene in Groundwater (µg/L)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µg/L)	1,1-DCA (µg/L)	1,2-DCA (µg/L)	Chloro- ethane (µg/L)	1,1-DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	<i>cis</i> - 1,2-DCE (µg/L)	<i>trans</i> - 1,2-DCE (µg/L)	Vinyl Chloride (µg/L)	Total CAHs (µg/L)	Ethane (µg/L)	Ethene (µg/L)
SMW-6 (20 feet) (Dup-1)	4/22/03	25,000	<50	<50	<50	570	<50	82	<50	<50	<50	25,652	NA	NA
	9/30/03	8,500	17	<5	<5	480	42	76	<5	<5	<5	9,115	0.21	0.05
	10/14/03	15,000	41	<5	<5	410	30	84	<5	<5	<5	15,564	0.40	0.11
	11/13/03	12,000	52	<20	<20	680	33	120	<20	<20	<20	12,885	0.60	0.48
	12/16/03	46	26	<0.5	<0.5	3.7	<0.5	<0.5	1.1	<0.5	<0.5	78	0.08	0.03
	2/18/04	150	1800	4.8	3200	210	12	7.6	110	<0.5	<0.5	5,495	0.12	0.09
	7/20/04	22	95	<0.5	35	37	1.5	1.8	11	<0.5	<0.5	204	0.02	0.02
	9/22/04	650	1400	<5	700	270	13	15	99	<5	<5	3,148	0.19	0.23
	9/22/04	540	930	<5	660	200	10	12	87	<5	<5	2,440	NA	NA
	4/21/05	440	410	<5	900	5.1	<5	<5	<5	<5	<5	1,756	0.58	39.65
SMW-7 (20 feet)	9/30/03	14,000	27	<20	<20	580	53	82	<20	<20	<20	14,742	1.16	0.49
	10/14/03	11,000	400	<20	<20	520	26	60	<20	<20	<20	12,006	1.12	0.42
	11/13/03	8,900	33	<20	<20	840	30	120	<20	<20	<20	9,923	0.71	0.32
	12/16/03	870	6,300	<20	<20	380	<20	<20	160	<20	<20	7,711	0.98	0.23
	2/18/04	4,000	4,300	63	1,900	380	54	41	120	<20	<20	10,859	0.15	0.09
	9/22/04	1,900	1,100	<50	1,000	400	<50	<50	120	<50	<50	4,521	0.13	0.15
	4/21/05	900	830	<50	1,100	94	<50	<50	<50	<50	<50	2,925	0.12	38.94
AIR STRIPPER														
Influent	9/29/03	3,100	19	<5	<5	150	14	71	<5	<5	<5	3,354	0.01	<0.01
	10/14/03	4,100	24	<5	<5	170	16	97	<5	<5	<5	4,407	0.04	<0.01
	11/13/03	3,300	46	<5	<5	320	31	110	9.4	<5	<5	3,816	0.29	0.26
	12/16/03	2,100	370	<5	<5	130	24	64	19	<5	<5	2,707	0.04	0.02
	2/18/04	2,000	530	20	270	130	11	82	27	<5	<5	3,070	0.01	<0.01
	9/22/04	4,800	250	<5	98	170	16	53	15	<5	22	5,424	<0.01	0.02
	4/21/05	870	140	<5	100	69	<5	45	8.4	<5	<5	1,232	0.02	0.88
Effluent	9/29/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.01	<0.01
	10/14/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.01	<0.01
	11/13/03	48	<0.5	<0.5	<0.5	4.3	<0.5	2.4	<0.5	<0.5	<0.5	54.7	NA	NA
	12/16/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.01	<0.01
	2/18/04	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.01	<0.01
	9/22/04	110	10	<0.5	2.9	3.0	0.61	2.5	0.69	<0.5	<0.5	129.7	<0.01	<0.01
	4/21/05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.01	0.15

TABLE 4-6
Summary of CAHs, Ethane, and Ethene in Groundwater (µg/L)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µg/L)	1,1-DCA (µg/L)	1,2-DCA (µg/L)	Chloro- ethane (µg/L)	1,1-DCE (µg/L)	PCE (µg/L)	TCE (µg/L)	<i>cis</i> - 1,2-DCE (µg/L)	<i>trans</i> - 1,2-DCE (µg/L)	Vinyl Chloride (µg/L)	Total CAHs (µg/L)	Ethane (µg/L)	Ethene (µg/L)
QA/QC														
Trip Blanks	4/22/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	9/29/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	10/14/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	11/13/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	12/16/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	2/18/04	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	9/22/04	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	4/21/05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
Rinse Blanks	9/30/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	10/14/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	11/13/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	12/16/03	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	2/18/04	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	9/22/04	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA
	4/21/05	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	NA	NA

TABLE 4-7
Summary of CAHs, Ethane, and Ethene (µM)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Date	1,1,1- TCA (µM)	1,1-DCA (µM)	1,2-DCA (µM)	Chloro- ethane (µM)	1,1-DCE (µM)	PCE (µM)	TCE (µM)	<i>cis</i> - 1,2-DCE (µM)	<i>trans</i> - 1,2-DCE (µM)	Vinyl Chloride (µM)	Total CAHs (µM)	Ethane (µM)	Ethene (µM)
UPGRADIENT MONITORING WELLS														
SMW-1 (25 feet)	9/30/03	127.44	0.40	<0.202	<0.31	12.38	0.66	1.22	<0.206	<0.206	<0.32	142.11	0.080	0.036
	10/14/03	97.45	2.73	<0.202	<0.31	10.32	0.31	1.29	<0.206	<0.206	<0.32	112.11	0.958	0.406
	11/13/03	69.72	1.11	<0.202	<0.31	9.39	0.13	2.51	0.27	<0.206	<0.32	83.13	0.051	0.011
	12/16/03	55.47	<0.202	<0.202	<0.31	7.53	<0.121	2.21	<0.206	<0.206	<0.32	65.21	0.013	0.005
	2/19/04	82.46	0.59	0.51	<0.31	8.46	0.30	2.44	<0.206	<0.206	<0.32	94.75	0.006	0.005
	9/21/04	59.22	0.84	<0.051	<0.078	8.67	0.12	1.98	0.24	<0.052	<0.083	71.06	0.005	0.004
	4/21/05	23.24	0.96	<0.051	<0.078	5.16	<0.030	1.67	0.19	<0.052	<0.083	31.22	0.007	0.008
SMW-2 (25 feet)	9/30/03	127.44	0.39	<0.202	<0.31	10.32	0.49	0.40	<0.206	<0.206	<0.32	139.04	0.143	0.069
	10/14/03	142.43	1.92	<0.202	<0.31	9.39	0.42	0.99	<0.206	<0.206	<0.32	155.14	0.153	0.060
	11/13/03	49.48	5.05	<0.202	<0.31	9.49	<0.121	0.56	<0.206	<0.206	<0.32	64.58	0.130	0.040
	12/16/03	63.72	<0.202	<0.202	<0.31	7.22	0.49	1.90	<0.206	<0.206	<0.32	73.34	0.026	0.007
	2/19/04	67.47	0.60	0.42	<0.31	7.12	0.35	1.52	<0.206	<0.206	<0.32	77.48	0.021	0.007
	7/20/04	59.22	0.41	<0.051	<0.078	6.91	0.24	1.52	0.12	<0.052	<0.083	68.43	0.018	0.010
	9/21/04	71.21	0.26	<0.051	<0.078	5.78	0.24	1.37	0.17	<0.052	<0.083	79.03	0.009	0.006
4/21/05	31.48	0.62	<0.051	<0.078	4.13	<0.030	1.22	0.13	<0.052	<0.083	37.58	0.002	0.002	
SMW-3 (25 feet) (Dup-1)	9/30/03	104.95	<0.202	<0.202	<0.31	5.37	0.31	0.61	<0.206	<0.206	<0.32	111.24	0.050	0.019
	10/14/03	59.97	1.92	<0.202	<0.31	2.79	0.13	0.46	<0.206	<0.206	<0.32	65.26	0.017	0.008
	11/13/03	36.73	<0.202	<0.202	<0.31	2.68	0.18	0.49	<0.206	<0.206	<0.32	40.08	0.084	0.030
	11/13/03	44.23	<0.202	<0.202	<0.31	3.10	0.18	0.62	<0.206	<0.206	<0.32	48.13	NA	NA
	12/16/03	82.46	<0.202	<0.202	<0.31	4.85	0.51	1.22	<0.206	<0.206	<0.32	89.04	0.007	0.004
	2/19/04	18.74	<0.202	0.76	<0.31	7.53	0.51	1.14	<0.206	<0.206	<0.32	28.68	0.001	0.001
	9/21/04	14.99	<0.051	<0.051	<0.078	0.91	0.05	0.18	<0.052	<0.052	<0.083	16.12	0.001	0.001
4/21/05	50.97	0.26	<0.051	<0.078	4.33	0.08	1.60	<0.052	<0.052	<0.083	57.25	0.003	0.004	
INJECTION WELLS														
IW-1 (Dup-1)	4/23/03	127.4	0.657	<0.505	<0.77	6.295	0.543	1.294	<0.516	<0.516	<0.80	136.2	NA	NA
	9/29/03	43.5	0.626	<0.051	<0.077	4.438	0.157	1.598	<0.052	<0.052	<0.08	50.3	0.012	0.004
	10/14/03	4.3	0.717	<0.051	<0.077	1.445	<0.030	0.122	0.094	<0.052	<0.08	6.7	0.039	0.015
	11/13/03	30.7	1.313	<0.051	<0.077	3.199	0.097	1.903	0.268	<0.052	<0.08	37.5	0.005	0.007
	12/16/03	2.0	14.141	<0.051	<0.077	1.651	<0.030	0.190	1.135	<0.052	<0.08	19.1	0.007	0.007
	12/16/03	2.5	16.162	<0.202	<0.31	1.548	<0.121	<0.152	1.342	<0.206	<0.32	21.6	NA	NA
	2/18/04	8.2	12.121	0.182	5.271	1.651	<0.030	0.282	0.774	<0.052	<0.08	28.5	0.005	0.005
	9/21/04	29.2	3.131	<0.051	5.891	4.747	0.066	0.837	0.877	<0.052	0.165	45.0	0.001	0.027
4/21/05	3.5	1.414	<0.051	2.171	1.135	<0.030	0.639	0.392	<0.052	<0.08	9.3	0.039	0.300	

TABLE 4-7
Summary of CAHs, Ethane, and Ethene (µM)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Date	1,1,1- TCA (µM)	1,1-DCA (µM)	1,2-DCA (µM)	Chloro- ethane (µM)	1,1-DCE (µM)	PCE (µM)	TCE (µM)	<i>cis</i> - 1,2-DCE (µM)	<i>trans</i> - 1,2-DCE (µM)	Vinyl Chloride (µM)	Total CAHs (µM)	Ethane (µM)	Ethene (µM)
IW-3	9/29/03	69.7	0.505	<0.051	<0.077	5.779	0.253	1.142	0.057	<0.052	<0.08	77.5	0.031	0.012
	10/14/03	9.0	1.414	<0.051	<0.077	1.858	<0.030	0.122	<0.052	<0.052	<0.08	12.4	0.065	0.026
	11/13/03	82.5	2.424	<0.051	<0.077	7.946	0.175	1.750	0.248	<0.052	<0.08	95.0	0.008	0.006
	12/16/03	1.2	14.141	<0.051	<0.077	1.754	<0.030	<0.038	1.135	<0.052	<0.08	18.2	0.015	0.013
	2/18/04	13.5	29.293	0.232	34.109	3.818	0.060	0.084	1.342	<0.052	<0.08	82.4	0.004	0.004
	9/21/04	6.2	15.152	<0.051	15.504	5.573	0.038	0.129	2.064	<0.052	0.182	44.9	0.002	0.003
	4/21/05	7.0	4.545	<0.051	9.302	1.858	<0.030	0.274	0.702	<0.052	1.207	24.9	0.002	0.539
IW-5	9/29/03	75.0	0.162	<0.051	<0.077	5.263	0.296	0.609	<0.052	<0.052	<0.08	81.3	0.011	0.004
	10/14/03	8.2	0.707	<0.051	<0.077	2.270	<0.030	0.071	<0.052	<0.052	<0.08	11.3	0.0697	0.0246
	11/13/03	52.5	0.152	<0.051	<0.077	4.747	0.139	0.700	0.089	<0.052	<0.08	58.3	0.0083	0.0043
	12/16/03	27.0	2.929	<0.051	<0.077	1.961	0.217	0.594	0.090	<0.052	<0.08	32.8	0.0500	0.0146
	2/18/04	24.7	16.162	0.253	<0.077	1.858	0.145	0.365	0.444	<0.052	<0.08	44.0	0.0043	0.0036
	7/19/04	13.5	7.576	<0.051	3.721	2.580	0.043	0.190	0.681	<0.052	<0.08	28.3	0.0023	0.0021
	9/21/04	17.2	6.667	<0.051	15.194	3.302	0.049	0.304	1.135	<0.052	<0.08	43.9	0.0017	0.0011
4/21/05	9.0	2.323	<0.051	6.202	1.961	<0.030	0.434	0.464	<0.052	<0.08	20.4	0.0013	0.1104	
IW-7	9/29/03	45.0	0.162	<0.051	<0.077	2.890	0.157	0.213	<0.052	<0.052	<0.08	48.4	0.014	0.003
	10/14/03	9.0	0.313	<0.051	<0.077	0.991	<0.030	0.065	<0.052	<0.052	<0.08	10.4	0.027	0.005
	11/13/03	29.2	0.222	<0.051	<0.077	2.374	0.163	0.335	<0.052	<0.052	<0.08	32.3	0.006	0.004
	12/16/03	11.2	<0.051	<0.051	<0.077	0.547	<0.030	0.107	<0.052	<0.052	<0.08	11.9	0.008	0.006
	2/18/04	30.0	14.141	0.242	<0.077	1.445	0.127	0.236	0.320	<0.052	<0.08	46.5	0.003	0.003
	2/18/04	33.7	14.141	0.566	<0.310	1.754	0.211	0.244	0.372	<0.206	<0.331	51.0	NA	NA
	9/21/04	24.0	7.475	<0.505	7.752	2.786	<0.302	<0.381	0.691	<0.516	<0.826	42.7	0.001	0.002
4/21/05	6.7	<0.302	<0.505	4.651	<0.516	<0.302	<0.381	<0.516	<0.516	<0.826	11.3	0.003	0.102	
IW-10	9/29/03	75.0	0.141	<0.051	<0.077	4.954	0.271	0.312	<0.052	<0.052	<0.08	80.6	0.006	0.003
	10/14/03	30.0	0.424	<0.051	<0.077	3.096	<0.030	0.175	<0.052	<0.052	<0.08	33.7	0.060	0.009
	11/13/03	34.5	2.626	<0.051	<0.077	2.580	0.308	0.510	<0.052	<0.052	<0.08	40.5	0.004	0.004
	12/16/03	11.2	24.24	<0.051	<0.077	1.858	0.121	0.259	0.537	<0.052	<0.08	38.3	0.007	0.003
	2/19/04	39.7	45.45	0.192	<0.077	4.128	0.175	0.304	1.135	<0.052	<0.08	91.1	0.001	0.002
	9/21/04	24.0	14.14	<0.051	11.318	3.509	0.097	0.175	0.970	<0.052	<0.08	54.2	0.001	0.001
	4/21/05	26.2	4.34	<0.051	8.527	4.954	<0.030	0.837	0.733	<0.052	<0.08	45.6	0.001	0.001

TABLE 4-7
Summary of CAHs, Ethane, and Ethene (µM)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Date	1,1,1- TCA (µM)	1,1-DCA (µM)	1,2-DCA (µM)	Chloro- ethane (µM)	1,1-DCE (µM)	PCE (µM)	TCE (µM)	<i>cis</i> - 1,2-DCE (µM)	<i>trans</i> - 1,2-DCE (µM)	Vinyl Chloride (µM)	Total CAHs (µM)	Ethane (µM)	Ethene (µM)
DOWNGRADIENT MONITORING WELLS														
MW-6 (7.5 feet)	9/30/03	42.73	0.067	<0.051	<0.077	2.786	0.151	0.274	<0.052	<0.052	<0.08	46	0.005	0.001
	10/14/03	39.73	0.094	<0.051	<0.077	2.270	0.109	0.297	<0.052	<0.052	<0.08	42	0.005	0.001
	11/13/03	13.49	0.072	<0.051	<0.077	1.548	0.038	0.190	<0.052	<0.052	<0.08	15.3	0.004	0.003
	12/16/03	2.02	1.212	<0.051	<0.077	0.079	<0.030	<0.038	<0.052	<0.052	<0.08	3.3	0.003	0.001
	2/18/04	1.80	16.162	<0.051	15.50	1.548	<0.030	<0.038	0.691	<0.052	<0.08	35.7	0.004	0.002
	9/22/04	7.20	6.162	<0.505	18.60	3.302	<0.302	<0.381	1.238	<0.516	<0.83	36.5	0.005	0.004
	4/21/05	7.50	2.222	<0.505	8.22	0.609	<0.302	<0.381	<0.516	<0.516	<0.83	18.5	0.003	0.364
SMW-4 (12.5 feet)	9/30/03	104.9	0.273	<0.202	<0.308	7.430	0.398	0.556	<0.206	<0.206	<0.32	113.6	0.028	0.008
	9/30/03	104.9	0.222	<0.202	<0.308	7.740	0.428	0.624	<0.206	<0.206	<0.32	114.0	NA	NA
	10/14/03	39.7	0.242	<0.202	<0.308	2.786	0.127	0.457	<0.206	<0.206	<0.32	43.3	0.045	0.020
	10/14/03	39.0	0.242	<0.202	<0.308	2.890	0.121	0.487	<0.206	<0.206	<0.32	42.7	NA	NA
	11/13/03	90.0	0.455	<0.202	<0.308	7.534	0.277	1.065	<0.206	<0.206	<0.32	99.3	0.018	0.011
	12/16/03	5.70	40.404	<0.202	<0.308	2.683	0.205	<0.152	1.445	<0.206	<0.32	50.4	0.004	0.003
	2/18/04	1.05	28.283	<0.202	24.806	3.302	<.120	<0.152	1.445	<0.206	<0.32	58.9	0.004	0.003
	7/19/04	15.0	5.859	<0.030	4.651	2.580	0.078	0.274	0.660	<0.052	<0.083	29.1	0.000	0.001
	9/22/04	27.7	8.283	<0.030	5.891	2.683	0.097	0.289	0.722	<0.052	<0.083	45.7	0.002	0.003
	4/21/05	2.2	4.040	<0.030	10.543	0.413	<0.030	0.099	0.217	<0.052	<0.083	17.6	0.004	0.857
4/21/05	2.3	4.242	<0.030	10.853	0.382	<0.030	0.091	0.206	<0.052	<0.083	18.1	NA	NA	
SMW-5 (20 feet)	9/30/03	104.95	0.465	<0.202	<0.308	8.153	0.392	1.142	<0.206	<0.206	<0.32	115.1	0.050	0.018
	10/14/03	74.96	0.465	<0.202	<0.308	5.263	0.211	1.065	<0.206	<0.206	<0.32	82.0	0.012	0.004
	11/13/03	82.46	0.929	<0.202	<0.308	10.320	0.205	1.826	<0.206	<0.206	<0.32	95.7	0.028	0.015
	12/16/03	5.70	62.626	<0.202	<0.308	6.089	<0.121	<0.152	2.580	<0.206	<0.32	77.0	0.006	0.004
	2/18/04	2.55	3.939	<0.202	134.88	6.398	<0.121	<0.152	2.064	<0.206	<0.32	149.8	0.007	0.003
	9/22/04	5.40	14.141	<0.505	23.26	4.334	<0.302	<0.381	1.342	<0.516	6.116	54.6	0.006	0.006
	4/21/05	1.65	2.727	<0.505	17.05	<0.516	<0.302	<0.381	<0.516	<0.516	<0.826	21.4	0.122	1.560

TABLE 4-7
Summary of CAHs, Ethane, and Ethene (µM)
Maryland Perchlorate Site

Well ID (Distance from barrier)	Date	1,1,1- TCA (µM)	1,1-DCA (µM)	1,2-DCA (µM)	Chloro- ethane (µM)	1,1-DCE (µM)	PCE (µM)	TCE (µM)	<i>cis</i> - 1,2-DCE (µM)	<i>trans</i> - 1,2-DCE (µM)	Vinyl Chloride (µM)	Total CAHs (µM)	Ethane (µM)	Ethene (µM)
SMW-6 (20 feet)	4/22/03	187.41	<0.505	<0.505	<0.77	5.882	<0.302	0.624	<0.516	<0.516	<0.80	193.9	<0.00033	<0.00036
	9/30/03	63.72	0.172	<0.051	<0.077	4.954	0.253	0.578	<0.052	<0.052	<0.08	69.7	0.007	0.002
	10/14/03	112.44	0.414	<0.051	<0.077	4.231	0.181	0.639	<0.052	<0.052	<0.08	117.9	0.013	0.004
	11/13/03	89.96	0.525	<0.202	<0.308	7.018	0.199	0.913	<0.206	<0.206	<0.32	98.6	0.020	0.017
	12/16/03	0.34	0.263	<0.005	<0.008	0.038	<0.003	<0.004	0.011	<0.005	<0.008	0.7	0.003	0.001
	2/18/04	1.12	18.182	0.048	49.61	2.167	0.072	0.058	1.135	<0.005	<0.008	72.4	0.004	0.003
	7/20/04	0.16	0.960	<0.005	0.54	0.382	0.009	0.014	0.114	<0.005	<0.008	2.2	0.001	0.001
	9/22/04	4.87	14.141	<0.051	10.85	2.786	0.078	0.114	1.022	<0.052	<0.08	33.9	0.006	0.008
	9/22/04	4.05	9.394	<0.051	10.23	2.064	0.060	0.091	0.898	<0.052	<0.08	26.8	NA	NA
4/21/05	3.30	4.141	4.141	13.95	0.053	<0.030	<0.038	<0.052		<0.08	21.4	0.019	1.416	
SMW-7 (20 feet)	9/30/03	104.95	0.273	<0.202	<0.308	5.986	0.320	0.624	<0.206	<0.206	<0.32	112.1	0.039	0.018
	10/14/03	82.46	4.040	<0.202	<0.308	5.366	0.157	0.457	<0.206	<0.206	<0.32	92.5	0.037	0.015
	11/13/03	66.72	0.333	<0.202	<0.077	8.669	0.181	0.913	<0.206	<0.052	<0.08	76.8	0.024	0.011
	12/16/03	6.52	63.636	<0.202	<0.077	3.922	<0.121	<0.152	1.651	<0.052	<0.08	75.7	0.033	0.008
	2/18/04	29.99	43.434	0.636	29.46	3.922	0.326	0.312	1.238	<0.052	<0.08	109.3	0.005	0.003
	9/22/04	14.24	11.111	<0.505	15.50	4.128	<0.302	<0.381	1.238	<0.516	<0.83	46.2	0.004	0.005
4/21/05	6.75	8.384	<0.505	17.05	0.970	<0.302	<0.381	<0.516	<0.516	<0.83	33.2	0.004	1.391	
AIR STRIPPER														
Influent	9/29/03	23	0.192	<0.051	<0.077	1.55	0.084	0.540	<0.052	<0.052	<0.08	25.6	0.0003	<0.00036
	10/14/03	30.73	0.242	<0.051	<0.077	1.75	0.10	0.738	<0.052	<0.052	<0.08	33.6	0.0013	<0.00036
	11/13/03	24.74	0.465	<0.051	<0.077	3.30	0.19	0.837	0.097	<0.052	<0.08	29.6	0.010	0.009
	12/16/03	15.74	3.737	<0.051	<0.077	1.34	0.14	0.487	0.196	<0.052	<0.08	21.6	0.001	0.001
	2/18/04	14.99	5.354	0.202	4.186	1.34	0.07	0.624	0.279	<0.052	<0.08	27.0	0.0003	<0.00036
	9/22/04	35.98	2.525	<0.051	1.52	1.75	0.10	0.403	0.155	<0.052	0.36	42.8	<0.00033	0.001
	4/21/05	6.52	1.414	<0.051	1.55	0.71	<0.03	0.342	0.087	<0.052	<0.08	10.6	<0.00033	0.031
Effluent	9/29/03	<0.004	<0.005	<0.005	<0.008	<0.005	<0.003	<0.004	<0.005	<0.005	<0.008	0	<0.00033	<0.00036
	10/14/03	<0.004	<0.005	<0.005	<0.008	<0.005	<0.003	<0.004	<0.005	<0.005	<0.008	0	<0.00033	<0.00036
	11/13/03	0.36	<0.005	<0.005	<0.008	0.04	<0.003	0.018	<0.005	<0.005	<0.008	0.4	<0.00033	<0.00036
	12/16/03	<0.004	<0.005	<0.005	<0.008	<0.005	<0.003	<0.004	<0.005	<0.005	<0.008	0	<0.00033	<0.00036
	2/18/04	<0.004	<0.005	<0.005	<0.008	<0.005	<0.003	<0.004	<0.005	<0.005	<0.008	0	<0.00033	<0.00036
	9/22/04	0.82	0.101	<0.005	0.045	0.031	0.004	0.019	0.007	<0.005	<0.008	1.0	<0.00033	<0.00036
	4/21/05	<0.004	<0.005	<0.005	<0.008	<0.005	<0.003	<0.004	<0.005	<0.005	<0.008	0	<0.00033	<0.00036

Notes:

Only data related to 1,1,1-TCA, PCE, TCE, and their daughter products are shown.

NA denotes not analyzed.

TABLE 4-8
Chlorine Numbers
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µM)	1,1-DCA (µM)	Chloro- ethane (µM)	Cl #	PCE (µM)	TCE (µM)	cis- 1,2-DCE (µM)	Vinyl Chloride (µM)	Ethene (µM)	Cl #
UPGRADIENT MONITORING WELLS											
SMW-1 (25 feet)	9/30/03	127.44	0.40	0	3.0	0.66	1.22	0	0	0.04	3.3
	10/14/03	97.45	2.73	0	3.0	0.31	1.29	0	0	0.41	2.6
	11/13/03	69.70	1.11	0	3.0	0.13	2.51	0.27	0	0.01	2.9
	12/16/03	55.50	0.00	0	3.0	0.00	2.21	0	0	0.01	3.0
	2/19/04	82.50	0.59	0	3.0	0.30	2.44	0	0	0.01	3.1
	9/21/04	59.20	0.84	0	3.0	0.12	1.98	0.24	0	0.00	2.9
	4/21/05	23.20	0.96	0	3.0	0.00	1.67	0.19	0	0.01	2.9
SMW-2 (25 feet)	9/30/03	127.44	0.39	0	3.0	0.50	0.40	0	0	0.07	3.3
	10/14/03	142.43	1.92	0	3.0	0.42	0.99	0	0	0.06	3.2
	11/13/03	49.50	5.05	0	2.9	0.00	0.56	0	0	0.04	2.8
	12/16/03	63.70	0.00	0	3.0	0.50	1.90	0	0	0.01	3.2
	2/19/04	67.50	0.60	0	3.0	0.35	1.52	0	0	0.01	3.2
	7/20/04	59.20	0.41	0	3.0	0.24	1.52	0.12	0	0.01	3.0
	9/21/04	71.20	0.26	0	3.0	0.24	1.37	0.17	0	0.01	3.0
4/21/05	31.50	0.62	0	3.0	0.00	1.22	0.13	0	0.00	2.9	
SMW-3 (25 feet)	9/30/03	104.95	0.00	0	3.0	0.31	0.61	0	0	0.02	3.3
	10/14/03	59.97	1.92	0	3.0	0.13	0.46	0	0	0.01	3.2
	11/13/03	36.73	0	0	3.0	0.18	0.49	0	0	0.03	3.1
	11/13/03	44.23	0	0	3.0	0.18	0.62	0	0	NA	3.2
	12/16/03	82.46	0	0	3.0	0.51	1.22	0	0	0.00	3.3
	2/19/04	18.74	0	0	3.0	0.51	1.14	0	0	0.00	3.3
	9/21/04	14.99	0	0	3.0	0.05	0.18	0	0	0.00	3.2
	4/21/05	50.97	0.26	0	3.0	0.08	1.60	0	0	0.00	3.0
INJECTION WELLS											
IW-1	4/23/03	127.44	0.66	0	3.0	0.54	1.29	0	0	NA	3.3
	9/29/03	43.48	0.63	0	3.0	0.16	1.60	0	0	0.004	3.1
	10/14/03	4.30	0.72	0	2.9	0	0.12	0.09	0	0.015	2.4
	11/13/03	30.70	1.31	0	3.0	0.10	1.90	0.27	0	0.007	2.9
	12/16/03	2.00	14.14	0	2.1	0	0.19	1.14	0	0.007	2.1
	12/16/03	2.50	16.16	0	2.1	0	0.00	1.34	0	NA	2.0
	2/18/04	8.20	12.12	5.27	2.1	0	0.28	0.77	0	0.005	2.3
	9/21/04	29.20	3.13	5.89	2.6	0.07	0.84	0.88	0.17	0.027	2.4
	4/21/05	3.50	1.41	2.17	2.2	0.00	0.64	0.39	0	0.300	2.0
IW-3	9/29/03	69.72	0.51	0	3.0	0.25	1.14	0.06	0	0.012	3.1
	10/14/03	9.00	1.41	0	2.9	0.00	0.12	0.00	0	0.026	2.5
	11/13/03	82.50	2.42	0	3.0	0.18	1.75	0.25	0	0.006	3.0
	12/16/03	1.20	14.14	0	2.1	0.00	0.00	1.14	0	0.013	2.0
	2/18/04	13.50	29.29	34.11	1.7	0.06	0.08	1.34	0	0.004	2.1
	9/21/04	6.20	15.15	15.50	1.7	0.04	0.13	2.06	0.18	0.003	2.0
4/21/05	7.00	4.55	9.30	1.9	0.00	0.27	0.70	1.21	0.539	1.3	
IW-5	9/29/03	74.96	0.16	0	3.0	0.30	0.61	0	0	0.004	3.3
	10/14/03	8.25	0.71	0	2.9	0	0.07	0	0	0.025	2.2
	11/13/03	52.50	0.15	0	3.0	0.14	0.70	0.09	0	0.004	3.0
	12/16/03	27.00	2.93	0	2.9	0.22	0.59	0.09	0	0.015	3.1
	2/18/04	24.70	16.16	0	2.6	0.15	0.37	0.44	0	0.004	2.7
	7/19/04	13.50	7.58	3.72	2.4	0.04	0.19	0.40	0	0.002	2.4
	9/21/04	17.20	6.67	15.19	2.1	0.05	0.30	0.66	0	0.001	2.4
	4/21/05	9.00	2.32	6.20	2.2	0	0.43	0.27	0	0.110	2.3

TABLE 4-8
Chlorine Numbers
Maryland Perchlorate Site

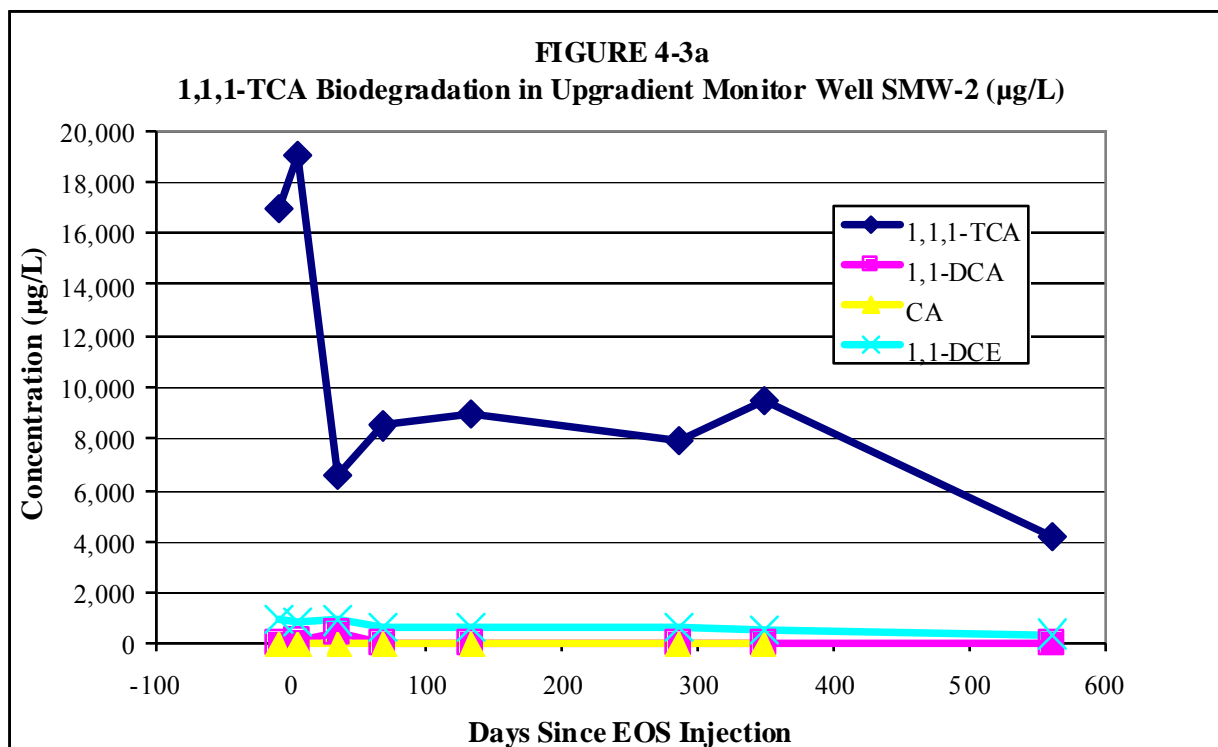
Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µM)	1,1-DCA (µM)	Chloro- ethane (µM)	Cl #	PCE (µM)	TCE (µM)	cis- 1,2-DCE (µM)	Vinyl Chloride (µM)	Ethene (µM)	Cl #
IW-7	9/29/03	45.00	0.16	0	3.0	0.16	0.21	0	0	0.003	3.4
	10/14/03	9.00	0.31	0	3.0	0.00	0.07	0	0	0.005	2.8
	11/13/03	29.20	0.22	0	3.0	0.16	0.34	0	0	0.004	3.3
	12/16/03	11.20	0	0	3.0	0.00	0.11	0	0	0.006	2.8
	2/18/04	30.00	8.44	0	2.8	0.13	0.24	0.19	0	0.003	2.9
	2/18/04	33.70	8.44	0	2.8	0.21	0.24	0.22	0	NA	3.0
	9/21/04	24.00	4.46	7.75	2.4	0	0	0.40	0	0.002	2.0
	4/21/05	6.70	0.00	4.65	2.2	0	0	0	0	0.102	0.0
IW-10	9/29/03	75.00	0.14	0	3.0	0.27	0.31	0	0	0.003	3.4
	10/14/03	30.00	0.42	0	3.0	0.00	0.18	0	0	0.009	2.9
	11/13/03	34.50	2.63	0	2.9	0.31	0.51	0	0	0.004	3.4
	12/16/03	11.20	24.24	0	2.3	0.12	0.26	0.54	0	0.003	2.5
	2/19/04	39.70	45.45	0	2.5	0.18	0.30	1.14	0	0.002	2.4
	9/21/04	24.00	14.14	11.31	2.3	0.10	0.18	0.97	0	0.001	2.3
	4/21/05	26.20	4.34	8.53	2.5	0.00	0.84	0.73	0	0.001	2.5
	DOWNGRADIENT MONITORING WELLS										
MW-6 (7.5 feet)	9/30/03	42.73	0.07	0	3.0	0.15	0.27	0	0	0.001	3.3
	10/14/03	39.73	0.09	0	3.0	0.11	0.30	0	0	0.001	3.3
	11/13/03	13.49	0.07	0	3.0	0.04	0.19	0	0	0.003	3.1
	12/16/03	2.02	1.21	0	2.6	0	0	0	0	0.001	0.0
	2/18/04	1.80	16.16	15.41	1.6	0	0	0.69	0	0.002	2.0
	9/22/04	7.20	6.16	18.49	1.6	0	0	1.24	0	0.004	2.0
	4/21/05	7.50	2.22	8.17	2.0	0	0	0	0	0.364	0.0
	SMW-4 (12.5 feet)	9/30/03	104.95	0.27	0	3.0	0.40	0.56	0	0	0.008
9/30/03		104.95	0.22	0	3.0	0.43	0.62	0	0	NA	3.4
10/14/03		39.73	0.24	0	3.0	0.13	0.46	0	0	0.020	3.1
10/14/03		38.98	0.24	0	3.0	0.12	0.49	0	0	NA	3.2
11/13/03		89.96	0.46	0	3.0	0.28	1.07	0	0	0.011	3.2
12/16/03		5.70	40.40	0	2.1	0.21	0	1.45	0	0.003	2.2
2/18/04		1.05	28.28	24.81	1.6	0	0	1.45	0	0.003	2.0
7/19/04		15.00	5.86	4.65	2.4	0.08	0.27	0.66	0	0.001	2.4
9/22/04		27.70	8.28	5.89	2.5	0.10	0.29	0.72	0	0.003	2.4
4/21/05		2.20	4.04	10.54	1.5	0	0.10	0.22	0	0.857	0.6
4/21/05	2.30	4.24	10.85	1.5	0	0.09	0.21	0	0	2.3	
SMW-5 (20 feet)	9/30/03	104.95	0.47	0	3.0	0.39	1.14	0	0	0.018	3.2
	10/14/03	74.96	0.47	0	3.0	0.21	1.07	0	0	0.004	3.2
	11/13/03	82.46	0.93	0	3.0	0.21	1.83	0	0	0.015	3.1
	12/16/03	5.70	62.63	0	2.1	0	0	2.58	0	0.004	2.0
	2/18/04	2.55	3.94	134.05	1.1	0	0	2.06	0	0.003	2.0
	9/22/04	5.40	14.14	23.11	1.6	0	0	1.34	6	0.006	1.2
	4/21/05	1.65	2.73	16.95	1.3	0	0	0	0	1.560	0.0
	SMW-6 (20 feet)	4/22/03	187.41	0	0	3.0	0.00	0.62	0	0	0
9/30/03		63.72	0.17	0	3.0	0.25	0.58	0	0	0.002	3.3
10/14/03		112.44	0.41	0	3.0	0.18	0.64	0	0	0.004	3.2
11/13/03		89.96	0.53	0	3.0	0.20	0.91	0	0	0.017	3.1
12/16/03		0.34	0.26	0	2.6	0.00	0.00	0.01	0	0.001	1.8
2/18/04		1.12	18.18	49.31	1.3	0.07	0.06	1.14	0	0.003	2.2
7/20/04		0.16	0.96	0.54	1.8	0.01	0.01	0.11	0	0.001	2.2
9/22/04		4.87	14.14	10.79	1.8	0.08	0.11	1.02	0	0.008	2.2
9/22/04		4.05	9.39	10.17	1.7	0.06	0.09	0.90	0	NA	2.2
4/21/05		3.30	4.14	13.87	1.5	0	0	0	0	1.416	0.0

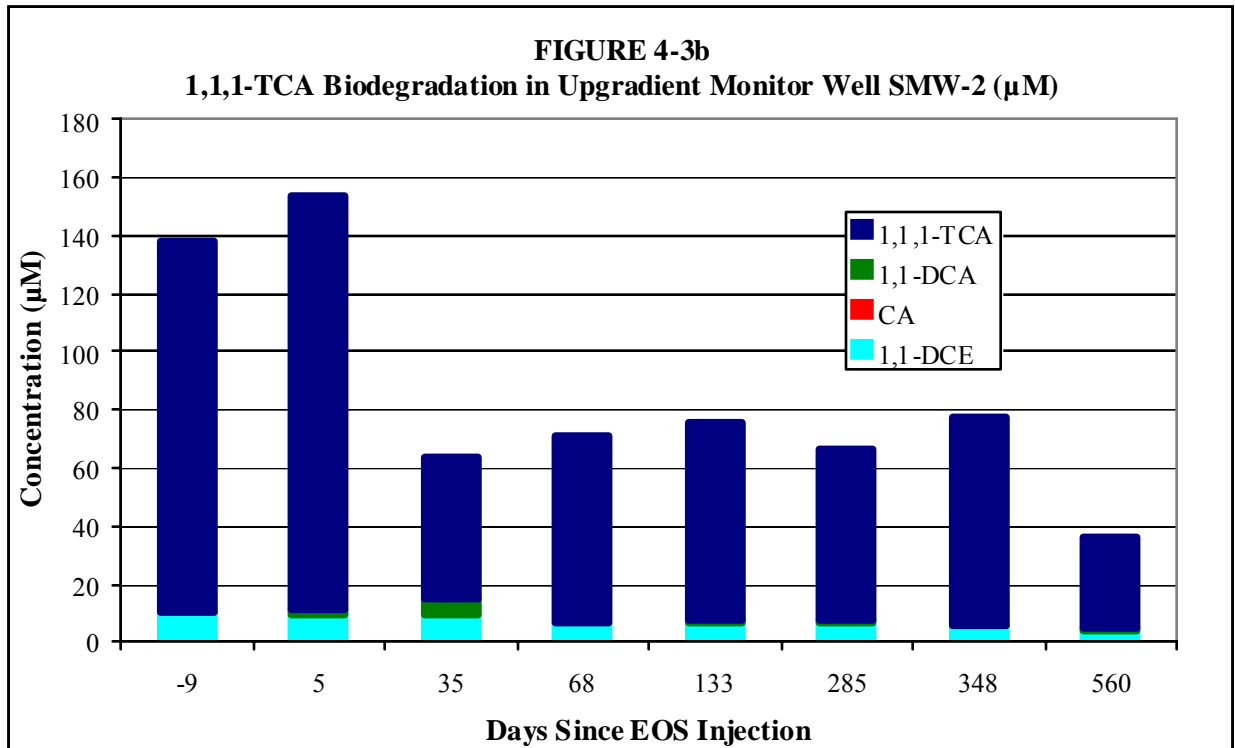
TABLE 4-8
Chlorine Numbers
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	1,1,1- TCA (µM)	1,1-DCA (µM)	Chloro- ethane (µM)	Cl #	PCE (µM)	TCE (µM)	<i>cis</i> - 1,2-DCE (µM)	Vinyl Chloride (µM)	Ethene (µM)	Cl #
SMW-7 (20 feet)	9/30/03	104.95	0.27	0	3.0	0.32	0.62	0	0	0.018	3.3
	10/14/03	82.46	4.04	0	3.0	0.16	0.46	0	0	0.015	3.2
	11/13/03	66.72	0.33	0	3.0	0.18	0.91	0	0	0.011	3.1
	12/16/03	6.52	63.64	0	2.1	0	0	1.65	0	0.008	2.0
	2/18/04	29.99	43.43	29.28	2.0	0.33	0.31	1.24	0	0.003	2.5
	9/22/04	14.24	11.11	15.41	2.0	0	0	1.24	0	0.005	2.0
	4/21/05	6.75	8.38	16.95	1.7	0	0	0	0	1.391	0.0
AIR STRIPPER											
Influent	9/29/03	23.00	0.19	0	3.0	0.08	0.54	0	0	0	3.1
	10/14/03	30.73	0.24	0	3.0	0.10	0.74	0	0	0	3.1
	11/13/03	24.74	0.47	0	3.0	0.19	0.84	0.10	0	0.009	3.1
	12/16/03	15.74	3.74	0	2.8	0.14	0.49	0.20	0	0.001	2.9
	2/18/04	14.99	5.35	4.16	2.4	0.07	0.62	0.28	0	0	2.8
	9/22/04	35.98	2.53	1.51	2.9	0.10	0.40	0.16	0	0.001	2.2
	4/21/05	6.52	1.41	1.54	2.5	0.00	0.34	0.09	0	0.031	2.6

Upgradient Monitor Wells

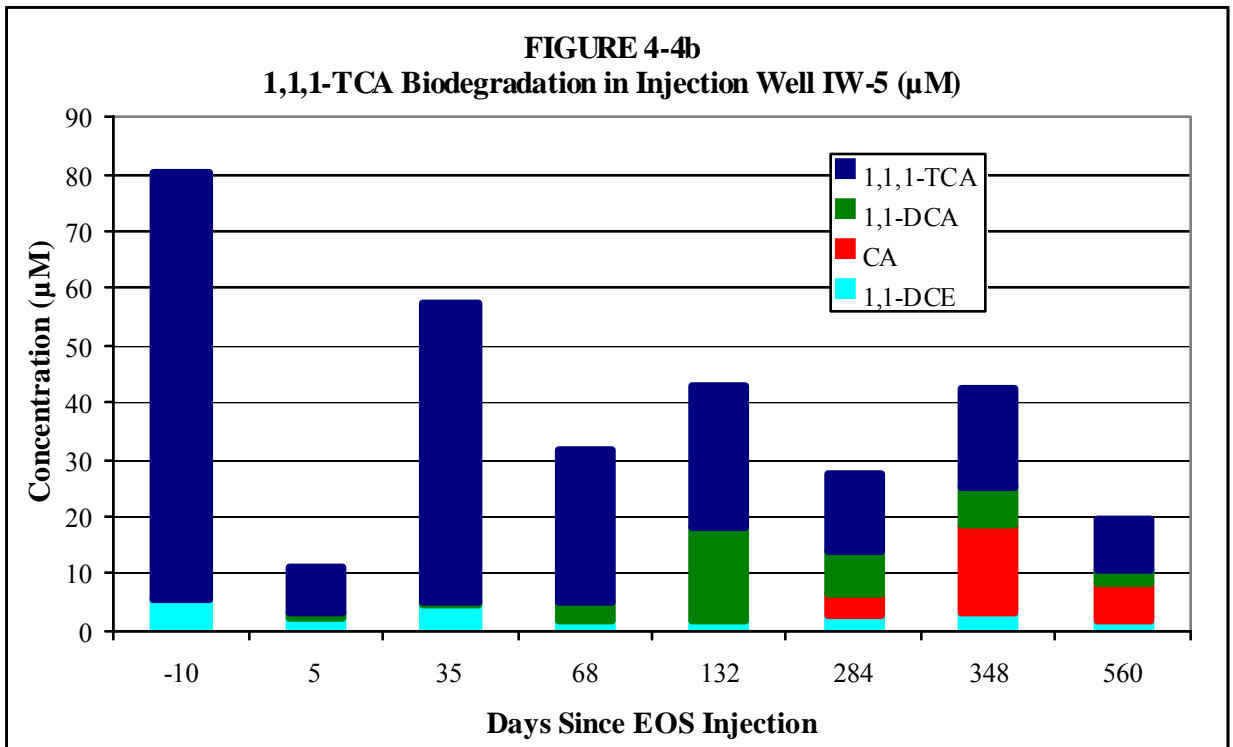
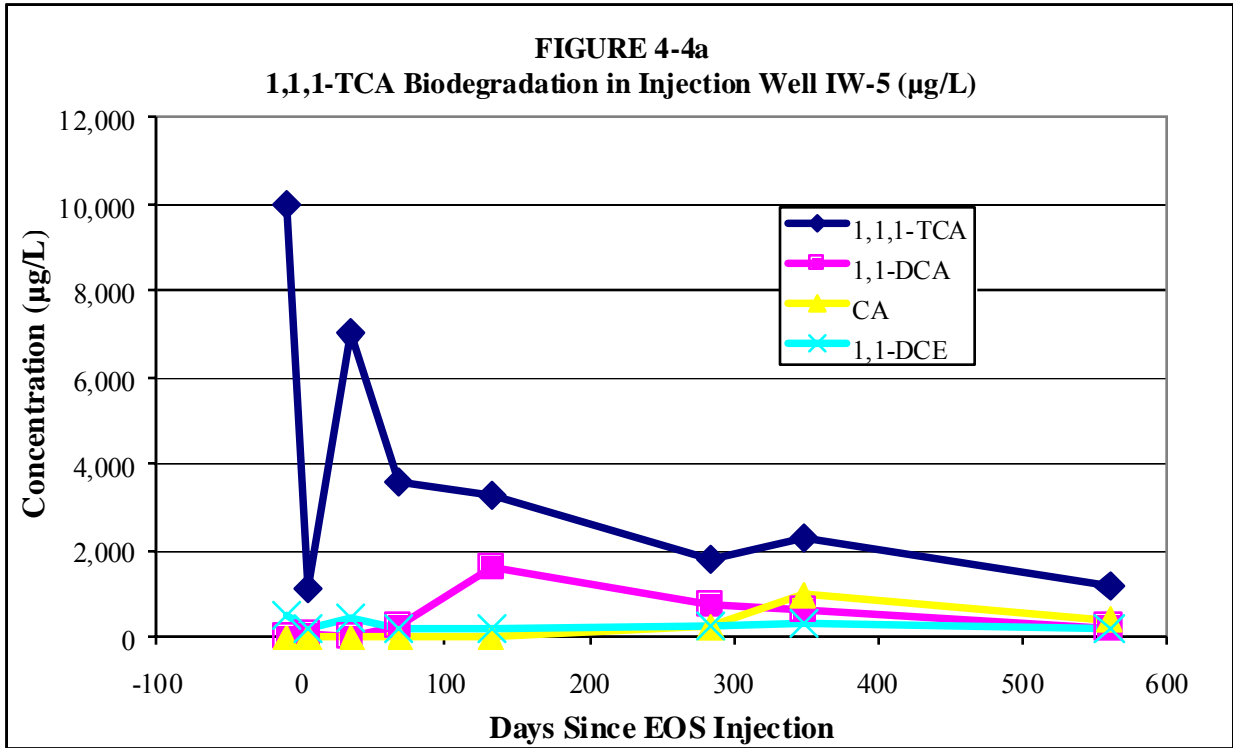
During the pilot test, 1,1,1-TCA concentrations fluctuated in the upgradient monitor wells with concentrations ranging between 2,000 $\mu\text{g/L}$ and 19,000 $\mu\text{g/L}$. In general, 1,1,1-TCA concentrations decreased over the course of the pilot test in the upgradient wells, but no corresponding increases in daughter products were observed. Low concentrations of 1,1-DCA were detected both pre- and post-injection, but chloroethane remained below the laboratory method detection limits throughout the pilot test. 1,1-DCE, an abiotic degradation product of 1,1,1-TCA, was more predominant than any of the biodegradation daughter products with concentrations ranging from 88 to 1,200 $\mu\text{g/L}$. These results are illustrated in Figures 4-3a and b for upgradient monitor well SMW-2. As shown in Table 4-8, the chlorine numbers remained at 3.0 in the upgradient wells throughout the pilot test indicating the biodegradation was not occurring. Overall, no impacts from the EOS[®] injection were observed in the upgradient monitor wells confirming that the concentrations detected in these wells are indicative of background influent concentrations to the PRB.



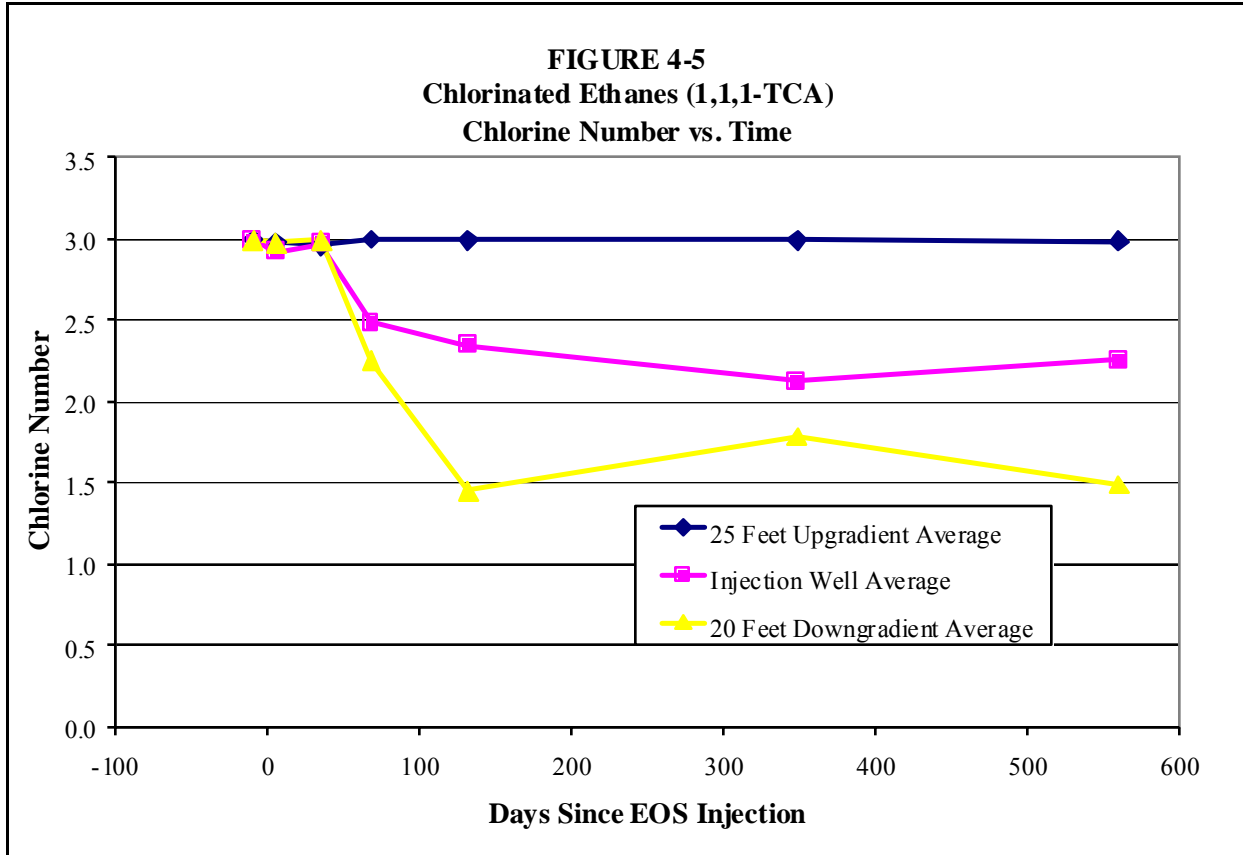


Injection Wells

Immediately after injection, decreases in 1,1,1-TCA were observed in all of the injection wells. These reductions were most likely due to sorption to the oil and/or dilution, since no substantial corresponding increases in daughter products were observed. Concentrations of 1,1,1-TCA in the injection wells rebounded at 1 month post-injection, but by 2 months post-injection degradation began to occur as evidenced by decreases in 1,1,1-TCA and increases in 1,1-DCA. By 4 months post-injection, further degradation to chloroethane was observed in some of the injection wells. Substantial concentrations of chloroethane were detected in all injection wells by 11 months post-injection. Substantial changes in ethane concentrations were not observed in the injection wells during the pilot test. The persistence of daughter products in these wells indicates that complete degradation had not occurred. However, overall, substantial degradation of 1,1,1-TCA was achieved within the PRB. Eighteen months following creation of the barrier, 1,1,1-TCA reductions ranged from 85% to 92% in the injection wells, with the exception of IW-10, which only indicated a 65% reduction compared to pre-injection levels. The trends observed in the injection wells for 1,1,1-TCA and its daughter products are illustrated on Figures 4-4a and 4-4b for IW-5.

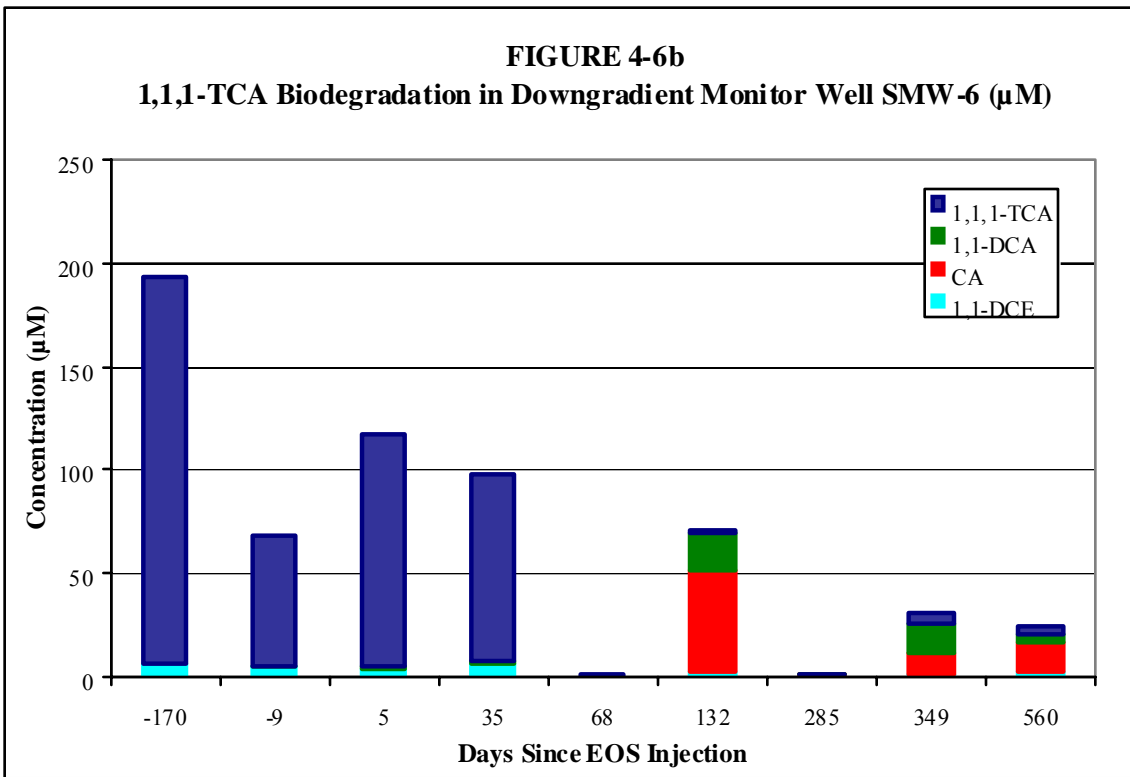
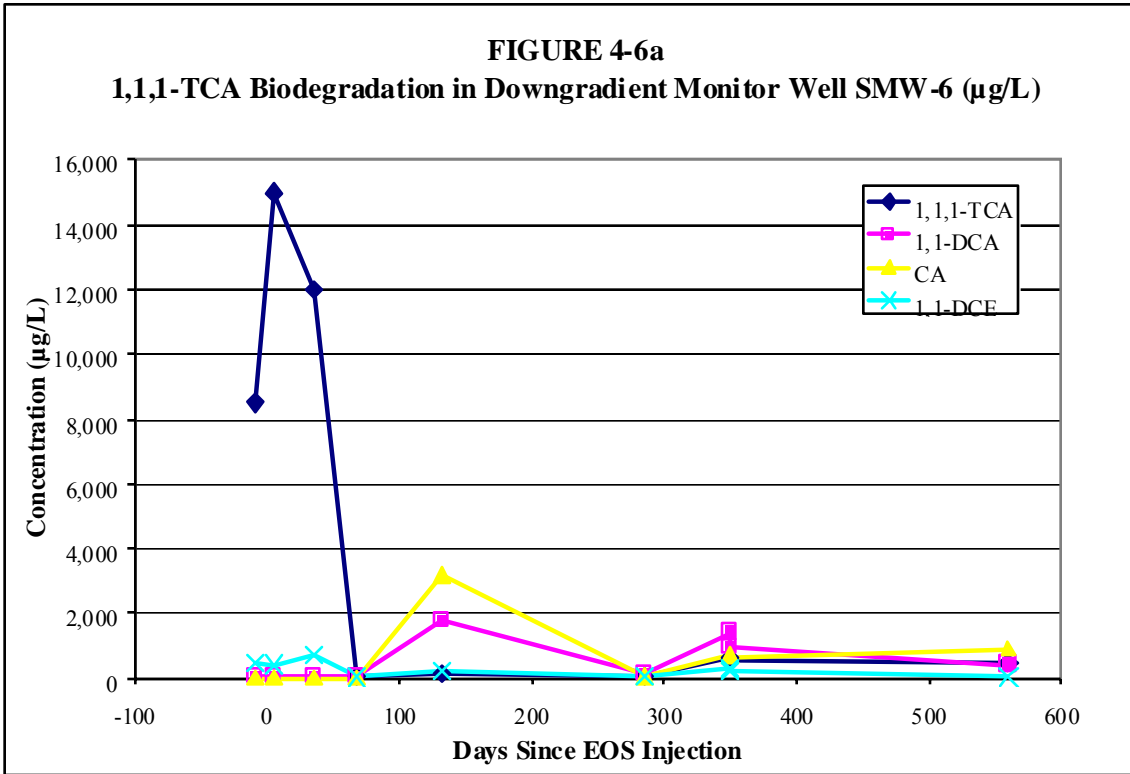


As shown in Table 4-8 and Figure 4-5, the chlorine numbers for the injection wells pre-injection were all 3.0. However, in contrast to the upgradient wells, the chlorine numbers decreased in all of the injection wells after EOS[®] injection confirming that the desired biodegradation processes were occurring. At 18 months post-injection, the average chlorine number in the five injection wells that were monitored was 2.2 indicating biodegradation was occurring in these wells.



Downgradient Monitor Wells

The downgradient monitor wells also showed substantial reductions in 1,1,1-TCA concentrations. In general, 1,1,1-TCA concentrations decreased during the pilot test with subsequent increases in 1,1-DCA and chloroethane. Eighteen months post-injection, 1,1,1-TCA was reduced by 94 to 98% twenty feet downgradient of the barrier. Figures 4-6a and 4-6b show the changes in 1,1,1-TCA and its daughter products for SMW-6 located approximately 20 feet downgradient of the PRB.



The chlorine numbers for the downgradient wells showed the greatest decrease over the 18-month pilot study (Table 4-8 and Figure 4-5). The pre-injection chlorine numbers were 3.0 for all downgradient wells pre-injection. At 18 months post-injection, the chlorine numbers had decreased to 2.0 in MW-6 (7.5 feet downgradient) and 1.5 in SMW-4 (12.5 feet downgradient). Twenty feet downgradient, the average chlorine number was 1.5. These results confirm that as groundwater migrates through the EOS[®] PRB, 1,1,1-TCA is being biodegraded to 1,1-DCA and then chloroethane. However, complete degradation to ethane was not observed indicating additional contact time may be needed to achieve complete dechlorination.

Mass Removal

Solutions-IES evaluated the mass of 1,1,1-TCA removed by the PRB by comparing the average concentrations in the three wells 25 feet upgradient to the average concentrations in the three wells 20 feet downgradient over the course of the 18-month pilot test using the same assumptions as indicated above for perchlorate. The mass flux calculations are summarized in Table 4-9 and indicate that the barrier removed a total of approximately 16 lbs of 1,1,1-TCA during the 18-month monitoring period.

TABLE 4-9
1,1,1-TCA Mass Removal
Maryland Perchlorate Site

Sample Date	Days Since Injection	Average Upgradient (µg/L)	Average Downgradient (µg/L)	Change (µg/L)	Change %		Mass removed (lbs/day)	Mass removed ¹ (lbs)
10/14/03	5	13,333	12,000	1,333	10%	increase	0.008	0.04
11/13/03	35	6,933	10,633	-3,700	-53%		-0.023	-0.68
12/16/03	68	8,967	559	8,408	94%		0.052	1.71
2/19/04	133	7,500	1,497	6,003	80%		0.037	2.40
9/21/04	348	6,467	1090	5,377	83%		0.033	7.10
4/21/05	560	4700	520	4180	89%		0.026	5.45
Total Mass of 1,1,1-TCA Removed by Emulsified Oil PRB =								16.01

Note:

1. Calculated as mass removed (lbs/day) times the number of days between each sampling event.

Solutions-IES also estimated the mass removal of 1,1,1-TCA by evaluating data for the air stripper which is fed by the interceptor trench located approximately 50 feet downgradient of the EOS[®] barrier. Historical air stripper monthly influent data were obtained from the facility. The data were evaluated from two years

before injection (September 2001) until the air stripper was shutdown in January 2005. Figure 4-7a shows the 1,1,1-TCA concentrations in the influent during this time period and illustrates that a substantial reduction in 1,1,1-TCA was observed after injection of the EOS[®]. Operational pumping data were used to determine the mass of 1,1,1-TCA in the air stripper influent. These data are presented on Table 4-10 and Figure 4-7b and show a substantial drop in 1,1,1-TCA mass after EOS[®] injection. For the two years pre-injection, an average of approximately 0.18 lbs/day of 1,1,1-TCA were entering the air stripper. Post-injection, the average mass flux of 1,1,1-TCA into the stripper was 0.15 lbs/day. Therefore, the mass flux was reduced by approximately 0.03 lbs/day. Based on these data, during the 18-month (560-day) monitoring period, approximately 25 pounds of 1,1,1-TCA were removed by the PRB.

Similar calculations were performed for 1,1-DCA and CA using the air stripper influent data. The air stripper influent data are shown on Figures 4-8a and b for 1,1-DCA and 4-9a and b for CA. Prior to injection, low levels of 1,1-DCA were detected in the air stripper influent. A large increase was observed after EOS[®] injection followed by a subsequent decrease as 1,1-DCA was further degraded to CA. CA was not detected in the air stripper influent prior to emulsion injection. Subsequently, CA concentrations increased over the course of the pilot test. Approximately 4.8 pounds of 1,1-DCA and 4.0 pounds of CA were created during the 18-month pilot test period. These amounts of 1,1-DCA and CA are equivalent to approximately 14.8 pounds of 1,1,1-TCA. Since 1,1-DCA and CA were essentially not present in the air stripper influent pre-injection, the mass estimates are probably more reliable.

TABLE 4-10
Mass Removal Evaluation Using Air Stripper Influent Data
Maryland Perchlorate Site

Month	Total Flow (gallons)	Days of Operation	1,1,1-TCA			1,1-DCA			Chloroethane		
			(µg/L)	(lbs/day)	(lbs/month)	(µg/L)	(lbs/day)	(lbs/month)	(µg/L)	(lbs/day)	(lbs/month)
Sep-01	266,990	30	2,450	0.18	5.45	29	0.00	0.06	0	-	-
Oct-01	221,000	31	2,260	0.13	4.16	27	0.00	0.05	0	-	-
Nov-01	176,970	30	2,170	0.11	3.20	41	0.00	0.06	0	-	-
Dec-01	273,295	31	1,770	0.13	4.03	39	0.00	0.09	0	-	-
Jan-02	309,395	31	1,120	0.09	2.89	37	0.00	0.10	0	-	-
Feb-02	388,630	28	1,780	0.21	5.76	28	0.00	0.09	0	-	-
Mar-02	434,480	31	2,400	0.28	8.69	16	0.00	0.06	0	-	-
Apr-02	394,470	30	2,680	0.29	8.81	28	0.00	0.09	0	-	-
May-02	316,510	31	2,510	0.21	6.62	27	0.00	0.07	0	-	-
Jun-02	485,920	30	2,340	0.32	9.47	33	0.00	0.13	0	-	-
Jul-02	314,910	31	3,570	0.30	9.36	30	0.00	0.08	0	-	-
Aug-02	125,110	31	3,740	0.13	3.90	33	0.00	0.03	0	-	-
Sep-02	103,390	30	2,450	0.07	2.11	29	0.00	0.02	0	-	-
Oct-02	166,180	31	3,200	0.14	4.43	39	0.00	0.05	0	-	-
Nov-02	248,840	30	2,990	0.21	6.20	32	0.00	0.07	0	-	-
Dec-02	251,860	31	3,390	0.23	7.11	22	0.00	0.05	0	-	-
Jan-03	230,310	31	4,630	0.29	8.88	24	0.00	0.05	0	-	-
Feb-03	209,703	28	3,610	0.23	6.31	18	0.00	0.03	0	-	-
Mar-03	252,770	31	4,320	0.29	9.10	20	0.00	0.04	0	-	-
Apr-03	441,600	30	-	-	-	-	-	-	-	-	-
May-03	263,376	31	-	-	-	-	-	-	-	-	-
Jun-03	259,200	30	-	-	-	-	-	-	-	-	-
Jul-03	351,939	31	5,230	0.49	15.33	21	0.00	0.06	0	-	-
Aug-03	15,535	31	6,040	0.03	0.78	21	0.00	0.00	0	-	-
Sep-03	79,370	30	5,590	0.12	3.70	28	0.00	0.02	0	-	-
Pre-Injection Averages			3,193	0.18	5.45	28.27	0.00	0.05	0	-	-
Oct-03	30,460	31	4,300	0.04	1.09	25	0.00	0.01	0	-	-
Nov-03	412,740	30	3,890	0.45	13.37	119	0.01	0.41	0	-	-
Dec-03	381,010	31	2,600	0.27	8.25	426	0.04	1.35	5.1	0.00	0.02
Jan-04	184,998	31	3,310	0.16	5.10	408	0.02	0.63	253	0.01	0.39
Feb-04	37,437	28	1,420	0.02	0.44	470	0.01	0.15	64	0.00	0.02
Mar-04	8,582	31	1,370	0.00	0.10	391	0.00	0.03	54	0.00	0.00
Apr-04	100,187	30	5,200	0.14	4.34	216	0.01	0.18	285	0.01	0.24
May-04	103,478	31	3,090	0.09	2.66	310	0.01	0.27	292	0.01	0.25
Jun-04	55,312	30	3,100	0.05	1.43	243	0.00	0.11	426	0.01	0.20
Jul-04	103,773	10	3,900	0.34	3.37	159	0.01	0.14	305	0.03	0.26
Aug-04	1	0	0	-	-	0	-	-	0	-	-
Sep-04	177,290	0	4,330	-	6.39	269	-	0.40	385	-	0.57
Oct-04	107,674	31	3,410	0.10	3.06	201	0.01	0.18	207	0.01	0.19
Nov-04	110,998	30	1,710	0.05	1.58	220	0.01	0.20	179	0.01	0.17
Dec-04	130,975	31	432	0.02	0.47	84	0.00	0.09	18	0.00	0.02
Jan-05	184,998	31	1,290	0.06	1.99	252	0.01	0.39	204	0.01	0.31
Post-Injection Averages			2,710	0.13	3.35	237.1	0.01	0.28	167.3	0.01	0.16

FIGURE 4-7a
1,1,1-TCA Concentrations in Air Stripper Influent vs. Time

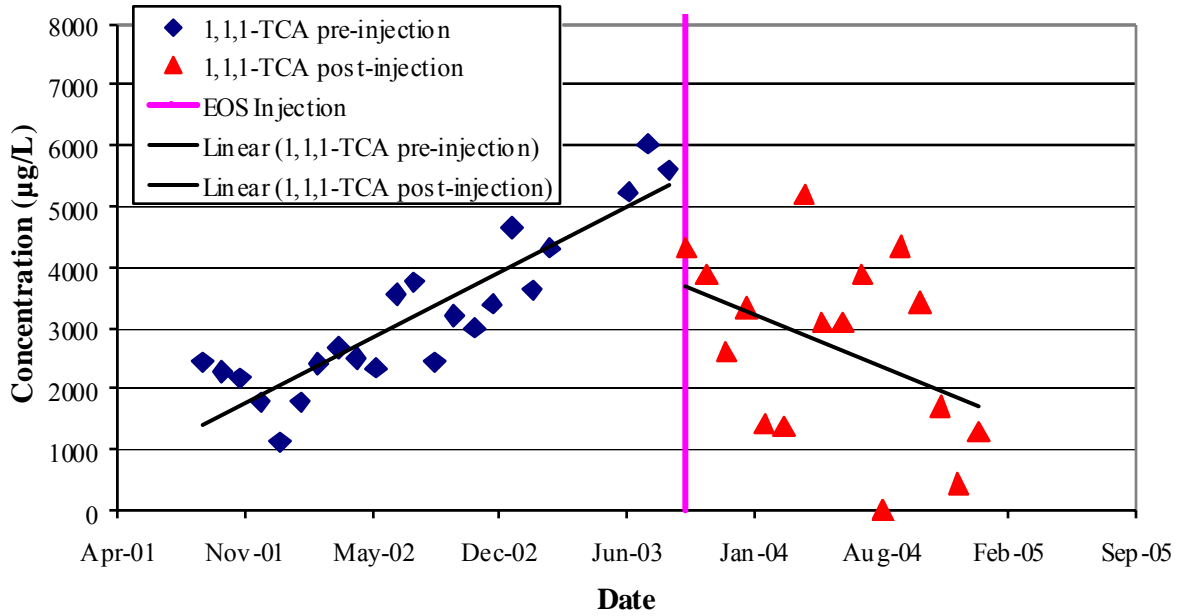
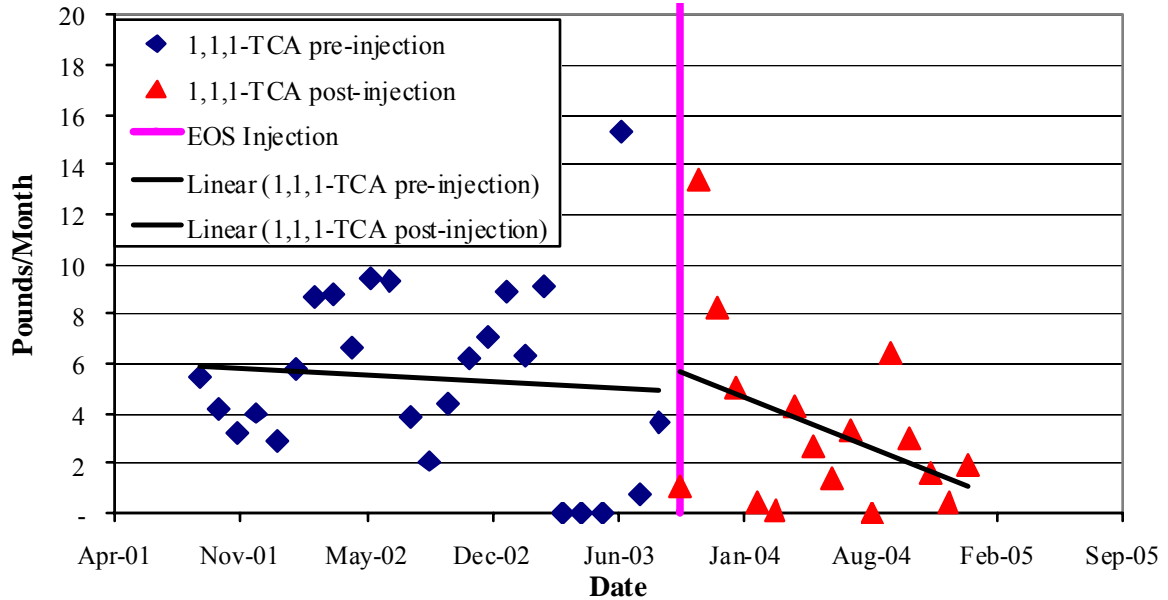
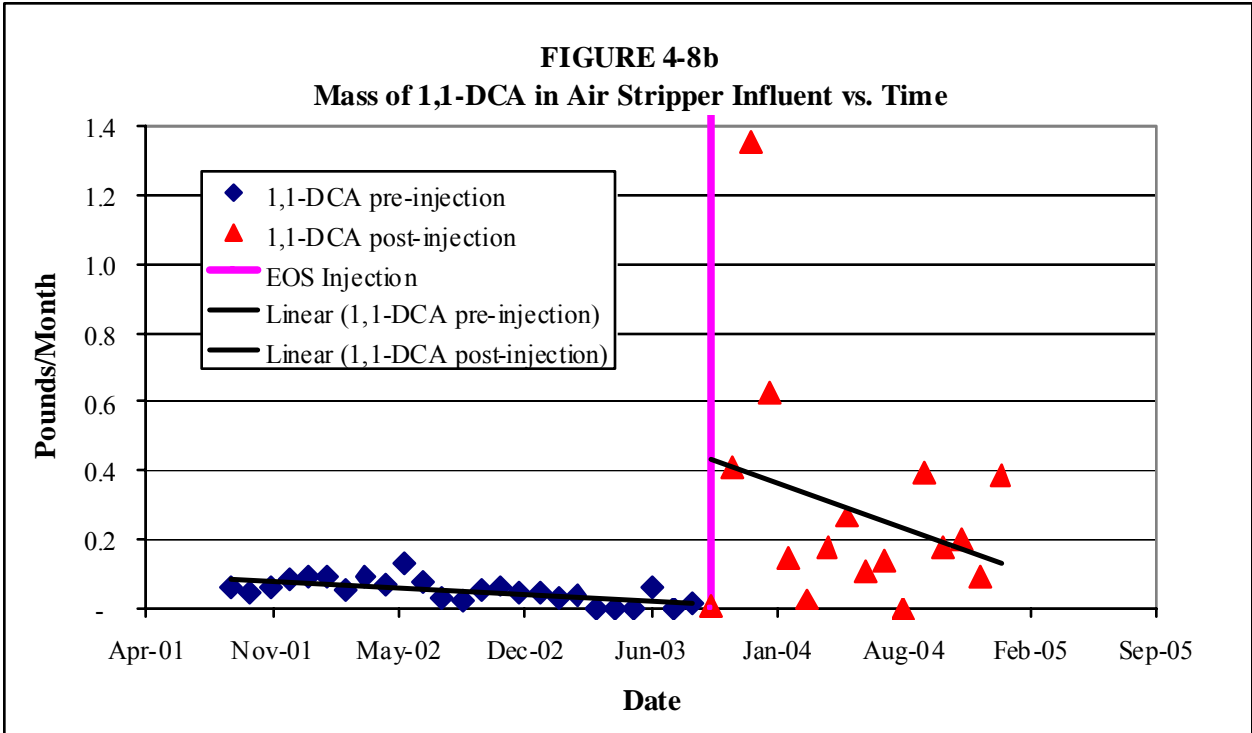
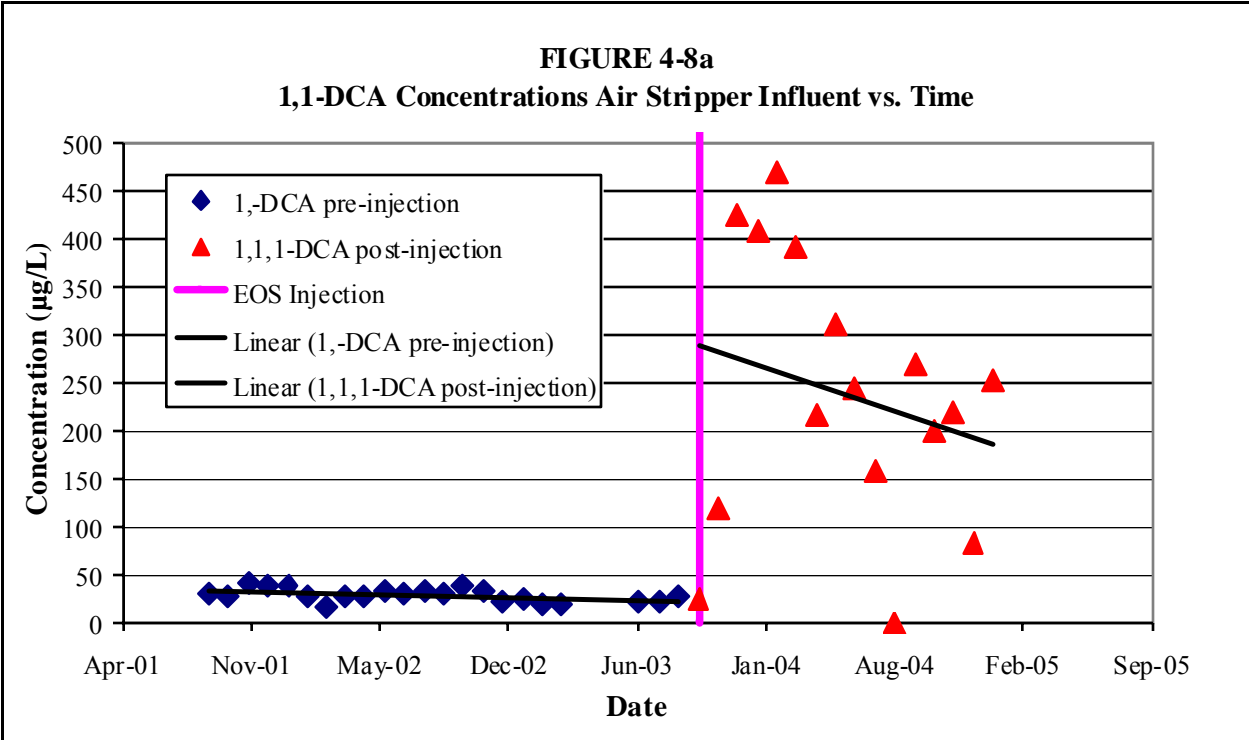
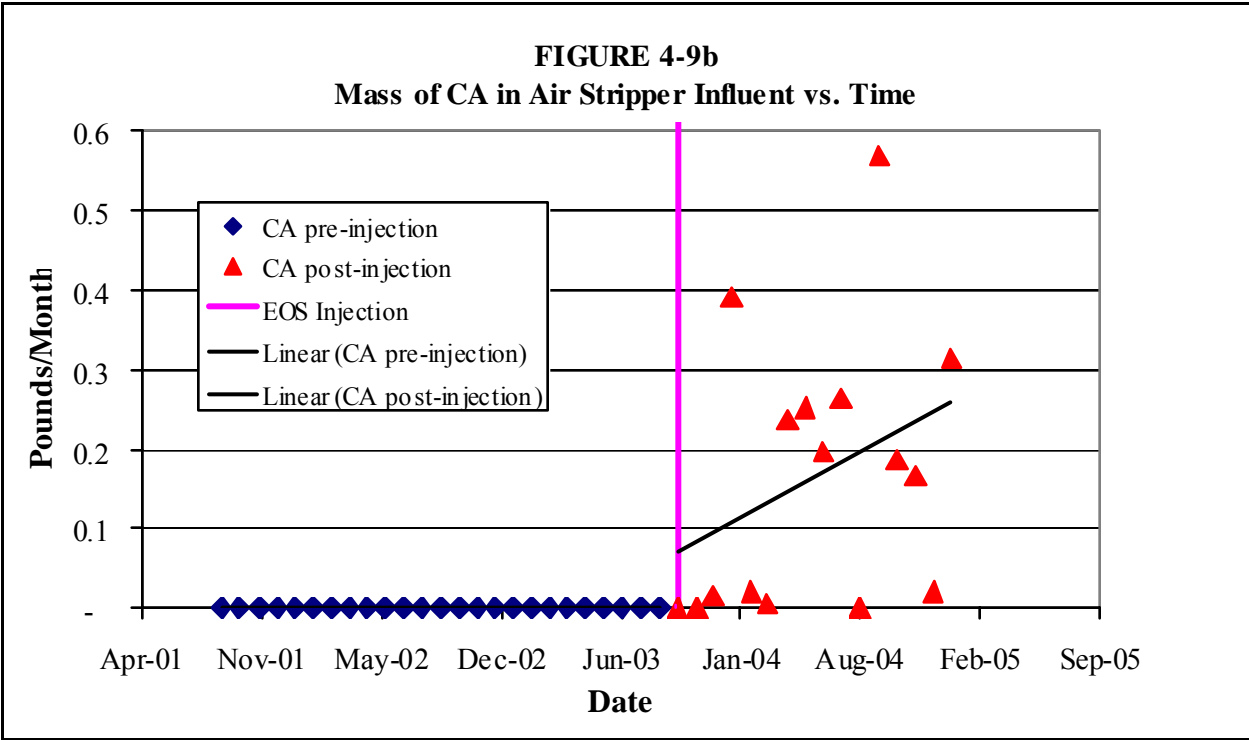
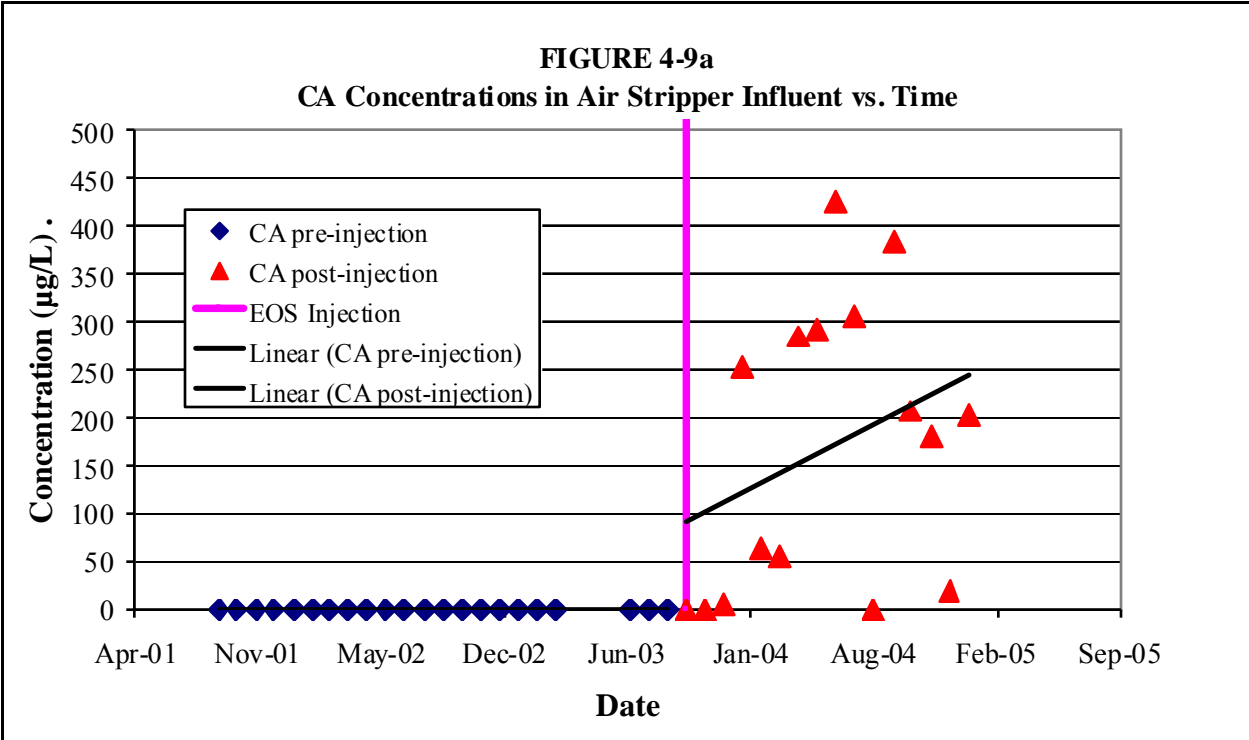


FIGURE 4-7b
Mass of 1,1,1-TCA in Air Stripper Influent vs. Time







4.3.1.3 Chlorinated Ethenes

The analytical results for PCE, TCE, and their daughter products are summarized in Table 4-6 and are presented in molar for in Table 4-7. Chlorine numbers were also calculated using the following equation:

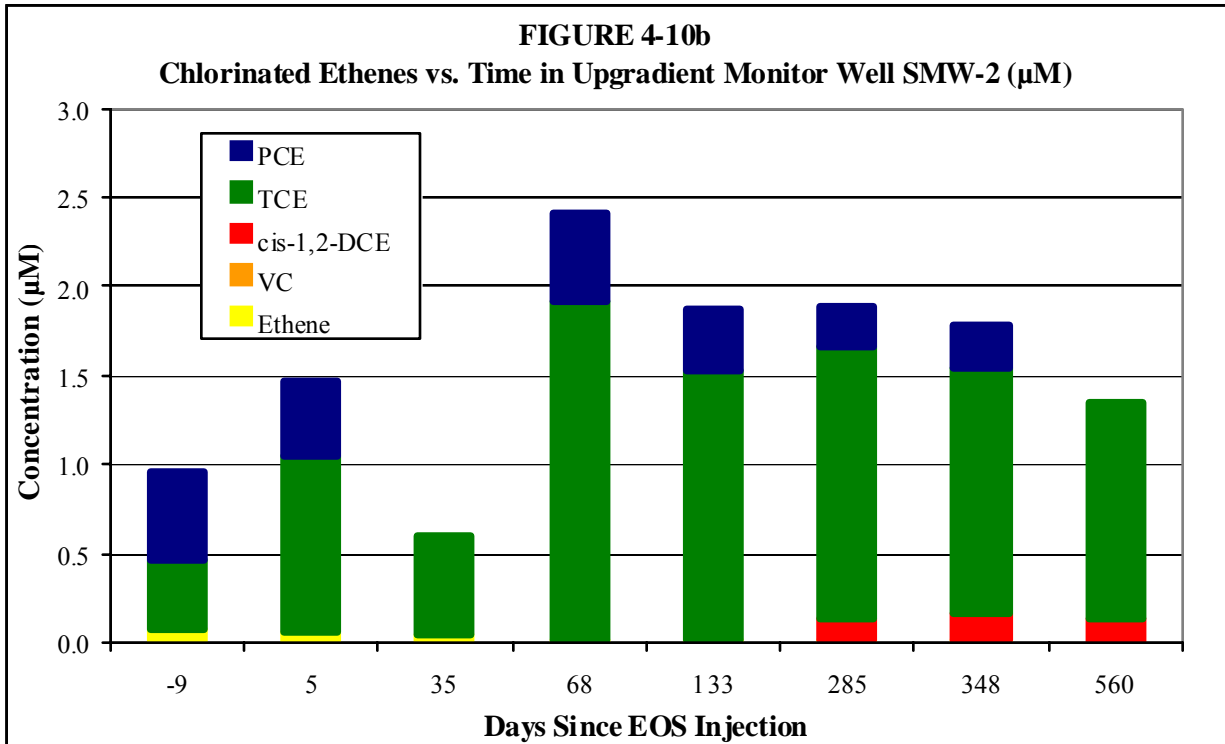
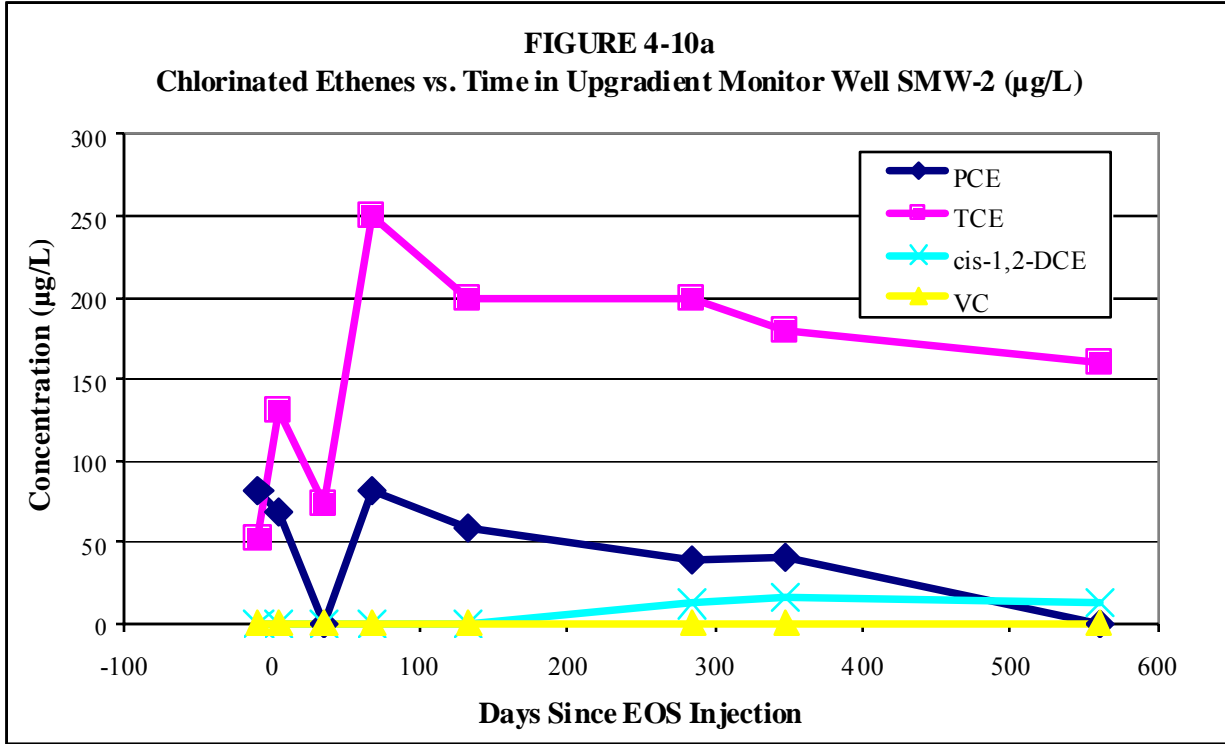
$$\text{Cl\#} = \frac{4 [\text{PCE}] + 3 [\text{TCE}] + 2 [\text{cis-1,2-DCE}] + [\text{VC}]}{[\text{PCE}] + [\text{TCE}] + [\text{cis-1,2-DCE}] + [\text{VC}] + [\text{Ethene}]}$$

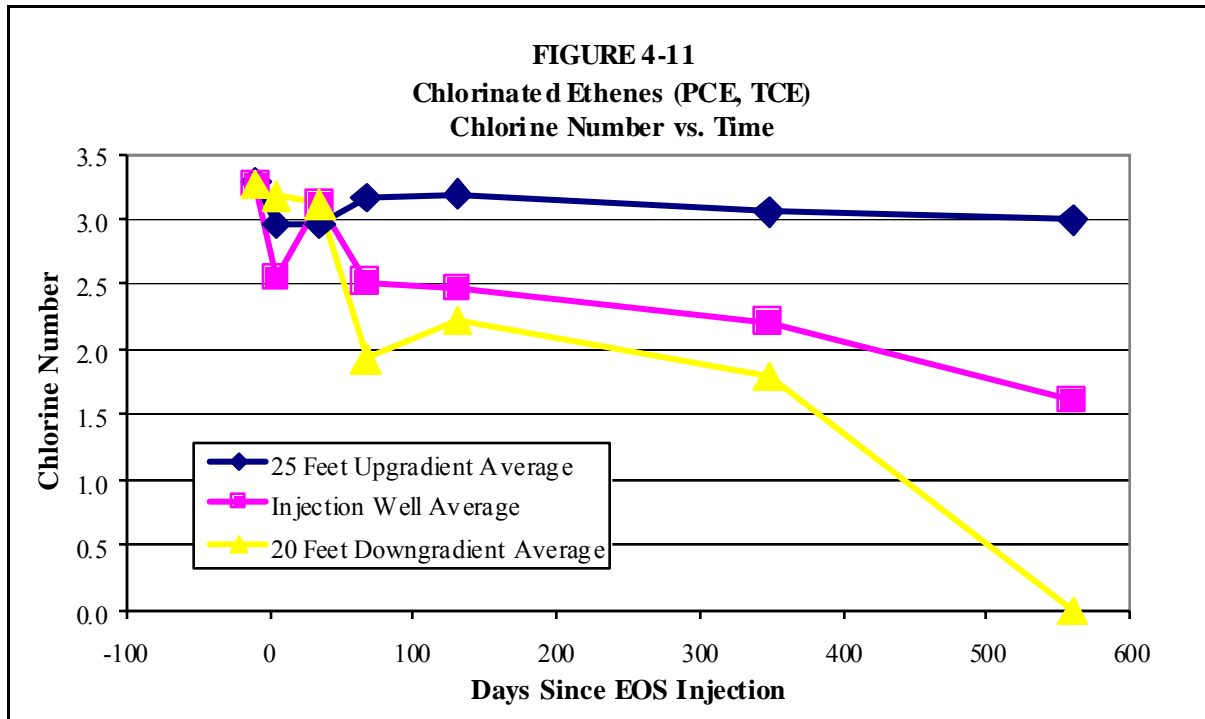
where [] indicates concentration in moles per liter. Groundwater containing only PCE would have a Cl# = 4.0. The chlorine numbers are tabulated in Table 4-8.

In general, the concentrations of chlorinated ethenes were substantially less than perchlorate or chlorinated ethanes with pre-injection concentrations of PCE ranging from 25 to 110 µg/L and TCE ranging from 28 to 210 µg/L. The following subsections discuss the chlorinated ethene results for the upgradient, injection, and downgradient wells during the 18-month pilot test.

Upgradient Monitor Wells

Throughout the pilot test, concentrations of chlorinated ethenes fluctuated in the upgradient monitor wells. PCE and TCE were the predominant chlorinated ethenes present in the upgradient wells. A few low concentrations of cis-1,2-DCE were detected, but vinyl chloride was not detected above the laboratory method detection limits. Figures 4-10a and b illustrate the chlorinated ethene results for upgradient monitor well SMW-2. As shown in these figures, although the chlorinated ethene concentrations fluctuated over time, the relative amounts of each chlorinated ethene compound remained similar. The chlorine numbers further illustrate this effect (Table 4-8 and Figure 4-11). The chlorine numbers for the upgradient wells fluctuated between 2.9 and 3.6 indicating that TCE was the predominant constituent.

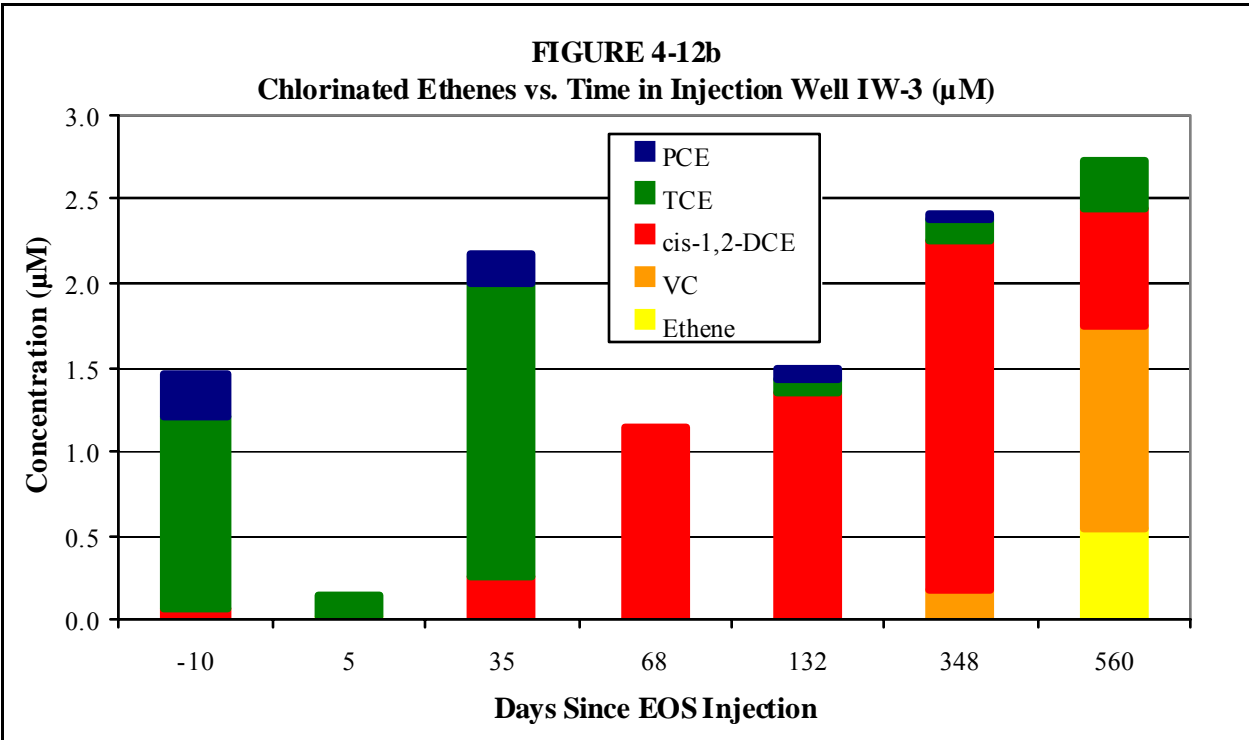
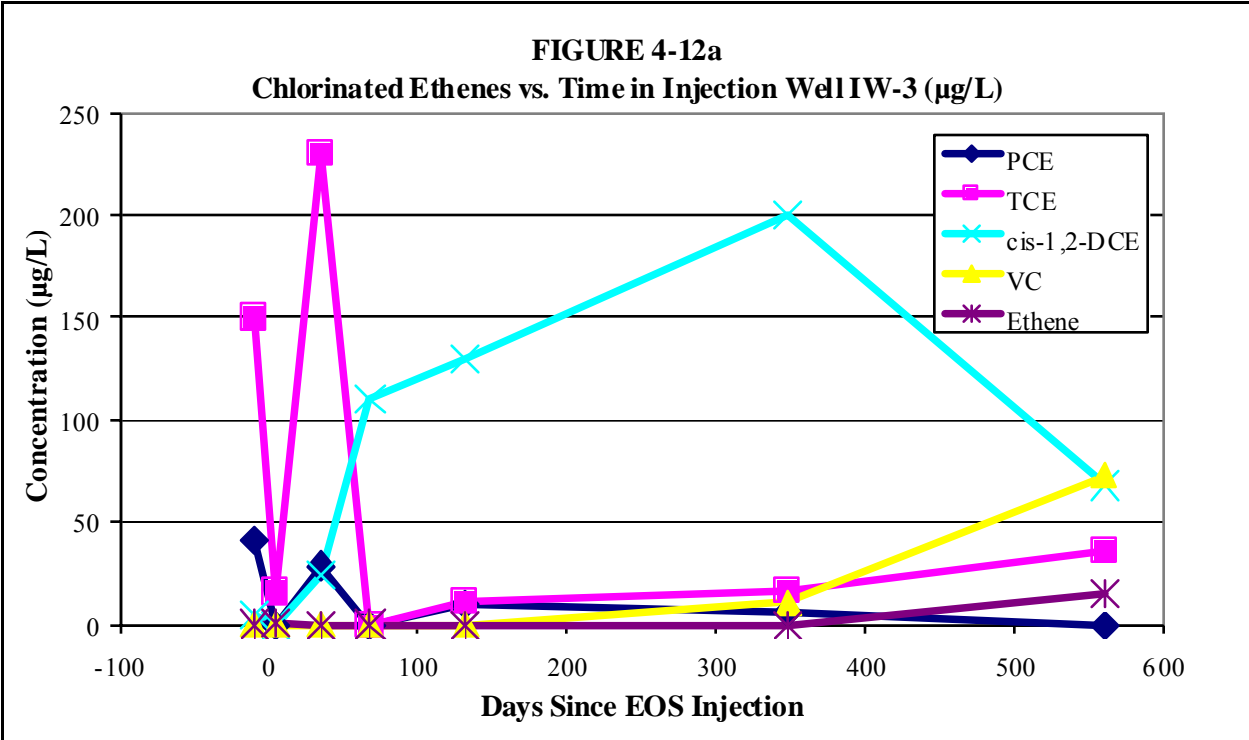




Injection Wells

In general, the chlorinated ethene results were similar to those for the chlorinated ethanes. Before injection, the chlorinated ethenes consisted of mostly PCE and TCE. Immediately after injection, PCE and TCE concentrations substantially reduced most likely due to sorption to the oil and/or dilution, since no substantial corresponding increases in daughter products were observed. PCE and TCE concentrations rebounded at 1 month post-injection and then reductive dechlorination activity was observed by 2 months post-injection. PCE and TCE concentrations decreased with corresponding production of cis-1,2-DCE. VC was only detected above the laboratory method detection limits in IW-1 and IW-3 near the end of the pilot test. During the 18-month sampling event, measurable increases in ethene concentrations were observed in IW-1, IW-3, IW-5, and IW-7 with concentrations ranging from 2.85 to 15.08 $\mu\text{g/L}$.

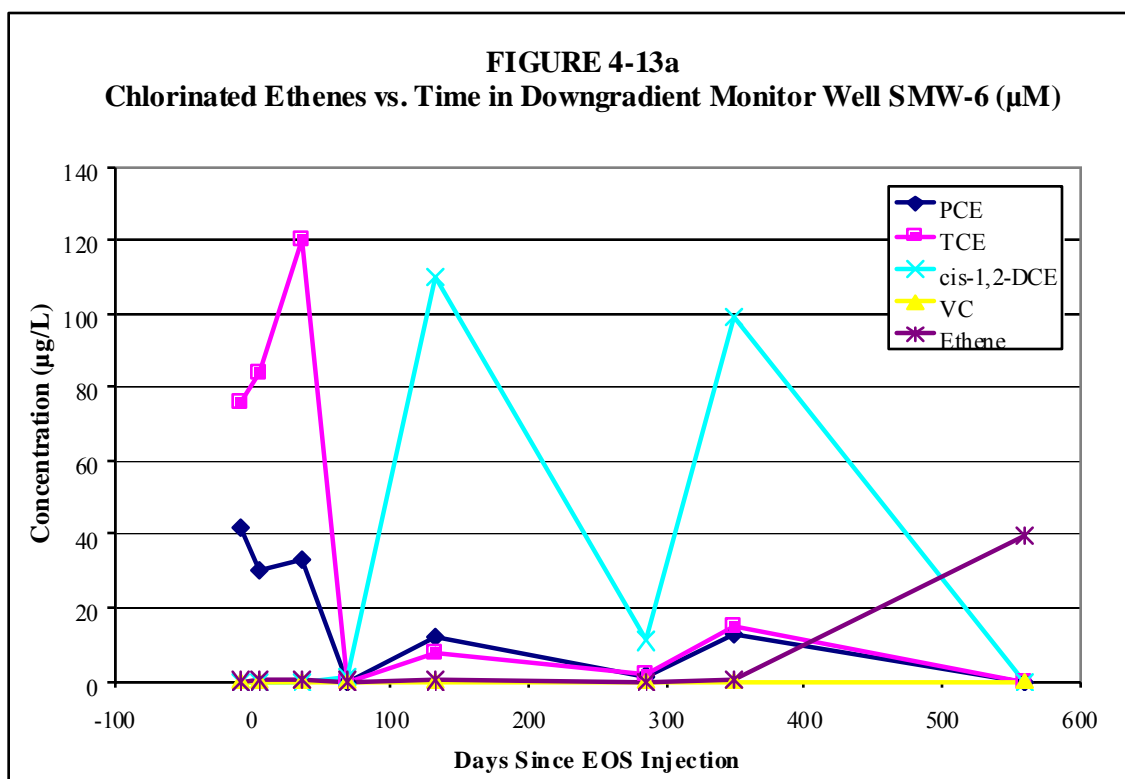
The chlorinated ethene results for IW-3 are displayed graphically on Figures 4-12a and b. These figures demonstrate the initial sorption of the solvents into the oil followed by desorption and subsequent biodegradation illustrating that sorption is a temporary effect and biodegradation is the ultimate reduction mechanism. This is confirmed by the changes in chlorine numbers for the injection wells (Table 4-8 and Figure 4-11). On average, the chlorine number was reduced from 3.3 to 1.6. These numbers indicate that before injection the groundwater consisted mostly of PCE and TCE and post-injection cis-1,2-DCE, VC, and ethene dominated.

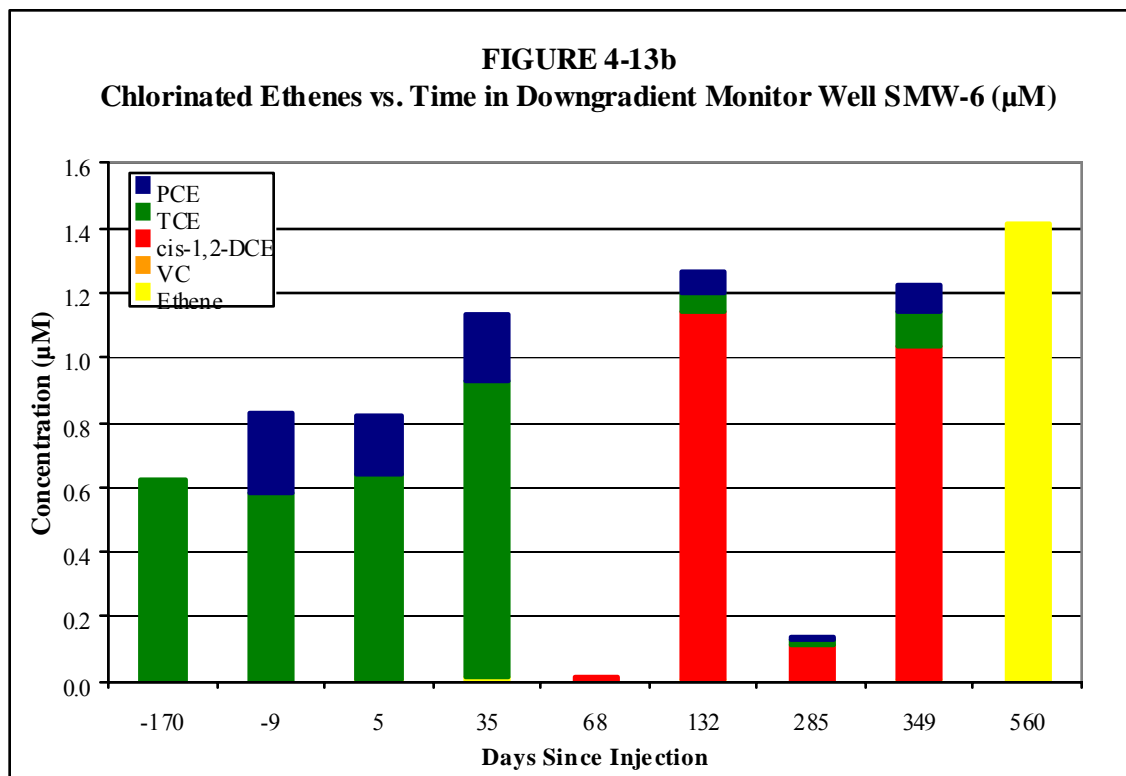


Downgradient Monitor Wells

Reductive dechlorination was observed in the downgradient monitor wells as groundwater moved through the emulsified oil PRB and the treated water appeared downgradient. Unlike the injection wells, a sharp decrease in PCE and TCE was not observed immediately after injection indicating that the sorption/dilution effects were limited to the vicinity of the injection wells. In general, the downgradient wells showed a decreasing trend in PCE and TCE followed by production of cis-1,2-DCE, VC, and ethene over the course of the 18-month pilot test. By 18 months post-injection, ethene predominated in the downgradient wells.

Figures 4-13a and b show the chlorinated ethene results for SMW-6 located 20 feet downgradient of the barrier. These figures illustrate the reduction of PCE and TCE, intermediate production of cis-1,2-DCE and VC, and subsequent production of ethene. Reductive dechlorination activity is confirmed by reductions in chlorine number. Twenty feet downgradient of the barrier, the average chlorine number decreased from 3.3 to 0 (see Table 4-8 and Figure 4-11) during the 18-month test period indicating complete dechlorination to non-toxic end products.





4.3.1.4 Biogeochemical Parameters

The goal of the EOS[®] injection was to create a reducing zone conducive to anaerobic biodegradation of perchlorate and chlorinated solvents. Various parameters can be indicative of reducing conditions. These parameters were monitored and evaluated over the course of the demonstration project to aid in interpretation of the contaminant data. The analytical results for the biogeochemical parameters that were evaluated at the site are summarized in Tables 4-11 and 4-12 and discussed in the following subsections.

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
UPGRADIENT MONITORING WELLS						
SMW-1 (25 feet)	7/21/03	NM	-97.4	6.04	21.5	346
	7/24/03	NM	3.3	6.27	22.7	269
	9/30/03	1.75	126.2	6.03	23.4	342
	10/13/03	0.83	97.3	5.95	22.0	395
	11/13/03	2.87	64	5.5	18.5	300
	12/16/03	1.91	103.3	5.8	14.3	300
	2/19/04	1.40	-199.4	5.8	9.0	286
	7/20/04	1.23	45.8	NM	22.1	200
	7/23/04	1.58	54.2	5.85	22.0	284
	9/21/04	1.00	112.9	5.84	23.7	286
	4/21/05	1.05	156.9	5.70	13.0	266
SMW-2 (25 feet)	7/21/03	NM	-19.4	5.82	19.7	291
	7/24/03	NM	60.4	5.89	20.4	228
	8/26/03	NM	204	6.5	21.8	310
	9/30/03	1.56	147.0	5.89	21.7	248
	10/13/03	1.36	104.1	5.81	20.5	283
	11/13/03	1.71	66	6.4	17.6	260
	12/16/03	0.92	119.2	5.9	13.6	270
	2/19/04	2.71	-143.6	5.9	8.3	220
	7/20/04	1.49	-42.3	NM	20.8	190
	7/23/04	1.00	72.5	5.92	20	253
	9/21/04	0.92	117.1	5.91	21.8	252
4/21/05	1.20	146.8	5.85	11.8	253	
SMW-3 (25 feet)	7/21/03	NM	-52.8	5.99	20.3	244
	7/24/03	NM	72.4	6.05	20.7	185
	9/30/03	1.50	116.0	6.19	20.3	234
	10/13/03	0.68	83.7	6.07	19.9	253
	11/13/03	2.96	22	6.0	16.6	230
	12/16/03	1.46	79.0	6.2	12.1	190
	2/19/04	3.10	-351.0	6.0	7.7	192.7
	7/20/04	1.28	-16.6	NM	20.2	160
	7/23/04	1.16	75.1	6.0	20.4	239
	9/21/04	1.45	111.7	6.15	21.9	192.9
	4/21/05	1.38	142.2	6.0	11.2	230
INJECTION WELLS						
IW-1	7/22/03	5.52	100.0	5.83	21.4	320
	7/24/03	NM	79.5	5.96	20.8	268
	8/26/03	NM	74	6.0	23.4	370
	9/29/03	2.44	101.8	6.01	22.3	242
	10/13/03	0.86	45.3	5.93	21.4	422
	11/13/03	2.07	<-100	6.2	18.2	470
	12/16/03	1.33	-95.4	6.8	12.6	420
	2/18/04	0.98	-528.9	5.9	9.6	412
	7/20/04	0.97	-42.6	NM	20.4	390
	7/23/04	0.90	-16.3	6.4	20.2	444
	9/21/04	0.82	-58.9	6.34	22.2	390
	4/21/05	1.34	80.4	6.24	12.1	295

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
IW-2	7/22/03	5.84	148.2	5.90	21.3	279
	7/24/03	NM	123.3	5.99	20.8	231
	8/26/03	NM	52	6.1	23.0	330
	9/29/03	4.52	106.8	5.98	21.9	241
	10/13/03	1.32	77.9	5.74	21.2	958
	11/13/03	1.59	-99	6.3	18.0	460
	12/16/03	1.04	-87.5	6.5	13.5	310
	2/18/04	1.29	-138.9	6.1	10.2	502
	7/20/04	1.14	-61.7	NM	20.3	510
	7/23/04	0.91	-41.1	6.54	20.1	595
	9/21/04	0.74	-88.3	6.54	22.6	592
	4/21/05	1.10	51.0	6.56	13.0	405
	IW-3	7/22/03	7.50	130.8	5.94	20.7
7/24/03		NM	118.0	6.03	20.7	458
8/26/03		NM	55	6.1	22.7	320
9/29/03		2.23	105.5	6.10	22.3	248
10/13/03		0.84	55.6	5.76	21.0	960
11/13/03		1.44	<-100	6.8	18.2	430
12/16/03		1.92	-124.6	6.5	14.8	440
2/18/04		1.40	-159.7	5.9	10.0	379
7/20/04		1.25	-56	NM	19.7	370
7/23/04		0.77	-27.9	6.38	19.1	783
9/21/04		1.07	-60.8	6.31	21.5	417
4/21/05		1.49	33.8	6.30	11.9	349
IW-4		7/22/03	6.02	164.4	5.79	21.0
	7/24/03	NM	150.9	5.81	20.8	353
	8/26/03	NM	110	6.2	22.3	260
	9/29/03	2.42	131.2	5.87	22.0	197
	10/13/03	1.25	97.0	5.68	21.0	394
	11/13/03	1.73	-89	5.7	17.8	380
	12/16/03	1.02	-83.2	6.2	13.6	420
	2/18/04	1.43	-125.7	5.8	9.8	445
	7/20/04	0.91	-54.1	NM	20.1	500
	7/23/04	0.81	-19.1	6.3	19.7	713
	9/21/04	0.74	-71.3	6.41	22.1	506
	4/21/05	1.15	39.7	6.50	12.1	342
	IW-5	7/22/03	5.98	165.8	5.86	19.5
7/24/03		NM	134.2	5.92	19.8	190.6
8/26/03		NM	118	6.5	21.8	280
9/29/03		3.77	132.7	5.84	20.9	197
10/13/03		0.91	71.4	5.72	21.0	379
11/13/03		1.41	-82	6.1	17.8	280
12/16/03		1.64	-106.4	6.1	13.4	290
2/18/04		0.87	-410	7.0	8.9	282
7/19/04		1.85	-84.8	6.2	20.1	310
7/23/04		0.97	-30.9	6.5	19.2	343
9/21/04		0.99	-54.9	6.47	21.7	402
4/21/05		1.23	4.6	6.44	11.5	301

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
IW-6	7/22/03	6.30	164.5	5.74	19.0	259
	7/24/03	NM	141.3	5.87	18.7	204
	8/26/03	NM	136	6.8	20.9	300
	9/29/03	4.48	128.5	5.95	20.3	215
	10/13/03	1.24	59.9	5.62	21.1	646
	11/13/03	1.09	-73	6.0	17.6	450
	12/16/03	1.22	-76.3	6.3	13.4	460
	2/18/04	1.32	-139.4	5.9	10.1	588
	7/20/04	0.95	-42.8	NM	19	340
	7/23/04	0.84	-29.5	6.44	18.2	416
	9/21/04	0.78	-48.3	6.18	22.0	435
	4/21/05	1.18	43.7	6.40	12.0	366
	IW-7	7/22/03	5.63	134.8	5.71	19.8
7/24/03		NM	127.1	5.81	19.8	185.3
9/29/03		3.46	136.8	5.98	20.7	180.2
10/13/03		2.00	73.8	5.56	20.4	449
11/13/03		1.42	-67	5.4	17.4	370
12/16/03		2.08	-83.6	6.2	12.7	390
2/18/04		0.98	-620	6.1	8.3	378
7/20/04		1.13	-49.2	NM	19.7	390
7/23/04		0.84	-34.5	6.41	18.9	410
9/21/04		1.18	-41.8	6.26	21.0	388
4/21/05		1.23	4.4	6.43	11.5	347
IW-8	7/22/03	5.90	131.9	5.69	19.9	233
	7/24/03	NM	119.6	5.82	18.9	190
	9/29/03	2.37	129.2	5.74	20.1	182.9
	10/13/03	1.03	81.0	5.68	20.5	615
	11/13/03	1.39	-70	5.6	17.1	410
	12/16/03	2.28	-88.2	6.5	13.2	430
	2/18/04	1.22	-743	6.6	8.7	328
	7/20/04	1.54	-39.1	NM	19	300
	7/23/04	0.89	-33.4	6.37	18.2	370
	9/21/04	0.91	-47.7	6.32	20.8	452
	4/21/05	1.31	31.7	6.55	12.1	317
IW-9	7/22/03	5.31	27.2	5.80	19.0	264
	7/24/03	NM	84.6	5.95	18.0	211
	9/29/03	1.89	129.2	5.89	19.7	201
	10/13/03	0.77	43.3	5.71	19.5	452
	11/13/03	1.87	-93	5.4	16.8	590
	12/16/03	2.64	-80.2	6.3	13.1	570
	2/18/04	1.45	-431	6.4	8.3	287
	7/20/04	1.48	-40	NM	18.4	240
	7/23/04	0.89	-34	6.35	17.8	318
	9/21/04	1.42	-40.1	6.24	20.0	293
	4/21/05	1.37	21.0	6.64	12.1	247

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
IW-10	7/22/03	5.48	119.3	5.79	18.9	234
	7/24/03	NM	118.3	5.90	17.8	186
	9/29/03	1.76	125.9	5.79	19.9	198
	10/13/03	0.84	32.4	5.85	19.5	394
	11/13/03	1.98	-65	5.2	17.0	260
	12/16/03	1.50	-75.5	6.5	12.3	260
	2/19/04	1.26	-481.7	5.9	8.2	272
	7/20/04	0.75	-36.5	NM	18.2	250
	7/23/04	0.90	-37.1	6.45	18	330
	9/21/04	1.26	-29.4	6.33	20.1	307
	4/21/05	1.11	-3.7	6.31	11.0	273
	DOWNGRADIENT MONITORING WELLS					
MW-6 (7.5 feet)	7/22/03	4.07	126.3	5.80	19.2	176.5
	7/24/03	NM	148.8	5.85	18.8	192.6
	8/26/03	NM	183	6.7	20.4	270
	9/30/03	5.83	153.5	5.79	21.3	157.7
	10/14/03	0.85	109.1	6.32	20.8	297
	11/13/03	3.56	-50	5.9	17.5	300
	12/16/03	2.84	16.9	6.7	13.4	300
	2/18/04	2.96	-154.0	6.0	8.2	227
	7/20/04	0.88	-37.9	NM	20.4	140
	7/23/04	0.44	-22.4	6.6	18.9	388
	9/22/04	0.51	-62.1	6.57	21.3	397
	4/21/05	0.39	-52.9	6.59	11.8	310
SMW-4 (12.5 feet)	7/21/03	NM	75.3	5.75	18.6	235
	7/24/03	NM	106.8	5.86	18.5	189
	8/26/03	NM	152	6.3	20.9	280
	9/30/03	1.54	153.5	5.64	20.7	225
	10/14/03	1.32	38.5	5.61	20.6	574
	11/13/03	1.49	<-100	5.8	17.8	390
	12/16/03	1.30	-90.3	6.6	14.0	370
	2/18/04	1.54	-48.9	6.3	9.0	317
	7/19/04	3.67	-45.9	7.37	19.0	280
	7/23/04	0.99	-27.9	6.88	18.4	386
	9/22/04	1.85	-59.7	6.80	20.5	387
	4/21/05	1.25	-20.7	6.80	11.3	374
SMW-5 (20 feet)	7/21/03	NM	81.7	5.70	18.8	283
	7/24/03	NM	98.5	5.89	18.0	221
	8/26/03	NM	167	6.7	20.8	310
	9/30/03	1.27	150.4	5.76	20.7	274
	10/14/03	0.69	59.8	5.85	20.5	439
	11/13/03	2.91	<-100	6.5	18.2	500
	12/16/03	1.79	-122.9	6.5	14.2	530
	2/18/04	3.90	-119.8	6.5	9.7	413
	7/20/04	0.64	-68.7	NM	17.8	380
	7/23/04	0.93	-46.2	6.89	17.9	533
	9/22/04	1.47	-85.6	6.83	20.4	489
	4/21/05	1.33	-53.1	6.84	11.8	417

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
SMW-6 (20 feet)	4/22/03	NM	NM	6.05	8.8	245
	7/22/03	NM	79.8	5.76	19.4	235
	7/24/03	NM	98.3	5.93	17.6	189.9
	8/26/03	NM	165	6.9	20.4	290
	9/30/03	4.66	153.7	5.39	20.4	145.1
	10/14/03	1.67	106.9	5.61	19.4	258
	11/13/03	2.94	-89	6.4	17.6	430
	12/16/03	3.11	12.2	6.2	14.0	450
	2/18/04	2.69	-153.5	6.1	10.1	199.2
	7/20/04	2.94	-58.9	5.66	18.8	80
	7/23/04	2.29	-11.7	5.97	18.5	176.1
	9/22/04	1.53	-71.4	6.66	20.0	404
	4/21/05	1.69	-7.8	6.45	12.1	233
	SMW-7 (20 feet)	7/21/03	NM	16.7	5.79	18.4
7/24/03		NM	84.5	5.90	17.1	203
9/30/03		1.72	146.0	5.79	19.2	228
10/14/03		1.36	115.1	5.70	18.9	254
11/13/03		1.09	<-100	6.3	17.1	440
12/16/03		0.94	-85.7	6.7	13.0	210
2/18/04		1.41	115.8	6.2	9.6	320
7/20/04		1.09	-99.9	NM	17.1	350
7/23/04		1.51	-33.0	6.85	17.6	490
9/22/04		1.17	-73.2	6.87	20.1	453
4/21/05		1.49	-21.8	6.81	11.6	383
TRACER TEST WELLS						
TT-1	4/22/03	NM	NM	6.30	9.7	266
	7/22/03	NM	9.4	6.07	21.2	274
	7/24/03	NM	70.7	6.04	19.63	216
	10/13/03	1.60	120.2	5.91	20.7	228
	7/20/04	1.64	55.3	NM	19.6	130
	7/23/04	3.13	80.2	6.04	19.2	235
	TT-2	7/21/03	NM	116.3	5.88	20.0
8/26/03		NM	123	6.6	22.1	320
9/30/03		1.50	116.0	6.19	20.3	234
10/13/03		1.71	128.2	5.86	21.3	269
11/13/03		4.94	81	5.9	17.8	260
12/16/03		1.58	44.9	6.2	13.5	250
2/18/04		4.21	-237.2	6.3	9.4	188.6
7/20/04		2.31	51.2	NM	20.2	180
7/23/04		2.76	-29.2	7.17	25.0	910
9/21/04		1.79	54.2	6.14	21.9	244
4/21/05		3.28	150.1	6.02	11.5	253

TABLE 4-11
Summary of Field Measurements
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Dissolved Oxygen (mg/L)	ORP (mV)	pH	Temperature (°C)	Conductivity (µS/cm)
AIR STRIPPER						
Influent	9/29/03	NM	146.8	5.69	20.8	168.5
	10/13/03	NM	NM	NM	NM	NM
	11/13/03	NM	NM	NM	NM	NM
	12/16/03	NM	NM	NM	NM	NM
	2/18/04	NM	-63	6.4	8.7	310
	9/22/04	NM	18.6	6.33	22.1	245
	4/21/05	1.35	12.0	6.29	14.8	177
	Effluent	9/29/03	NM	132.0	6.91	18.3
10/13/03		NM	NM	NM	NM	NM
11/13/03		NM	NM	NM	NM	NM
12/16/03		NM	NM	NM	NM	NM
2/18/04		NM	-70	6.4	8.9	320
9/22/04		NM	49.4	6.72	21.0	245
4/21/05		10.35	17.5	7.08	15.2	17.5

Note:
 NM denotes not measured.

TABLE 4-12
Summary of Measured Groundwater Biogeochemical Parameters
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Sulfate (mg/L)	Phosphate (mg/L)	Dissolved Iron (mg/L)	Arsenic (mg/L)	Manganese (mg/L)	Methane (µg/L)
UPGRADIENT MONITORING WELLS										
SMW-1 (25 feet)	7/21/03	17.6	16.2	<0.5	35.2	<0.5	NA	NA	NA	NA
	7/24/03	16.6/16.7	15.5/15.6	<0.5/<0.5	32.6/32.3	<0.5/<0.5	NA	NA	NA	NA
	9/30/03	17.6	11.0	<0.5	34.3	1.3	NA	NA	NA	0.4
	10/13/03	30.1	10.6	<0.5	42.0	1.8	NA	NA	NA	5.6
	11/13/03	18.8/18.8	10.4/10.4	<0.5/<0.5	32.1/31.8	1.6/1.8	NA	NA	NA	0.4
	12/16/03	21.9	10.9	<0.5	26.9	2.0	NA	NA	NA	1.0
	2/19/04	22.0	10.2	<0.5	31.7	2.5	NA	NA	NA	2.2
	7/20/04	19.1	8.2	<0.5	29.1	2.4	NA	NA	NA	NA
	7/23/04	18.7	7.1	<0.5	29.8	2.7	NA	NA	NA	NA
	9/21/04	20.7	6.5	<0.5	28.6	<10	NA	NA	NA	4.9
	4/21/05	21.8	7.0	<0.5	31.7	2.2	NA	NA	NA	7.1
	SMW-2 (25 feet)	7/21/03	16.1	16.2	<0.5	34.2	<0.5	NA	NA	NA
7/24/03		15.1	15.6	<0.5	31.2	<0.5	NA	NA	NA	NA
8/26/03		15.8/16.1	9.2/9.2	<0.5/<0.5	32.4/32.6	2.0/2.1	NA	NA	NA	NA
9/30/03		17.9	7.4	<0.5	34.4	1.8	<0.5	<0.010	0.36	0.6
10/13/03		19.3	8.5	<0.5	33.6	3.9	1.9	<0.010	0.35	0.5
11/13/03		20.0	9.8	<0.5	33.4	1.6	<0.5	<0.010	0.28	1.3
12/16/03		16.2	6.7	<0.5	23.8	1.2	<0.5	<0.010	0.18	1.0
2/19/04		17.8	10.0	<0.5	27.8	2.7	<0.5	<0.010	0.18	0.6
7/20/04		16.9	6.0	<0.5	29.1	1.9	NA	NA	NA	3.7
7/23/04		16.2	5.9	<0.5	28.3	3.1	NA	NA	NA	NA
8/24/04		17.1	4.5	<0.5	28.3	<0.5	NA	NA	NA	NA
9/21/04		18.9/19.2	6.0/6.1	<0.5/<0.5	25.9/25.3	<10/<10	<0.5	<0.010	0.13	3.6
4/21/05	19.7	7.2	<0.5	26.6	2.4	<0.10	<0.010	0.17	1.7	
SMW-3 (25 feet)	7/21/03	14.2	6.9	<0.5	34.3	<0.5	NA	NA	NA	NA
	7/24/03	14.4	4.6	<0.5	31.3	<0.5	NA	NA	NA	NA
	9/30/03	14.1/14.8	7.0/7.2	<0.5/<0.5	26.4/26.5	2.0/2.2	NA	NA	NA	0.5
	10/13/03	16.2	4.2	<0.5	35.4	<0.5	NA	NA	NA	<0.2
	11/13/03	16.8/16.5	14.6/14.5	<0.5/<0.5	28.2/28.0	0.9/<0.5	NA	NA	NA	0.5
	12/16/03	18.3/17.8	11.0/11.0	<0.5/<0.5	24.3/24.2	1.7/1.8	NA	NA	NA	0.4
	2/19/04	17.0	15.2	<0.5	24.1	2.0	NA	NA	NA	<0.2
	7/20/04	13.5	8.7	<0.5	22.7	2.5	NA	NA	NA	NA
	7/23/04	13.8/13.6	8.7/8.7	<0.5/<0.5	23.4/23.4	2.6/1.9	NA	NA	NA	NA
	9/21/04	10.0	6.9	<0.5	18.8	<10	NA	NA	NA	0.9
	4/21/05	17.8	6.4	<0.5	24.0	1.7	NA	NA	NA	4.6
	INJECTION WELLS									
IW-1	7/22/03	17.2/16.7	16.4/16.7	<0.5/<0.5	28.4/28.2	<0.5/<0.5	NA	NA	NA	NA
	7/24/03	12.0	12.2	<0.5	19.3	<0.5	NA	NA	NA	NA
	8/26/03	18.9	14.7	<0.5	28.0	<0.5	NA	NA	NA	NA
	9/29/03	18.0	13.9	<0.5	28.1	<0.5	NA	NA	NA	0.8
	10/13/03	19.0/18.6	<0.5/<0.5	<0.5/<0.5	23.2/23.0	<0.5/<0.5	NA	NA	NA	<0.2
	11/13/03	12.2/12.2	<0.5/<0.5	<0.5/<0.5	1.1/0.4	<0.5/<0.5	NA	NA	NA	8.3
	12/16/03	13.7/16	<0.5/<0.5	<0.5/<0.5	1.2/1.6	<0.5/<0.5	NA	NA	NA	166.0
	2/18/04	18.9	<0.5	<0.5	6.3	<0.5	NA	NA	NA	1047.1
	7/20/04	14.6	<0.5	<0.5	6.9	<0.5	NA	NA	NA	NA
	7/23/04	16.4	<0.5	<0.5	10.2	<0.5	NA	NA	NA	NA
	8/24/04	15.6/15.7	<0.5/<0.5	<0.5/<0.5	11.0/11.2	<0.5/<0.5	NA	NA	NA	NA
	9/21/04	15.8	1.5	<0.5	12.0	<10	NA	NA	NA	3636.9
	4/21/05	21.5	0.5	<0.5	15.7	<1	NA	NA	NA	3436.7

TABLE 4-12
Summary of Measured Groundwater Biogeochemical Parameters
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Sulfate (mg/L)	Phosphate (mg/L)	Dissolved Iron (mg/L)	Arsenic (mg/L)	Manganese (mg/L)	Methane (µg/L)
IW-2	7/22/03	14.0	19.8	<0.5	28.6	<0.5	NA	NA	NA	NA
	7/24/03	13.3/13.6	18.7/18.5	<0.5/<0.5	27.7/28.3	<0.5/<0.5	NA	NA	NA	NA
	8/26/03	15.9	14.7	<0.5	29.6	<0.5	NA	NA	NA	NA
	7/20/04	14.7	<0.5	<0.5	<0.5	<0.5	NA	NA	NA	NA
	7/23/04	14.2	<0.5	<0.5	<0.5	<0.5	NA	NA	NA	NA
	8/24/04	10.3	<0.5	<0.5	<0.5	<0.5	NA	NA	NA	NA
IW-3	7/22/03	13.8	17.3	<0.5	30.9	<0.5	NA	NA	NA	NA
	7/24/03	11.9	11.7	<0.5	21.6	<0.5	NA	NA	NA	NA
	8/26/03	15.1/15.3	14.5/14.6	<0.5/<0.5	36.0/30.5	<0.5/<0.5	NA	NA	NA	NA
	9/29/03	16.9	12.9	<0.5	30.1	<0.5	<0.5	<0.010	0.052	0.5
	10/13/03	13.1	<0.5	<0.5	27.6	<0.5	0.86	<0.010	3.6	0.5
	11/13/03	18.3	<0.5	<0.5	7.7	<0.5	69	0.011	16	2.7
	12/16/03	13.4	<0.5	<0.5	1.9	<0.5	24	<0.010	8.9	141.8
	2/18/04	23.0	<0.5	<0.5	1.4	<0.5	11	<0.010	4.1	395.4
	7/20/04	20.2	<0.5	<0.5	<0.5	<0.5	NA	NA	NA	NA
	7/23/04	18.6/18.6	<0.5/<0.5	<0.5/<0.5	1.4/1.5	<0.5/<0.5	NA	NA	NA	NA
	8/24/04	16.8	<0.5	<0.5	<0.5	<0.5	NA	NA	NA	NA
	9/21/04	23.8	<0.5	<0.5	2.7	<10	33	<0.010	3.1	2043.0
	4/21/05	22.7	<0.5	<0.5	11.0	<1	30	0.0054 J	3.1	3890.7
IW-4	7/22/03	9.5	15.6	<0.5	25.7	<0.5	NA	NA	NA	NA
	7/24/03	8.8	10.8	<0.5	14.9	<0.5	NA	NA	NA	NA
	8/26/03	12.2	9.7	<0.5	26.5	<0.5	NA	NA	NA	NA
	7/20/04	10.9/11.0	<0.5/<0.5	<0.5/<0.5	2.2/2.3	<0.5/<0.5	NA	NA	NA	NA
	7/23/04	13.0	<0.5	<0.5	4.6	<0.5	NA	NA	NA	NA
	8/24/04	10.8	<0.5	<0.5	1.8	<0.5	NA	NA	NA	NA
IW-5	7/22/03	10.8	14.5	<0.5	25.6	<0.5	NA	NA	NA	NA
	7/24/03	10.6	13.8	<0.5	25.5	<0.5	NA	NA	NA	NA
	8/26/03	14.0	11.3	<0.5	29.4	1.0	NA	NA	NA	NA
	9/29/03	11.3	10.9	<0.5	23.9	2.7	NA	NA	NA	<0.2
	10/13/03	9.2	<0.5	<0.5	19.9	0.8	NA	NA	NA	0.9
	11/13/03	11.9	<0.5	<0.5	10.1	<0.5	NA	NA	NA	2.3
	12/16/03	9.0/10.0	<0.5/<0.5	<0.5/<0.5	2.0/2.3	<0.5/<0.5	NA	NA	NA	58.7
	2/18/04	13.1	<0.5	<0.5	2.7	<0.5	NA	NA	NA	136.0
	7/19/04	15.6/16.1	<0.5/<0.5	<0.5/<0.5	5.0/5.1	<0.5/<0.5	NA	NA	NA	2250.5
	7/23/04	14.0	<0.5	<0.5	6.4	<0.5	NA	NA	NA	NA
	8/24/04	13.6	<0.5	<0.5	4.0	<0.5	NA	NA	NA	NA
	9/21/04	17.9/18.5	<0.5/<0.5	<0.5/<0.5	6.3/6.6	<10/<10	NA	NA	NA	5394.3
4/21/05	16.5	0.9	<0.5	16.3	<1	NA	NA	NA	2919.3	
IW-6	7/22/03	13.9/15.0	17.2/18.9	<0.5/<0.5	27.2/31.0	<0.5/<0.5	NA	NA	NA	NA
	7/24/03	14.5	16.7	<0.5	30.3	<0.5	NA	NA	NA	NA
	8/26/03	15.6	10.8	<0.5	31.1	1.9	NA	NA	NA	NA
	7/20/04	18.0	<0.5	<0.5	5.6	<0.5	NA	NA	NA	NA
	7/23/04	16.8	<0.5	<0.5	6.8	<0.5	NA	NA	NA	NA
	8/24/04	17.5/18.8	<0.5/<0.5	<0.5/<0.5	5.5/5.8	<0.5/<0.5	NA	NA	NA	NA

TABLE 4-12
Summary of Measured Groundwater Biogeochemical Parameters
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Sulfate (mg/L)	Phosphate (mg/L)	Dissolved Iron (mg/L)	Arsenic (mg/L)	Manganese (mg/L)	Methane (µg/L)
IW-7	7/22/03	12.3	15.1	<0.5	28.8	<0.5	NA	NA	NA	NA
	7/24/03	12.9/12.7	12.6/12.5	<0.5	30.1/29.5	<0.5	NA	NA	NA	NA
	9/29/03	12.5/13.3	6.1/6.5	<0.5/<0.5	26.9/28.5	0.7/0.6	<0.5	<0.010	0.60	<0.2
	10/13/03	9.9	<0.5	<0.5	24.8	0.8	<0.5	<0.010	2.4	1.1
	11/13/03	11.0	<0.5	<0.5	11.9	<0.5	78	<0.010	13	24.9
	12/16/03	7.2	<0.5	<0.5	1.9	<0.5	26	<0.010	10	129.0
	2/18/04	13.3/13.7	<0.5/<0.5	<0.5/<0.5	4.4/4.4	<0.5/<0.5	29	<0.010	7.0	207.5
	7/20/04	10.9	<0.5	<0.5	4.3	<0.5	NA	NA	NA	NA
	7/23/04	14.3	<0.5	<0.5	8.5	<0.5	NA	NA	NA	NA
	9/21/04	18.0	<0.5	<0.5	12.0	<10	45	<0.010	5.0	4,637.6
4/21/05	11.6/11.8	0.8/0.8	<0.5/<0.5	10.9/10.9	<1/<1	38	0.0081 J	5.4	3,878.5	
IW-8	7/22/03	13.4	14.8	<0.5	30.4	<0.5	NA	NA	NA	NA
	7/24/03	12.1	11.9	<0.5	26.5	<0.5	NA	NA	NA	NA
	7/20/04	9.8	<0.5	<0.5	5.1	<0.5	NA	NA	NA	NA
	7/23/04	16.2/16.1	<0.5/<0.5	<0.5/<0.5	8.5/8.5	<0.5/<0.5	NA	NA	NA	NA
IW-9	7/22/03	15.3	19.3	<0.5	28.9	<0.5	NA	NA	NA	NA
	7/24/03	15.3	17.5	<0.5	29.3	<0.5	NA	NA	NA	NA
	7/20/04	16.8	<0.5	<0.5	1.6	<0.5	NA	NA	NA	NA
	7/23/04	20.9	<0.5	<0.5	5.2	<0.5	NA	NA	NA	NA
IW-10	7/22/03	13.4	11.9	<0.5	27.1	<0.5	NA	NA	NA	NA
	7/24/03	14.2	10.1	<0.5	31.3	<0.5	NA	NA	NA	NA
	9/29/03	12.3	5.5	<0.5	27.5	1.7	NA	NA	NA	<0.2
	10/13/03	17.4	<0.5	<0.5	30.3	2.2	NA	NA	NA	0.3
	11/13/03	15.9	<0.5	<0.5	7.4	<0.5	NA	NA	NA	0.3
	12/16/03	17.3	<0.5	<0.5	2.6	<0.5	NA	NA	NA	0.8
	2/19/04	21.5	<0.5	<0.5	2.3	<0.5	NA	NA	NA	17.7
	7/20/04	16.9/16.9	<0.5/<0.5	<0.5/<0.5	4.9/4.8	<0.5/<0.5	NA	NA	NA	NA
	7/23/04	19.4	<0.5	<0.5	8.2	<0.5	NA	NA	NA	NA
	9/21/04	19.1	<0.5	<0.5	12.4	<10	NA	NA	NA	1279.0
4/21/05	20.9	0.5	<0.5	17.5	<1	NA	NA	NA	1013.0	
DOWNGRADIENT MONITORING WELLS										
MW-6 (7.5 feet)	7/22/03	8.5/8.8	11.9/12.0	<0.5/<0.5	22.9/22.7	<0.5/<0.5	NA	NA	NA	NA
	7/24/03	11.5	15.1	<0.5	27.5	<0.5	NA	NA	NA	NA
	8/26/03	12.9/13.0	10.3/10.2	<0.5/<0.5	28.4/28.6	0.9/0.8	NA	NA	NA	NA
	9/30/03	6.6	4.6	<0.5	18.3	0.6	<0.5	<0.010	0.11	<0.2
	10/14/03	11.1/11.2	<0.5/<0.5	<0.5/<0.5	27.9/27.8	<0.5/<0.5	<0.5	<0.010	46	<0.2
	11/13/03	9.9	<0.5	<0.5	11.1	<0.5	1.8	<0.010	22	0.2
	12/16/03	1.5/1.8	<0.5/<0.5	<0.5/<0.5	9.4/12.7	<0.5/<0.5	1.3	<0.010	11	1.9
	2/18/04	2.5	<0.5	<0.5	12.6	<0.5	<0.5	<0.010	12	74.8
	7/20/04	3.3	<0.5	<0.5	13.1	<0.5	NA	NA	NA	NA
	7/23/04	11.0/11.3	<0.5/<0.5	<0.5/<0.5	10.5/10.5	<0.5/<0.5	NA	NA	NA	NA
	8/24/04	8.5	<0.5	<0.5	9.5	<0.5	NA	NA	NA	NA
	9/22/04	19.4	<0.5	<0.5	7.4	<10	37	<0.010	9.3	5,223.4
	4/21/05	17.2	<0.5	<0.5	8.7	<1	19	0.014	9.7	1,463.8

TABLE 4-12
Summary of Measured Groundwater Biogeochemical Parameters
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Sulfate (mg/L)	Phosphate (mg/L)	Dissolved Iron (mg/L)	Arsenic (mg/L)	Manganese (mg/L)	Methane (µg/L)
SMW-4 (12.5 feet)	7/21/03	11.8	16.6	<0.5	26.8	<0.5	NA	NA	NA	NA
	7/24/03	12.0	16.1	<0.5	28.1	<0.5	NA	NA	NA	NA
	8/26/03	14.4	10.7	<0.5	31.2	1.2	NA	NA	NA	NA
	9/30/03	14.8/12.6	12.6/10.8	<0.5/<0.5	29.4/26.6	1.0/0.9	<0.5	<0.010	0.14	<0.2
	10/14/03	12.1/13.8	<0.5/<0.5	<0.5/<0.5	42.4/43.8	1.1/0.6	1.2	<0.010	4.8	0.2
	11/13/03	15.9	<0.5	<0.5	8.0	<0.5	22.0	<0.010	14.0	0.6
	12/16/03	11.2	<0.5	<0.5	<0.5	<0.5	3.5	<0.010	19	0.5
	2/18/04	16.0/16.1	<0.5/<0.5	<0.5/<0.5	1.5/1.6	<0.5/<0.5	1.0	<0.010	15	75.7
	7/19/04	15.7	<0.5	<0.5	12.4	<0.5	NA	NA	NA	261.2
	7/23/04	15.7	<0.5	<0.5	11.4	<0.5	NA	NA	NA	NA
	8/24/04	14.7	<0.5	<0.5	10.2	<0.5	NA	NA	NA	NA
	9/22/04	16.8	<0.5	<0.5	12.6	<10	<0.5	<0.010	18	2,977.9
4/21/05	17.4/17.2	<0.5/<0.5	<0.5/<0.5	8.2/8.2	<1/<1	23	0.0098 J	5.5	3,551.5	
SMW-5 (20 feet)	7/21/03	13.0	15.8	<0.5	25	<0.5	NA	NA	NA	NA
	7/24/03	14.3	18.0	<0.5	31.4	<0.5	NA	NA	NA	NA
	8/26/03	15.2	13.1	<0.5	31.1	<0.5	NA	NA	NA	NA
	9/30/03	17.2	13.9	<0.5	31.6	<0.5	NA	NA	NA	0.4
	10/14/03	17.9/17.4	<0.5/<0.5	<0.5/<0.5	37.2/37.7	<0.5/<0.5	NA	NA	NA	<0.2
	11/13/03	25.4	<0.5	<0.5	5.2	<0.5	NA	NA	NA	0.6
	12/16/03	21.2	<0.5	<0.5	1.8	<0.5	NA	NA	NA	1.9
	2/18/04	23.4	<0.5	<0.5	2.2	<0.5	NA	NA	NA	497.9
	7/20/04	19.3	<0.5	<0.5	3.1	<0.5	NA	NA	NA	NA
	7/23/04	18.4	<0.5	<0.5	3.0	<0.5	NA	NA	NA	NA
	8/24/04	19.7	<0.5	<0.5	4.2	<0.5	NA	NA	NA	NA
	9/22/04	22.5	<0.5	<0.5	6.2	<10	NA	NA	NA	4,149.5
4/21/05	24.8	<0.5	<0.5	0.9	<1	NA	NA	NA	3,117.0	
SMW-6 (20 feet)	7/22/03	13.4	17.4	<0.5	27.1	<0.5	NA	NA	NA	NA
	7/24/03	13.0/13.2	18.3/17.9	<0.5/<0.5	28.4/28.5	<0.5/<0.5	NA	NA	NA	NA
	8/26/03	14.8	11.3	<0.5	31.2	0.8	NA	NA	NA	NA
	9/30/03	11.5	<0.5	<0.5	23.3	<0.5	<0.5	<0.010	0.11	0.3
	10/14/03	13.8	<0.5	<0.5	26.3	<0.5	<0.5	<0.010	1.3	<0.2
	11/13/03	13.8/14.2	<0.5	<0.5	5.6/5.7	<0.5	2.6	<0.010	1.4	0.5
	12/16/03	2.2	0.9	<0.5	12.7	<0.5	4.1	<0.010	2.4	<0.2
	2/18/04	14.6	<0.5	<0.5	6.8	<0.5	<0.5	<0.010	6.7	97.2
	7/20/04	3.1	<0.5	<0.5	8.4	<0.5	NA	NA	NA	500.4
	7/23/04	8.2	<0.5	<0.5	7.2	<0.5	NA	NA	NA	NA
	8/24/04	8.5/8.6	<0.5/<0.5	<0.5/<0.5	10.7/10.8	<0.5/<0.5	NA	NA	NA	NA
	9/22/04	15.7/17.7	0.8/<0.5	<0.5/>0.5	6.6/8.9	<10/<10	NA	<0.010	11	4,466.8
4/21/05	15.4	<0.5	<0.5	6.5	<1	13	0.0049 J	3.6	2,194.3	
SMW-7 (20 feet)	7/21/03	14.9	17.8	<0.5	31.0	<0.5	NA	NA	NA	NA
	7/24/03	12.3	14.4	<0.5	22.1	<0.5	NA	NA	NA	NA
	9/30/03	14.3	8.4	<0.5	26.4	1.0	NA	NA	NA	<0.2
	10/14/03	25.2	4.1	<0.5	51.5	<0.5	NA	NA	NA	<0.2
	11/13/03	19.9	<0.5	<0.5	6.9	<0.5	NA	NA	NA	0.4
	12/16/03	13.6	<0.5	<0.5	9.8	<0.5	NA	NA	NA	0.5
	2/18/04	22.4	<0.5	<0.5	9.5	<0.5	NA	NA	NA	20.2
	7/20/04	19.7	<0.5	<0.5	2.9	<0.5	NA	NA	NA	NA
	7/23/04	18.4	<0.5	<0.5	3.4	<0.5	NA	NA	NA	NA
	9/22/04	21.0/20.6	<0.5/<0.5	<0.5/<0.5	8.5/8.5	<10/<10	NA	NA	NA	3,002.3
	4/21/05	20.8	<0.5	<0.5	8.2	<1	NA	NA	NA	3,358.6

Competing Electron Acceptors

Various electron acceptors can potentially compete with reductive dechlorination, including dissolved oxygen, nitrate, sulfate, iron (III), manganese (IV), and carbon dioxide (methanogenesis). These parameters or their byproducts (e.g., Fe(II), Mn(II), methane) were measured to assess conditions at the site. A brief discussion of each parameter is provided below.

Dissolved Oxygen

Dissolved oxygen is used by microbes as an electron acceptor for the biodegradation of organic carbon. Perchlorate degradation and reductive dechlorination are anaerobic processes. DO concentrations <0.5 mg/L are favorable for anaerobic biodegradation.

The DO data are shown on Table 4-11. In general, DO levels have decreased across the entire pilot test area. The DO concentrations do not indicate strongly anaerobic conditions; however, the results for the other biogeochemical parameters and for the constituents of concern indicate that conditions favorable for anaerobic biodegradation have been established.

Nitrate

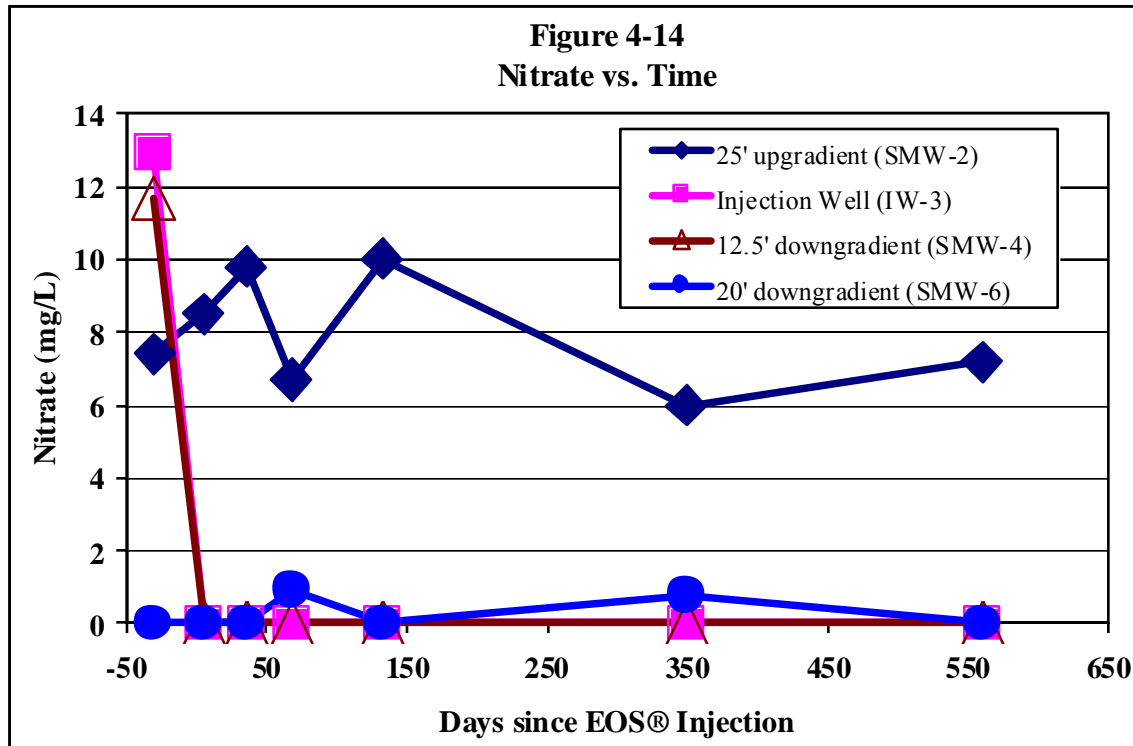
Nitrate reduction is another indicator of anaerobic conditions favorable for biodegradation. Following depletion of oxygen, denitrification can occur resulting in decreased nitrate concentrations in the aquifer.

Prior to EOS[®] injection, the average nitrate concentration in the injection wells was 9.9 mg/L. Immediately after injection, nitrate was not detected (<0.5 mg/L) in any of the injection wells. Nitrate remained at non-detectable levels in all of the injection wells until the 11-month post-injection sampling event when nitrate was detected in IW-1 at a concentration of 1.5 mg/L. During the 18-month sampling event, low levels of nitrate (<1 mg/L) were detected in all of the four sampled injection wells except IW-3 which was still non-detect (<0.5 mg/L).

Within 1 month of EOS[®] injection, nitrate was below detection (<0.5 mg/L) in all of the down gradient monitor wells. All down gradient monitor wells continued to show non-detectable levels of nitrate throughout the 18-month pilot test with the exception of two low detections observed in SMW-6. Nitrate concentrations have remained essentially unchanged in the up gradient wells with concentrations fluctuating between 16 mg/L and 4 mg/L over the course of the pilot test.

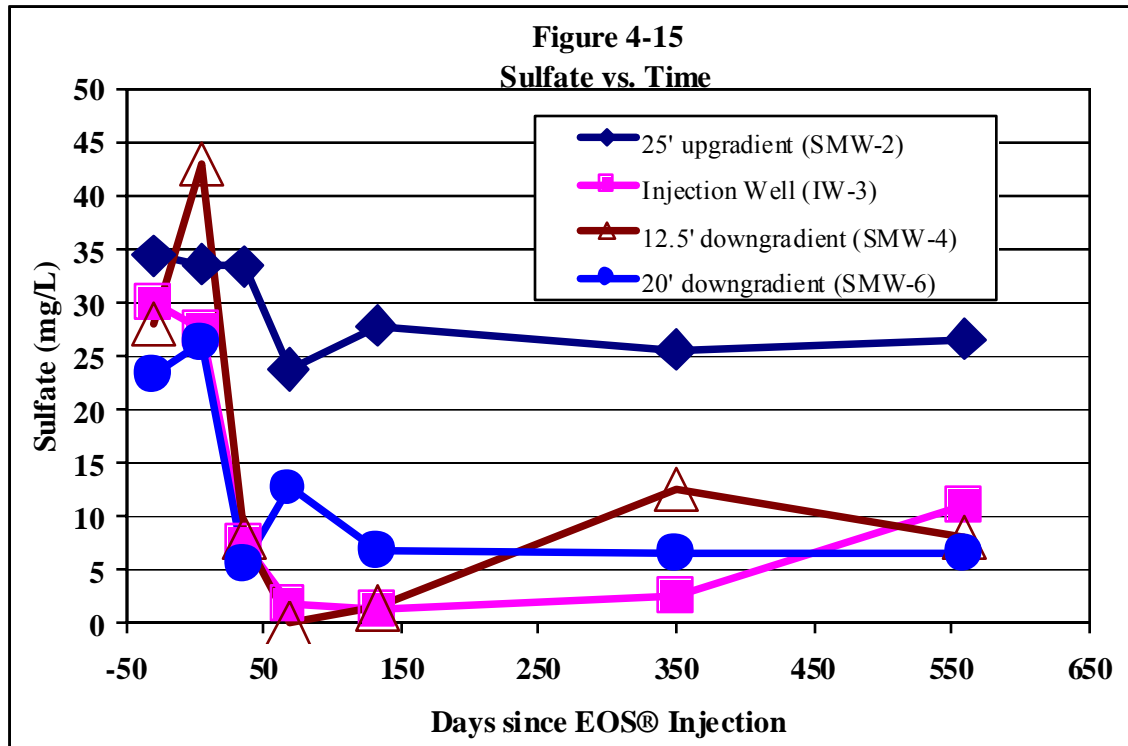
Figure 4-14 shows the changes in nitrate concentrations during the demonstration in up gradient well SMW-2, injection well IW-3, and

downgradient wells SMW-4 and SMW-6. The figure confirms the trends noted above. Overall, EOS[®] injection quickly resulted in nitrate reducing conditions within and downgradient of the barrier. However, low levels of nitrate started to appear in some of the injection wells near the end of the monitoring period indicating that the substrate consumption was decreasing the efficiency of the barrier.



Sulfate

Sulfate reduction is another indicator of favorable anaerobic conditions. As shown in Table 4-12 and Figure 4-15, sulfate concentrations were quickly reduced in the injection and downgradient wells with sustained higher concentrations upgradient. Near the end of the pilot test, sulfate levels in the injection wells appeared to be rebounding slightly, but reduced levels were still observed downgradient.



Iron and Manganese

Iron and manganese reduction are anaerobic processes in which Fe(III) is reduced to Fe(II) and Mn(IV) is reduced to Mn(II). The reduced forms of iron and manganese are soluble in water. Thus, increases in dissolved iron and dissolved manganese can be indicators of anaerobic biodegradation.

Prior to injection, dissolved iron was not detected (<0.5 mg/L) in any of the pilot test wells. EOS[®] injection created iron reducing conditions as indicated by substantial increases in dissolved iron in the injection wells with concentrations as high as 78 mg/L. Increased levels of dissolved iron were also detected in the downgradient monitor wells, but to a lesser extent than the changes observed in the injection wells. Manganese reduction was also observed in the PRB area with increases in manganese observed in all of the injection and downgradient wells following EOS[®] injection. The dissolved iron and manganese results are presented in Table 4-12 and depicted graphically on Figures 4-16 and 4-17, respectively.

Figure 4-16
Dissolved Iron vs. Time

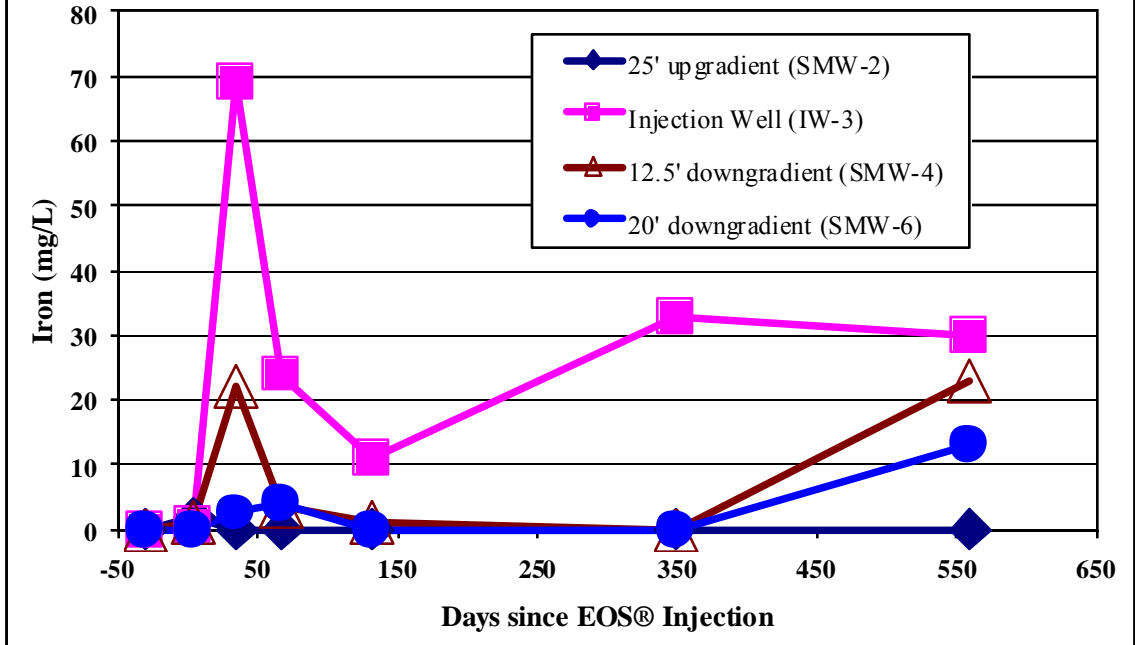
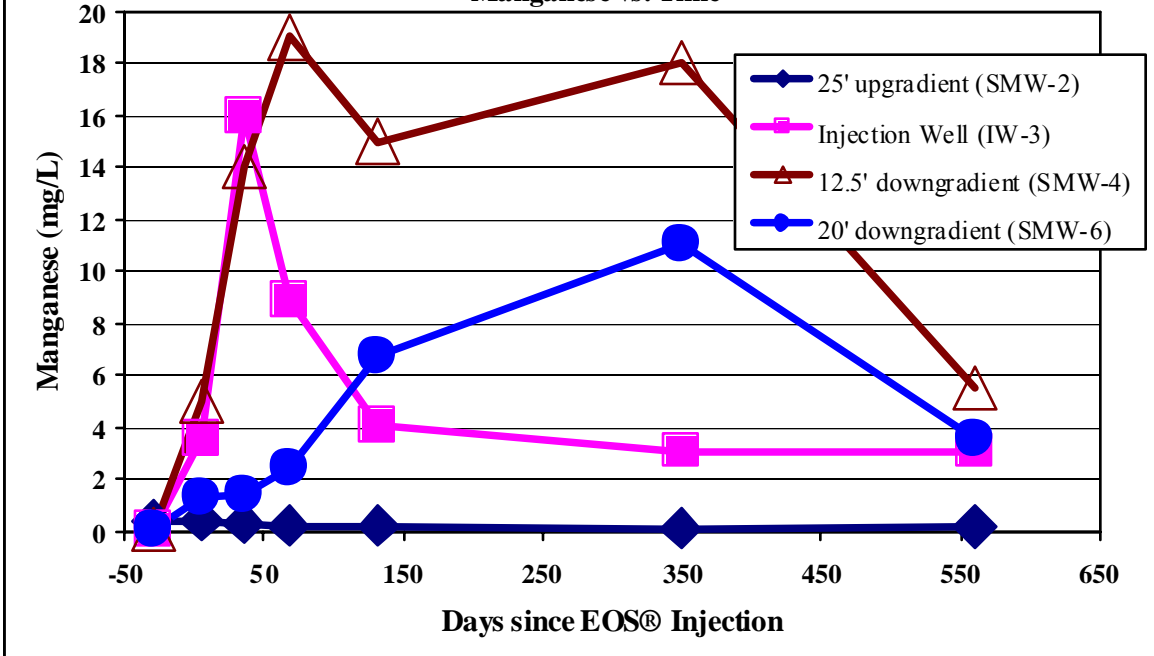
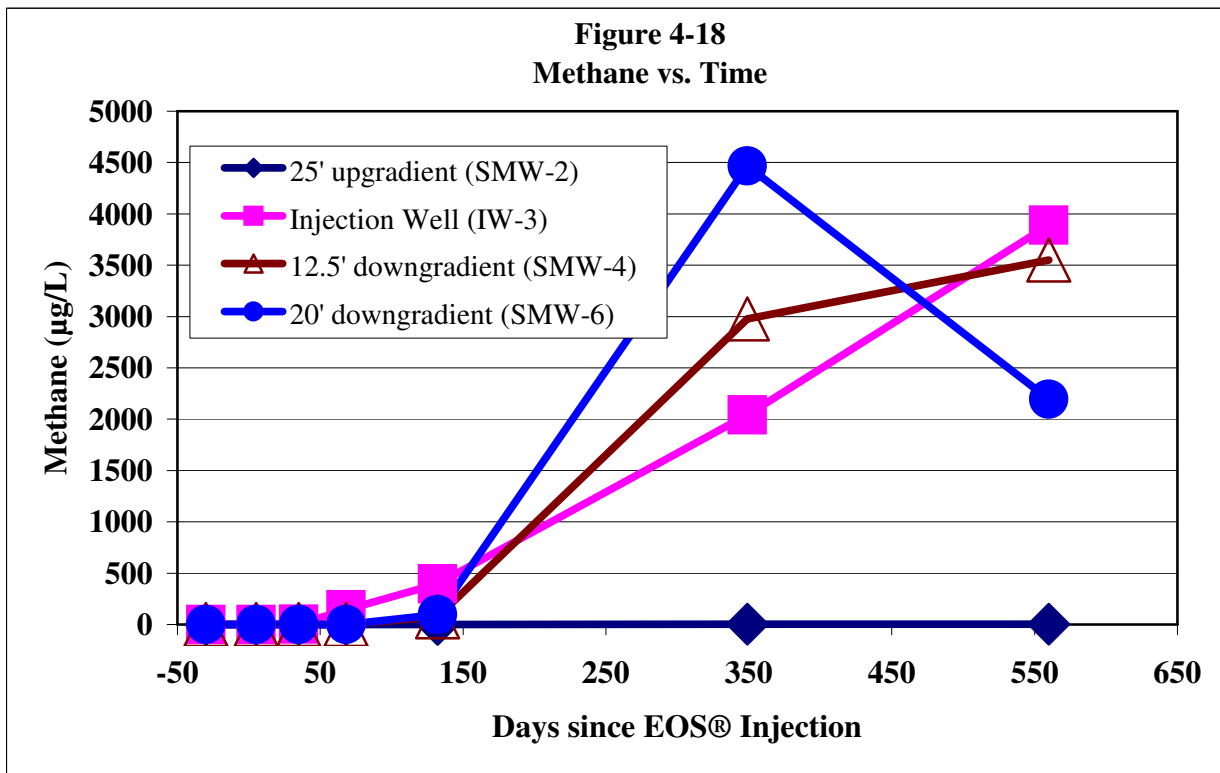


Figure 4-17
Manganese vs. Time



Methane

The presence of methane above background conditions indicates microbial degradation (methanogenesis) is occurring and strongly reducing conditions have been established. Before EOS[®] injection, methane concentrations were <1 µg/L in all of the pilot test wells. Throughout the pilot test, methane levels remained low (<8 µg/L) in all of the upgradient monitor wells. In the injection wells, methane generation was observed by two months post-injection. Within 11 months, methane concentrations were >1,000 µg/L in all injection wells with concentrations as high as 5,400 µg/L in IW-5. By four months post-injection, increased methane levels were observed in all downgradient monitor wells. Table 4-12 and Figure 4-18 present the methane results for the pilot test.

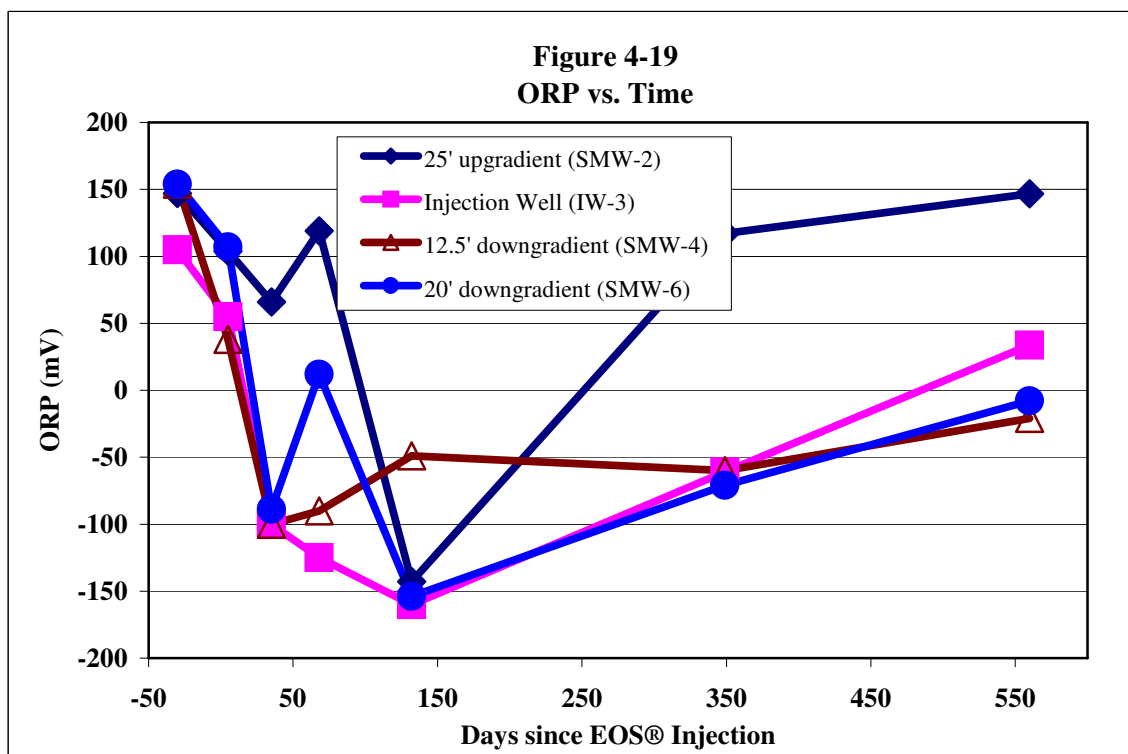


Indicator Parameters

Parameters that are indicators of conditions favorable for anaerobic biodegradation of perchlorate and chlorinated solvents include ORP, pH, and temperature. Chloride (a by-product) and ethene/ethane (end products) can also serve as indicators of biodegradation. These parameters were evaluated as part of the demonstration project, and the results are discussed below.

Oxidation-Reduction Potential

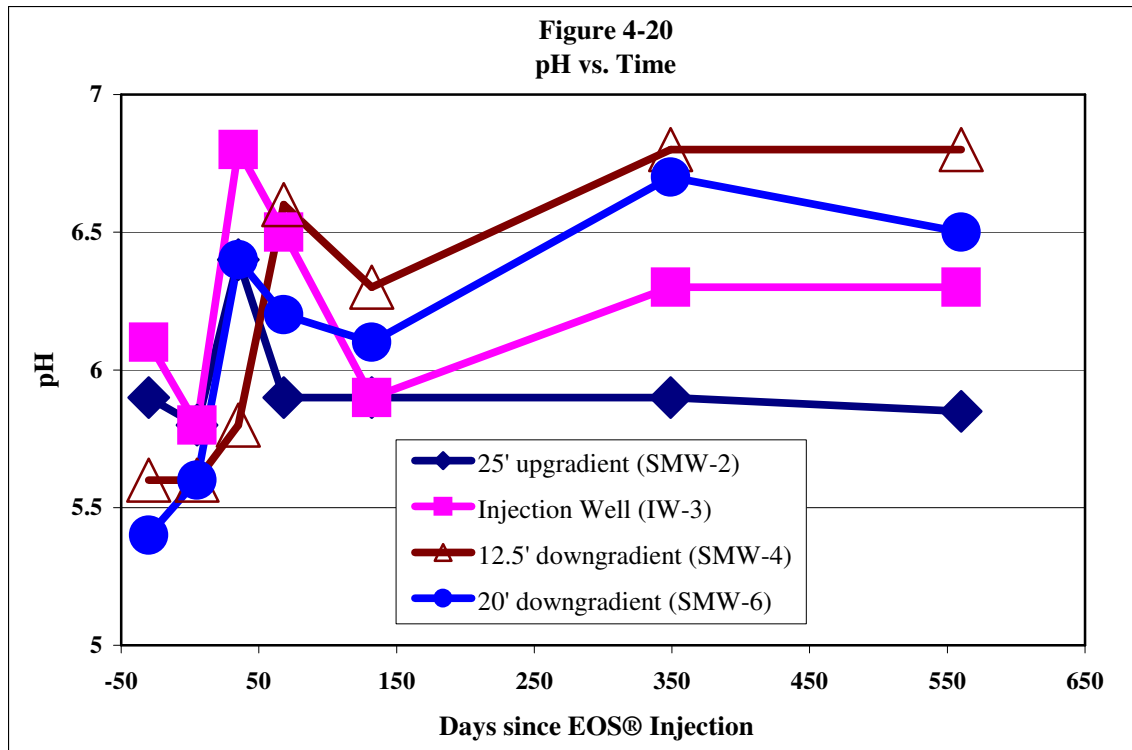
ORP is a measure of the electron activity of the groundwater. At ORP levels less than +50 mV, reductive dechlorination pathways are possible; below – 100 mV conditions are most conducive for supporting reductive dechlorination pathways. ORP measurements collected at the site are summarized in Table 4-11, and data for upgradient well SMW-2, injection well IW-3, and downgradient wells SMW-4 and SMW-6 are shown on Figure 4-19. ORP decreased in all of the site monitoring and injection wells following EOS[®] injection. Within 1 month of injection, negative ORP values were detected in all injection wells and downgradient monitor wells. The lowest values were observed in the injection wells 4 months post-injection. Eighteen months post-injection, ORP levels remain less than +50 mV in all injection and downgradient monitor wells, except for IW-1 (80.4 mV) and IW-2 (51 mV), indicating that reducing conditions favorable for anaerobic biodegradation remain in most of the pilot test area.



pH

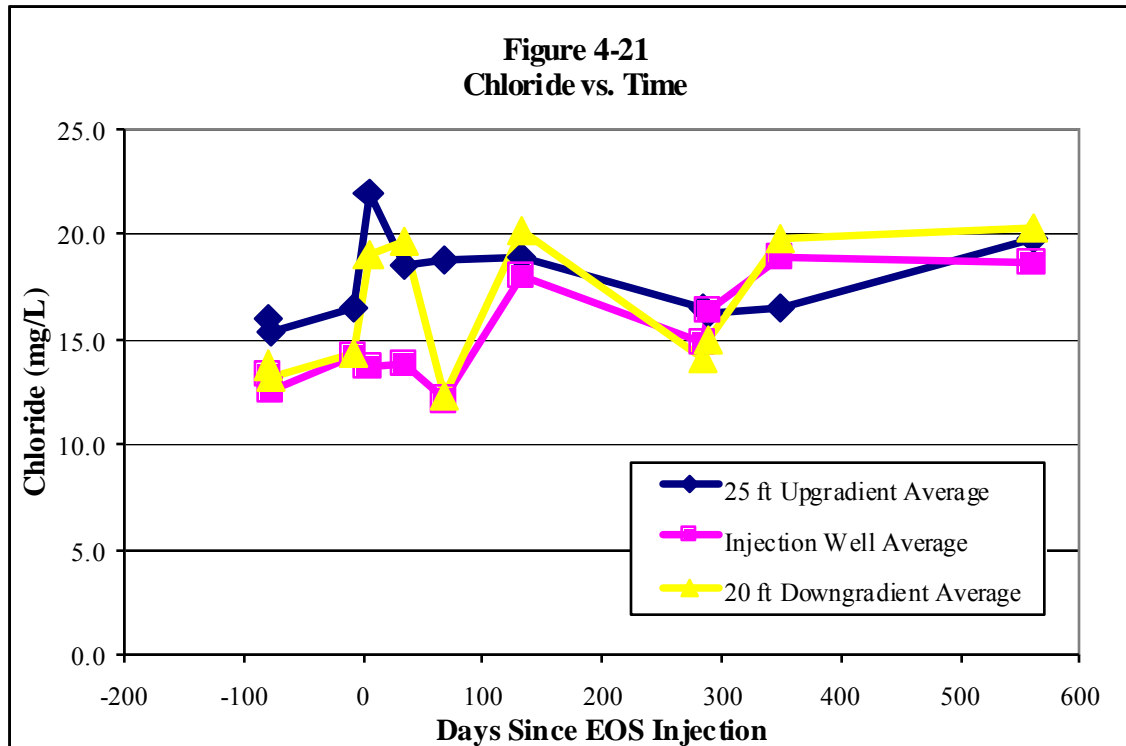
pH values ranging from 6 to 8 standard units are generally preferable for anaerobic biodegradation. pH changes are a concern when conducting enhanced anaerobic bioremediation projects, because of the sensitivity of the

microbial population. The EOS[®] substrate used in the injection has a low pH (~3.5); however, over the course of the 18-month pilot test, the pH levels in the injection and downgradient monitor wells increased to more favorable levels with pre-injection levels around 6.0 and post-injection readings around 6.5 (Table 4-11 and Figure 4-20). In the upgradient wells, pH readings remained around 6.0 throughout the pilot test. The increase observed within and downgradient of the PRB is likely associated with the reduction of iron and manganese.



Chloride

As perchlorate and chlorinated solvents are biodegraded, chlorine atoms are released resulting in increased chloride concentrations. Background concentrations of chloride are commonly too high to notice the production of chloride due to biodegradation. The chloride data are presented in Table 4-12, and the average upgradient, injection well, and downgradient concentrations over time are graphed on Figure 4-21. As shown in the figure, no clear increasing trend in chloride concentrations was observed within or downgradient of the PRB compared to upgradient (background) levels.



Ethene/Ethane

Ethene and ethane are the non-toxic end products of reductive dechlorination of chlorinated ethenes and ethanes. Both of these constituents were monitored during the pilot test to evaluate biodegradation processes. As shown in Table 4-6, upgradient concentrations of ethene generally ranged between 0.03 and 1.9 $\mu\text{g/L}$, while ethane concentrations ranged between 0.04 and 4.6 $\mu\text{g/L}$. The only exception is one data set for SMW-1 on October 14, 2003 (5 days after EOS[®] injection) which indicated concentrations of 11.4 and 28.7 for ethene and ethane, respectively. Concentrations of ethane in the injection and downgradient wells remained within the range detected in the upgradient wells during the entire 18-month monitoring period indicating that complete dechlorination of 1,1,1-TCA was not occurring within the pilot test area. However, a substantial increase in ethene was observed in injection wells IW-1 and IW-3 and in all of the downgradient monitor wells during the 18-month post-injection monitoring event. The average ethene concentration 20 feet downgradient of the PRB was 40.8 $\mu\text{g/L}$ indicating complete dechlorination of chlorinated ethenes (e.g., PCE and TCE) was occurring.

4.3.2 Distribution of EOS[®] in the Aquifer

The objective of the EOS[®] injection was to distribute emulsion in the subsurface to create a PRB approximately 50 feet long perpendicular to groundwater flow, 5 feet wide parallel to groundwater flow, and 10 feet high in the vertical direction. The EOS[®] was distributed

by injecting diluted emulsion followed by a water chase. The goal of the injection was for the emulsion to sorb to the sediment and provide a slow release of TOC to stimulate biodegradation.

The distribution of EOS[®] in the aquifer was evaluated through soil and groundwater TOC data. The TOC data for soil samples collected 6 and 9 months post-injection are summarized in Table 4-13, along with pre-injection data. Samples were collected throughout the pilot test area and at several background locations (see Figure 3-10). The TOC data were evaluated for two different vertical zones, 5 to 10 feet bgs and 10 to 15 feet bgs. The average TOC concentrations in the pre-injection and background soil samples were 172 mg/kg (5-10 ft bgs) and 648 mg/kg (10-15 ft bgs). In contrast, soil samples collected at 6 and 9 months post-injection from within the PRB had average TOC concentrations of 829 mg/kg (5-10 ft bgs) and 1,274 mg/kg (10-15 ft bgs) indicating the presence of emulsion. Figures 4-22a and b show the TOC data for the upper and lower zones. The figures show that the highest TOC concentrations were detected within and near the barrier, with the exception of one outlier in the lower zone.

Groundwater samples were collected during the injection process to monitor for the presence of emulsion in nearby wells. During the first injection phase, IW-1, IW-3, IW-5, IW-7, and IW-9 were injected and groundwater samples were collected from IW-6 for visual observation and TOC analysis. In the second phase, IW-2, IW-4, IW-6, IW-8, and IW-10 were injected and monitoring was conducted at SMW-4. These TOC data are summarized in Table 4-14, and the data from the first injection phase are illustrated on Figure 4-23. During the first injection phase, emulsion was quickly detected in IW-6 located 5 feet from the nearest injection point. At the start of the second injection phase, elevated TOC was already present in SWM-4 (12.5 feet downgradient from the injection wells) and continued to increase during the injection.

TOC groundwater data were collected during each performance monitoring event (Table 4-15) and during the six-month post-injection Geoprobe sampling event (Table 4-4 and Figure 3-11). Figure 4-24 shows the TOC concentrations in upgradient well SMW-2, injection well IW-3, and downgradient wells SMW-4 and SMW-6. The figure illustrates a substantial increase in TOC in the injection and 12.5-foot downgradient well with concentrations leveling off in these wells around 50 mg/L and 20 mg/L, respectively. A smaller increase in TOC is observed 20 feet downgradient, and little change is observed upgradient. These results indicate that the initial injection spread emulsion up to 12.5 feet 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.

Groundwater TOC data from the six-month post-injection Geoprobe sampling event are shown on Figure 4-25. Assuming background TOC levels are generally less than 3 mg/L, elevated TOC levels were detected in a wide area downgradient of the PRB extending as far as 35 feet in the direction of groundwater flow.

Table 4-13
TOC Soil Sample Results
Maryland Perchlorate Site

Sample Location	Distance from Barrier (ft)	Sample Type	Sample Depth (feet bgs)	Sample Date	Total Organic Carbon Wet Wt. (mg/kg)	Total Organic Carbon Dry Wt. (mg/kg)	Percent Solids (%)	Notes
Pre-Injection and Background Locations								
TT-1		Comp	8-12	4/22/2003	440	559	78.7%	
		Comp	12-14	4/22/2003	<1.0	<1.0	80.4%	
IW-10		Comp	6-8	4/23/2003	200	214	93.3%	
		Comp	12-14	4/23/2003	920	1030	89.3%	
IW-1		Comp	14-15	4/22/2003	<1.0	<1.0	77.4%	
BKG		Comp 1	5 - 10	4/21/2004	33	37	88.8%	
		Comp 2	10 - 15	4/21/2004	2,890	3,631	79.6%	
RI-11	30	Comp 1	5 - 10	9/22/2004	143	172	83.0%	
RI-12	29	Comp 1	5 - 10	9/22/2004	<1.0	<1.0	80.1%	
RI-13	44	Comp 1	5 - 10	9/22/2004	103	119	86.4%	
		Comp 2	10 - 15	9/22/2004	103	137	75.2%	
RI-14	22.5	Comp 1	5 - 10	9/22/2004	123	153	80.4%	
		Comp 2	10 - 15	9/22/2004	605	677	89.4%	
RI-15	35	Comp 1	5 - 10	9/22/2004	320	370	86.5%	
RI-18	21.5	Comp 1	5 - 10	9/22/2004	190	206	92.3%	
		Comp 2	10 - 15	9/22/2004	15	17	89.9%	
Background Average			5 - 10		172	203		
			10 - 15		648	784		
Upgradient Pilot Study Locations								
RI-1	5	Comp 1	5 - 10	4/19/2004	90	108	83.5%	
		Grab	7.5	4/19/2004	110	120	91.8%	
		Comp 2	10 - 15	4/19/2004	110	136	80.6%	
		Grab	10.5	4/19/2004	193	231	83.5%	
RI-2	10	Comp 1	5 - 10	4/21/2004	118	138	85.7%	
		Comp 2	10 - 15	4/21/2004	117	133	88.2%	
Barrier Pilot Study Locations								
RI-3	0	Comp 1	5 - 10	4/19/2004	138	154	89.9%	
		Grab	8.5	4/19/2004	115	127	90.9%	
		Grab	12	4/19/2004	1,302	1,426	91.3%	black staining
RI-4	0	Comp 1	5 - 10	4/21/2004	95	106	89.3%	
		Comp 2	10 - 15	4/21/2004	515	627	82.2%	
		Grab	11.5	4/21/2004	3,020	3,344	90.3%	black staining
RI-16	0	Comp 1	5 - 10	9/22/2004	1,450	1,576	92.0%	
		Grab	9 - 10	9/22/2004	2,928	3,579	81.8%	
		Comp 2	10 - 15	9/22/2004	1,668	2,155	77.4%	
		Grab	14 - 15	9/22/2004	180	232	77.6%	
RI-19	0	Comp 1	5 - 10	9/22/2004	150	168	89.4%	
		Grab	7 - 8	9/22/2004	928	1,055	88.0%	
		Comp 2	10 - 15	9/22/2004	1,215	1,440	84.4%	
		Grab	11 - 12	9/22/2004	1,020	1,126	90.6%	
Barrier Average			5 - 10		829	966		
			10 - 15		1,274	1,478		
Downgradient Pilot Study Locations								
RI-5	2.5	Comp 1	5 - 10	4/21/2004	343	392	87.5%	
		Grab	8 - 10	4/21/2004	23	29	76.6%	
		Comp 2	10 - 15	4/21/2004	210	252	83.3%	
RI-6	5	Comp 1	5 - 10	4/21/2004	100	112	89.6%	
		Comp 2	10 - 15	4/21/2004	328	374	87.7%	
RI-7	7.5	Comp 1	5 - 10	4/21/2004	125	142	87.9%	
		Comp 2	10 - 15	4/21/2004	250	282	88.5%	
		Grab	10 - 12	4/21/2004	365	442	82.5%	
RI-8	10	Comp 1	5 - 10	4/21/2004	95	114	83.5%	
		Grab	8 - 10	4/21/2004	60	75	80.2%	
		Comp 2	10 - 15	4/21/2004	590	818	72.1%	
		Grab	14 - 15	4/21/2004	838	956	87.7%	
RI-9	15	Comp 1	5 - 10	4/21/2004	340	453	75.1%	
		Comp 2	10 - 15	4/21/2004	710	852	83.3%	
RI-10	20	Comp 1	5 - 10	4/21/2004	28	31	90.3%	
		Comp 2	10 - 15	4/21/2004	278	311	89.3%	

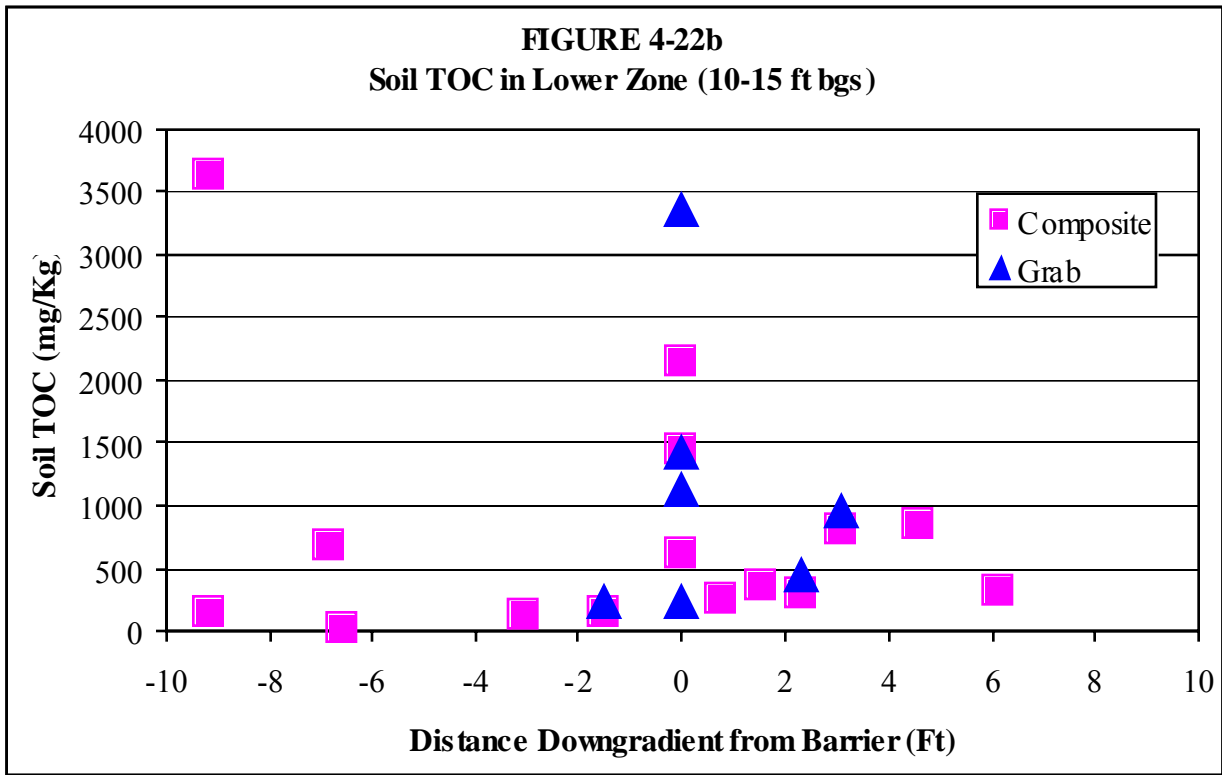
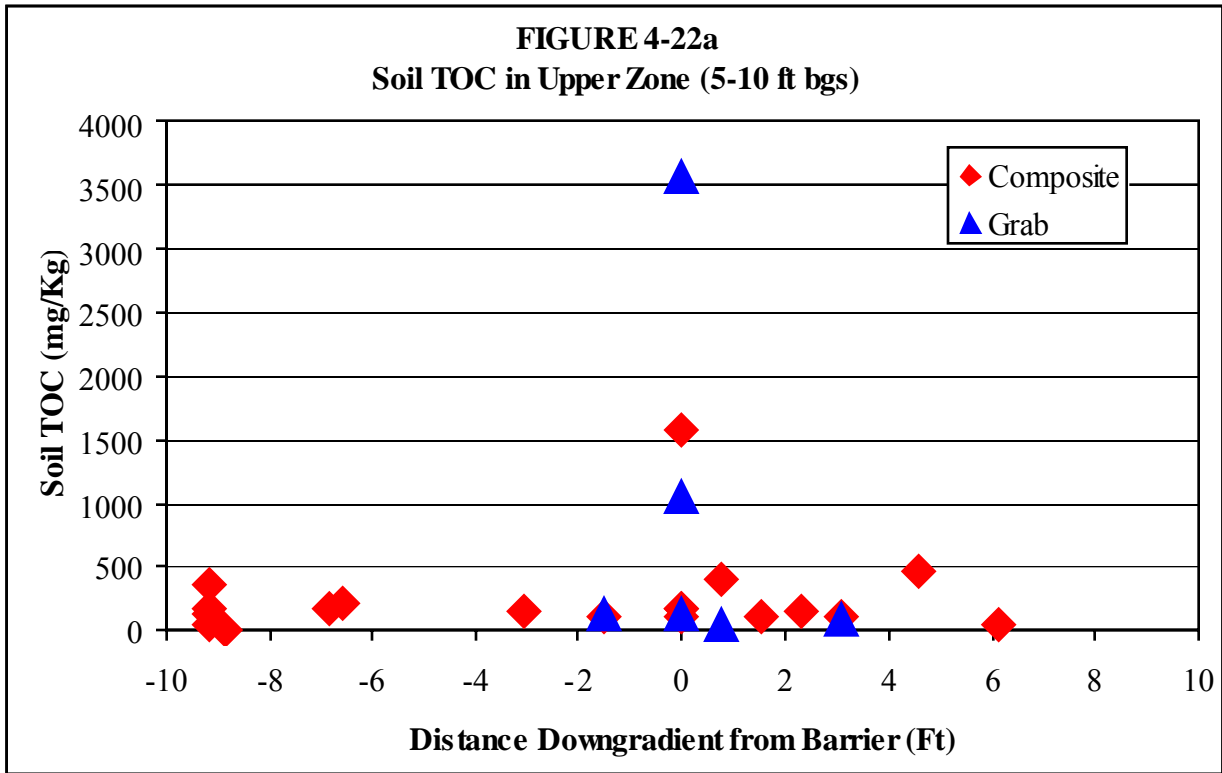


TABLE 4-14
TOC vs Time During Injection
Maryland Perchlorate Site

Well ID	Sample Date	Sample Time	Time Since Start of Injection (minutes)	Total Organic Carbon (mg/L)
IW-6	10/7/2003	15:15	0	1.34
		16:15	59	18.4
		17:15	119	161
		18:15	179	219
		18:50	214	220
SMW-4	10/8/2003	15:20	0	65.1
		16:50	45	73.2
		17:50	105	74.0
		18:50	165	75.7

Notes:

1. On 10/7/03, injection started on wells IW-1, IW-3, IW-5, IW-7, and IW-9 at 15:16.
2. On 10/8/03, injection started on wells IW-2, IW-4, IW-6, IW-8, and IW-10 at 16:05.

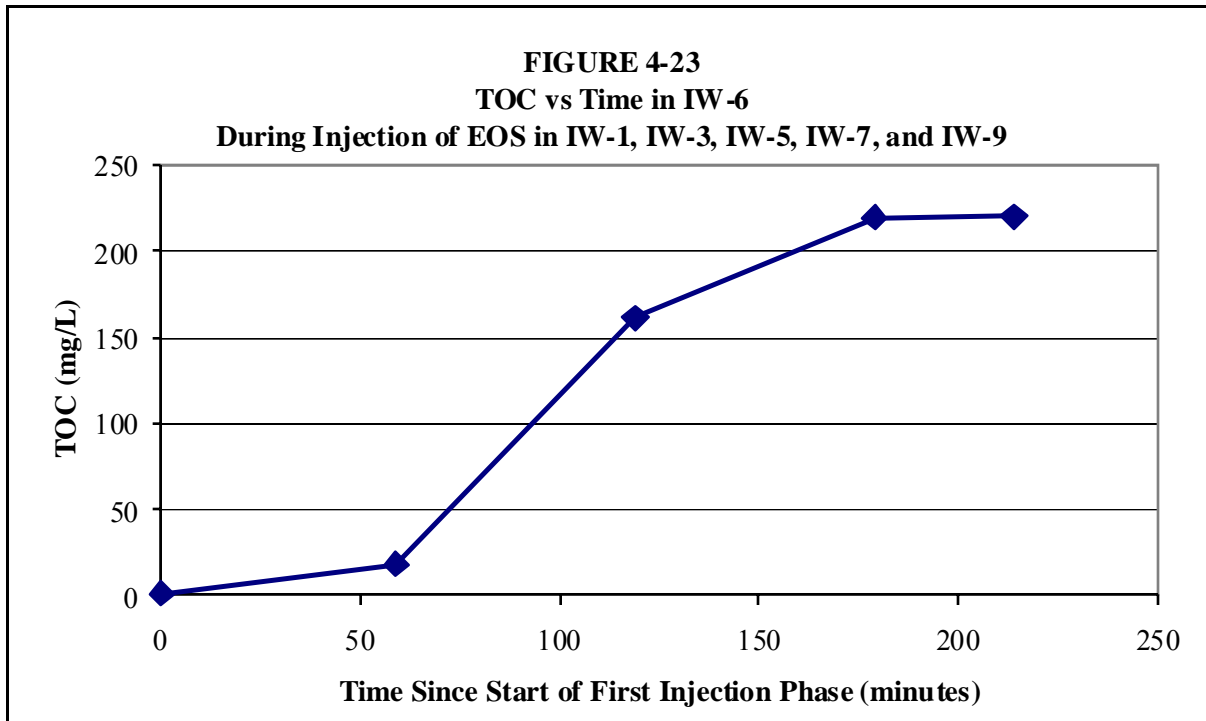


TABLE 4-15
Total Organic and Inorganic Carbon in Groundwater
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Days Since Injection	Total Organic Carbon (mg/L)	Total Inorganic Carbon (mg/L)	TOC and TIC (mg/L)
UPGRADIENT MONITORING WELLS					
SMW-1 (25 feet)	9/30/03	-9	1.39	27.9	29.3
	10/13/03	4	1.95	24.7	26.7
	11/13/03	35	1.75	22.0	23.8
	12/16/03	68	<1.0	23.9	23.9
	2/19/04	133	1.12	23.1	24.2
	9/21/04	348	1.18	24.5	25.7
	4/21/05	560	1.42	26.1	27.5
SMW-2 (25 feet)	9/30/03	-9	<1.0	20.5	20.5
	10/13/03	4	1.48	18.2	19.7
	11/13/03	35	1.62	24.1	25.7
	12/16/03	68	<1.0	22.6	22.6
	2/19/04	133	<1.0	16.4	16.4
	9/21/04	348	<1.0	21.4	21.4
	4/21/05	560	<1.0	22.6	22.6
SMW-3 (25 feet)	9/30/03	-9	1.08	21.1	22.2
	10/13/03	4	3.43	18.5	21.9
	11/13/03	35	1.82	9.77	11.6
	12/16/03	68	<1.0	17.3	17.3
	2/19/04	133	<1.0	14.3	14.3
	9/21/04	348	<1.0	13.3	13.3
	4/21/05	560	1.28	21.5	22.8
Average 25 ft Upgradient	9/30/03	-9	0.82	23.17	24.0
	10/13/03	4	2.29	20.47	22.8
	11/13/03	35	1.73	18.62	20.4
	12/16/03	68	<1.0	21.27	21.3
	2/19/04	133	0.37	17.93	18.3
	9/21/04	348	0.39	19.73	20.1
	4/21/05	560	0.90	23.40	24.3
INJECTION WELLS					
IW-1	9/29/03	-10	1.15	24.2	25.4
	10/13/03	4	100	42.0	142.0
	11/13/03	35	62.5	47.7	110.2
	12/16/03	68	61.8	53.6	115.4
	2/18/04	132	36.2	29.9	66.1
	9/21/04	348	17.6	35.4	53.0
	4/21/05	560	10.8	28.7	39.5
IW-3	9/29/03	-10	1.15	25.1	26.3
	10/13/03	4	418	52.8	470.8
	11/13/03	35	48.4	45.8	94.2
	12/16/03	68	73.2	51.3	124.5
	2/18/04	132	49.1	27.6	76.7
	9/21/04	348	53.2	28.4	81.6
	4/21/05	560	21.7	29.1	50.8

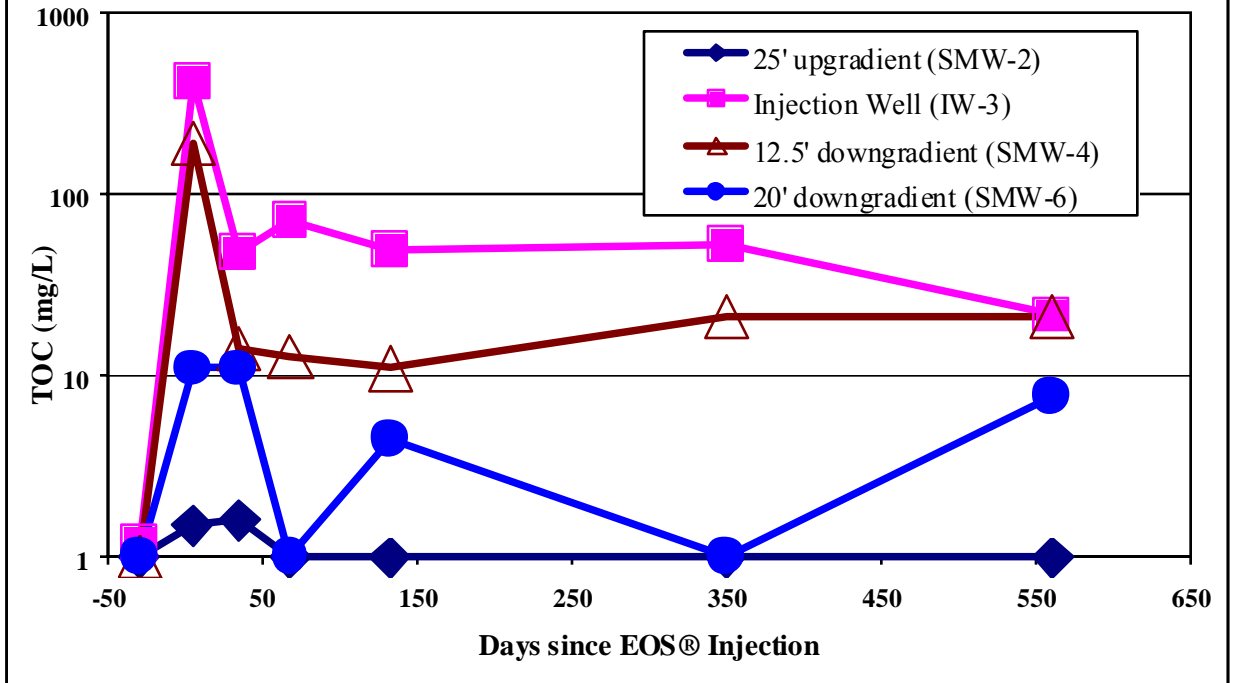
TABLE 4-15
Total Organic and Inorganic Carbon in Groundwater
Maryland Perchlorate Site

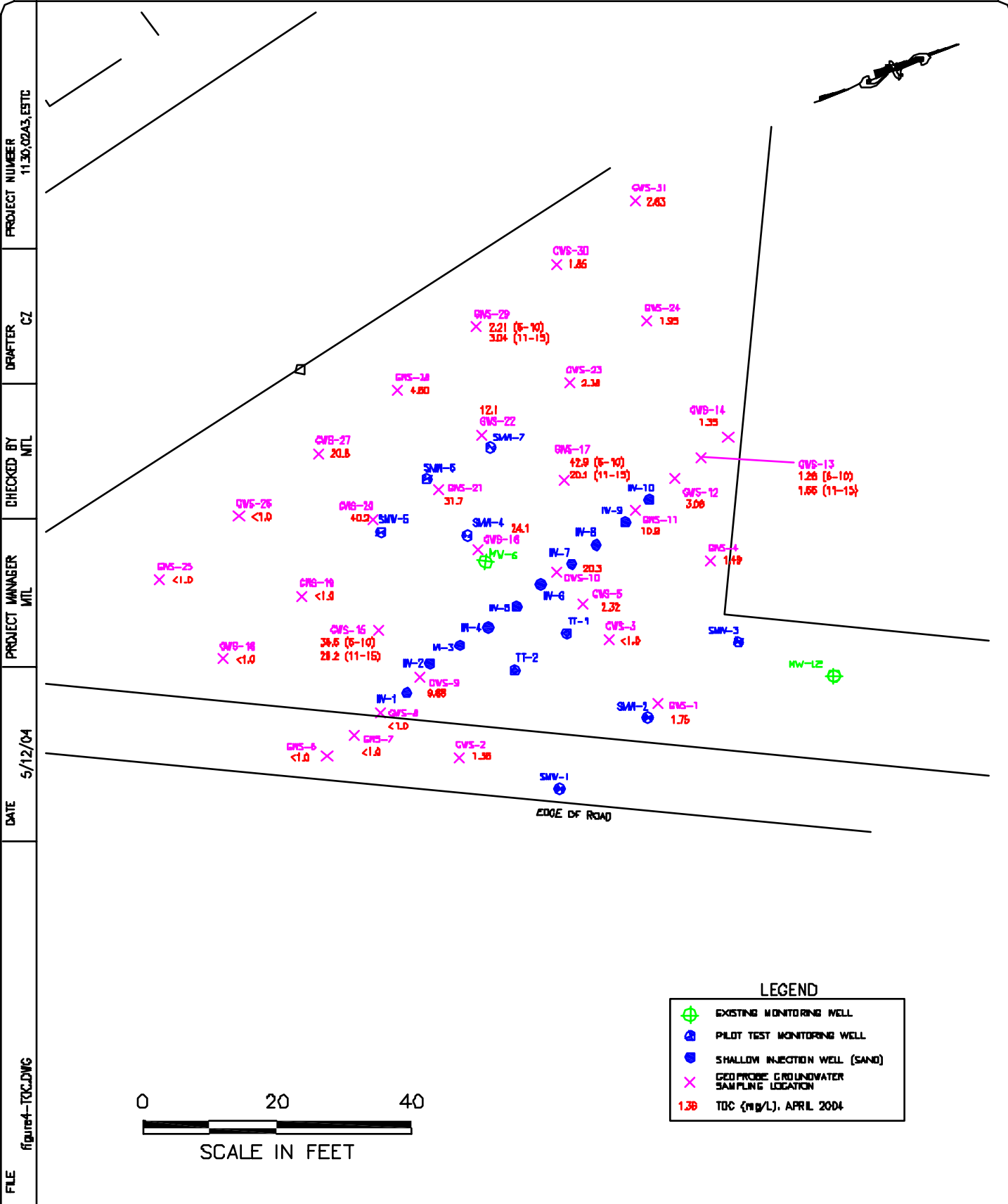
Well ID (Distance from Barrier)	Sample Date	Days Since Injection	Total Organic Carbon (mg/L)	Total Inorganic Carbon (mg/L)	TOC and TIC (mg/L)
IW-5	9/29/03	-10	<1.0	24.0	24.0
	10/13/03	4	151	43.8	194.8
	11/13/03	35	25.2	37.1	62.3
	12/16/03	68	29.3	<1.0	29.3
	2/18/04	132	28.0	24.6	52.6
	9/21/04	348	52.3	28.6	80.9
	4/21/05	560	13.1	27.1	40.2
IW-7	9/29/03	-10	1.16	20.6	21.8
	10/13/03	4	176	39.8	215.8
	11/13/03	35	89.0	47.8	136.8
	12/16/03	68	96.9	68.5	165.4
	2/18/04	132	64.7	32	96.7
	9/21/04	348	48.8	31.6	80.4
	4/21/05	560	38.1	37.8	75.9
IW-10	9/29/03	-10	<1.0	21.0	21.0
	10/13/03	4	451	38.7	489.7
	11/13/03	35	39.5	25.9	65.4
	12/16/03	68	24.8	28.8	53.6
	2/19/04	133	18.2	25.8	44.0
	9/21/04	348	29.7	20.5	50.2
	4/21/05	560	19.0	26.6	45.6
Average Injection Well	9/29/03	-10	0.7	23.0	23.7
	10/13/03	4	259.2	43.4	302.6
	11/13/03	35	52.9	40.9	93.8
	12/16/03	68	57.2	50.6	97.6
	2/19/04	133	39.2	28.0	67.2
	9/21/04	348	40.3	28.9	69.2
	4/21/05	560	20.5	29.9	50.4
DOWNGRADIENT MONITORING WELLS					
MW-6 (7.5 feet)	9/30/03	-9	<1.0	21.9	21.9
	10/14/03	5	48.6	50.6	99.2
	11/13/03	35	8.7	<1.0	8.7
	12/16/03	68	1.12	32.6	33.7
	2/18/04	132	8.42	26.6	35.0
	9/22/04	349	80.2	18.2	98.4
	4/21/05	560	14.1	27.0	41.1
SMW-4 (12.5 feet)	9/30/03	-9	<1.0	24.0	24.0
	10/14/03	5	190	44.0	234.0
	11/13/03	35	14.1	37.0	51.1
	12/16/03	68	12.6	35.7	48.3
	2/18/04	132	10.7	28.5	39.2
	9/22/04	349	21.2	21.1	42.3
	4/21/05	560	21.4	26.4	47.8

TABLE 4-15
Total Organic and Inorganic Carbon in Groundwater
Maryland Perchlorate Site

Well ID (Distance from Barrier)	Sample Date	Days Since Injection	Total Organic Carbon (mg/L)	Total Inorganic Carbon (mg/L)	TOC and TIC (mg/L)
SMW-5 (20 feet)	9/30/03	-9	<1.0	25.4	25.4
	10/14/03	5	59.8	30.6	90.4
	11/13/03	35	20.0	60.3	80.3
	12/16/03	68	11.0	36.3	47.3
	2/18/04	132	16.8	28.6	45.4
	9/22/04	349	50.9	24.8	75.7
	4/21/05	560	22.9	29.0	51.9
SMW-6 (20 feet)	9/30/03	-9	<1.0	20.7	20.7
	10/14/03	5	11.3	27.0	38.3
	11/13/03	35	11.3	40.5	51.8
	12/16/03	68	<1.0	19.1	19.1
	2/18/04	132	4.53	24.4	28.9
	9/22/04	349	29.7	22.4	52.1
	4/21/05	560	7.80	24.1	31.9
SMW-7 (20 feet)	9/30/03	-9	<1.0	21.7	21.7
	10/14/03	5	2.36	17.6	20.0
	11/13/03	35	10.9	61.5	72.4
	12/16/03	68	4.91	33.6	38.5
	2/18/04	132	2.01	29.0	31.0
	9/22/04	349	35.0	25.9	60.9
	4/21/05	560	19.4	29.1	48.5
Average 20 ft Downgradient	9/30/03	-9	<1.0	22.60	22.6
	10/14/03	5	24.49	25.07	49.6
	11/13/03	35	14.07	54.10	68.2
	12/16/03	68	7.96	29.67	35.0
	2/18/04	132	7.78	27.33	35.1
	9/22/04	349	38.53	24.37	62.9
	4/21/05	560	16.70	27.40	44.1

Figure 4-24
TOC vs. Time





Volatile fatty acids (VFAs) were also analyzed as part of the performance monitoring activities and provide an indication of the breakdown of the soybean oil and lactate that was in the emulsion. The VFA results are summarized in Table 4-16. No VFAs were detected in any of the upgradient wells. In the injection wells, acetic, propionic, and butyric acids were detected immediately after EOS[®] injection suggesting that the soybean oil is being fermented to organic acids in the vicinity of the injection wells. Eighteen months post-injection high levels of acetic acid were still being detected in the injection wells. Lactic acid was not detected in the injection wells despite the presence of sodium lactate in the emulsion. However, lactic acid was detected in all of the down gradient wells immediately after injection. Acetic acid was consistently detected in the downgradient wells with occasional detections of propionic and butyric acids.

TABLE 4-16
Volatile Fatty Acids in Groundwater
Maryland Perchlorate Site

Well ID	Sample Date	Pyruvic Acid (mg/L)	Lactic Acid (mg/L)	Formic Acid (mg/L)	Acetic Acid (mg/L)	Propionic Acid (mg/L)	Butyric Acid (mg/L)
Upgradient Monitoring Wells							
SMW-2 (25 feet)	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	<1	<1	<1	<1	<1
	11/13/2003	<4	<1	<1	<1	<1	<1
	12/16/2003	<4	<1	<1	<1	<1	<1
	2/18/2004	<4	<1	<1	<1	<1	<1
	9/21/2004	<4	<1	<1	<1	<1	<1
	4/21/2005	<4	<1	<1	<1	<1	<1
Injection Wells							
IW-3	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	<1	<1	111.4	35.3	129.5
	11/13/2003	<4	<1	<1	41.0	12.3	1.5
	12/16/2003	<4	<1	<1	80.7	18.2	3.0
	2/18/2004	<4	<1	<1	59.9	5.1	2.3
	9/21/2004	<4	<1	<1	116.6	<1	5.2
	4/21/2005	<4	<1	<1	52.7	<1	<1
IW-7	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	<1	<1	63.6	35.8	45.5
	11/13/2003	<4	<1	<1	77.7	50.7	7.6
	12/16/2003	<4	<1	<1	80.0	44.2	5.9
	2/18/2004	<4	<1	<1	70.8	17.5	5.9
	9/21/2004	<4	<1	<1	69.8	<1	<1
	4/21/2005	<4	<1	<1	67.4	<1	<1
Downgradient Monitoring Wells							
MW-6 (7.5 feet)	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	57.3	<1	22.6	3.3	1.9
	11/13/2003	<4	<1	<1	<1	2.9	<1
	12/16/2003	<4	<1	<1	<1	<1	<1
	2/18/2004	<4	<1	<1	14.0	<1	<1
	9/22/2004	<4	<1	<1	158.0	<1	1.4
	4/21/2005	<4	<1	<1	28.6	<1	<1
SMW-4 (12.5 feet)	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	268.2	<5	40.4	5.5	43.2
	11/13/2003	<4	<1	<1	19.9	<1	<1
	12/16/2003	<4	<1	<1	21.3	1.8	<1
	2/18/2004	<4	<1	<1	21.9	<1	<1
	9/22/2004	<4	<1	<1	45.3	<1	<1
	4/21/2005	<4	<1	<1	53.9	<1	<1
SMW-6 (20 feet)	9/29/2003	<4	<1	<1	<1	<1	<1
	10/14/2003	<4	15.3	<1	5.8	<1	<1
	11/13/2003	<4	<1	<1	1.7	1.2	<1
	12/16/2003	<4	<1	<1	2.6	<1	<1
	2/18/2004	<4	<1	<1	6.4	<1	<1
	9/22/2004	<4	<1	<1	63.7	<1	<1
	4/21/2005	<4	<1	<1	6.4	<1	<1

4.3.3 Permeability Impacts of the EOS[®] Injection

The impacts of the EOS[®] injection on aquifer permeability were evaluated by comparing pre- and post-injection hydraulic conductivity values and pre- and post-injection bromide tracer tests. Performance monitoring data were also reviewed to assess permeability impacts. The hydraulic conductivity data are presented in Table 4-17 and Figure 4-26. In the upgradient wells, the hydraulic conductivity essentially remained unchanged during the pilot test, while the injection wells showed a decrease in hydraulic conductivity over time. The downgradient wells did not show much change 4 months after injection, but by 18 months post-injection the hydraulic conductivity had decreased by approximately 50%.

The tracer test data are summarized in Table 4-18. The pre-injection and post-injection bromide tracer test data are similar, as shown in Figures 4-27a and b. Therefore, groundwater flow through the barrier does not appear to have been substantially affected by the measured changes in hydraulic conductivity. Although the permeability impacts are not dramatic, the performance monitoring data suggest some flow around the edges of the barrier is occurring. As discussed in Section 4.3.1.1, low levels of perchlorate reappeared in downgradient monitor well SM W-5 approximately 2 months after EOS[®] injection. These low levels are likely the result of untreated groundwater mixing with treated groundwater along the edges of the treatment zone.

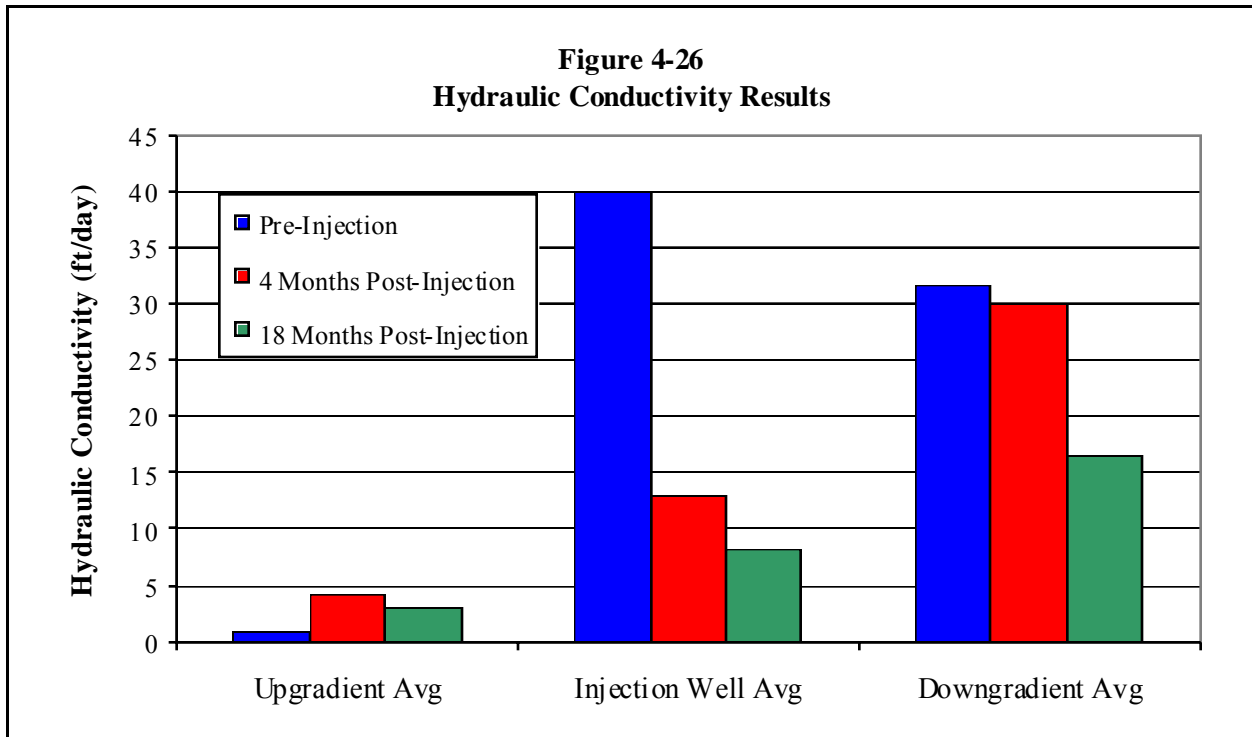


TABLE 4-17
Summary of Hydraulic Conductivity Tests
Maryland Perchlorate Site

Well ID	Test Date	Test Before or After Injection	Type of Test	Hydraulic Conductivity	
				cm/sec	ft/day
Upgradient Monitoring Wells					
SMW-2	2/19/2004	Post-Injection	Spec Capacity	1.96E-03	5.56
	4/20/2005	Post-Injection	Spec Capacity	1.39E-03	3.94
TT-1	4/14/2003	Pre-Injection	Slug In	3.46E-04	0.98
	4/14/2003	Pre-Injection	Slug In	4.27E-04	1.21
	4/23/2003	Pre-Injection	Spec Capacity	1.90E-04	0.54
	2/19/2004	Post-Injection	Spec Capacity	1.04E-03	2.95
	4/20/2005	Post-Injection	Spec Capacity	6.75E-04	1.91
Upgradient Average	Pre-Injection			3.21E-04	0.91
	4 Months Post-Injection			1.50E-03	4.25
	18 Months Post-Injection			1.03E-03	2.93
Injection Wells					
IW-1	6/24/2003	Pre-Injection	Spec Capacity	1.76E-02	49.89
	2/19/2004	Post-Injection	Spec Capacity	2.76E-03	7.82
	4/20/2005	Post-Injection	Spec Capacity	9.95E-04	2.82
IW-2	6/24/2003	Pre-Injection	Spec Capacity	1.09E-02	30.90
	4/20/2005	Post-Injection	Spec Capacity	1.31E-03	3.70
IW-3	6/24/2003	Pre-Injection	Spec Capacity	1.90E-02	53.86
	2/19/2004	Post-Injection	Spec Capacity	5.30E-03	15.02
	4/20/2005	Post-Injection	Spec Capacity	4.61E-03	13.07
IW-4	6/24/2003	Pre-Injection	Spec Capacity	1.47E-02	41.67
	4/20/2005	Post-Injection	Spec Capacity	1.94E-03	5.50
IW-5	6/24/2003	Pre-Injection	Spec Capacity	1.11E-02	31.46
	2/19/2004	Post-Injection	Spec Capacity	5.19E-03	14.71
	4/20/2005	Post-Injection	Spec Capacity	3.33E-03	9.44
IW-6	6/24/2003	Pre-Injection	Spec Capacity	4.18E-03	11.85
	4/20/2005	Post-Injection	Spec Capacity	8.88E-04	2.52
IW-7	6/24/2003	Pre-Injection	Spec Capacity	1.13E-02	32.03
	2/19/2004	Post-Injection	Spec Capacity	4.91E-03	13.92
	4/20/2005	Post-Injection	Spec Capacity	1.39E-03	3.93
IW-8	6/24/2003	Pre-Injection	Spec Capacity	1.79E-02	50.74
	4/20/2005	Post-Injection	Spec Capacity	2.51E-03	7.11
IW-9	6/24/2003	Pre-Injection	Spec Capacity	1.79E-02	50.74
	4/20/2005	Post-Injection	Spec Capacity	7.45E-03	21.13
IW-10	6/24/2003	Pre-Injection	Spec Capacity	1.69E-02	47.90
	4/20/2005	Post-Injection	Spec Capacity	4.26E-03	12.09
Injection Well Average	Pre-Injection			1.41E-02	40.10
	4 Months Post-Injection			4.54E-03	12.87
	18 Months Post-Injection			2.87E-03	8.13
Downgradient Monitoring Wells					
SMW-4	2/19/2004	Post-Injection	Spec Capacity	4.53E-03	12.84
	4/20/2005	Post-Injection	Spec Capacity	5.00E-03	14.16
SMW-6	4/14/2003	Pre-Injection	Slug In	3.29E-03	9.32
	4/14/2003	Pre-Injection	Slug In	1.80E-03	5.09
	4/23/2003	Pre-Injection	Spec Capacity	3.05E-03	8.65
	2/19/2004	Post-Injection	Spec Capacity	3.19E-03	9.04
	4/20/2005	Post-Injection	Spec Capacity	1.90E-03	5.38

TABLE 4-17
Summary of Hydraulic Conductivity Tests
Maryland Perchlorate Site

Well ID	Test Date	Test Before or After Injection	Type of Test	Hydraulic Conductivity	
				cm/sec	ft/day
MW-6	4/14/2003	Pre-Injection	Slug In	1.30E-02	36.91
	4/14/2003	Pre-Injection	Slug Out	1.90E-02	53.73
	4/14/2003	Pre-Injection	Slug In	1.90E-02	53.73
	4/14/2003	Pre-Injection	Slug Out	1.90E-02	53.73
	2/19/2004	Post-Injection	Spec Capacity	1.80E-02	51.02
	4/20/2005	Post-Injection	Spec Capacity	1.06E-02	30.12
Downgradient Average		Pre-Injection		1.11E-02	31.59
		4 Months Post-Injection		8.57E-03	24.30
		18 Months Post-Injection		5.84E-03	16.56

TABLE 4-18
Bromide Tracer Test Results
Perchlorate Site
Elkton, Maryland

Well ID (Distance from Barrier)	Pre-Injection Tracer Test			Post-Injection Tracer Test		
	Sample Date	Days After Tracer Injection	Bromide (mg/L)	Sample Date	Days After Tracer Injection	Bromide (mg/L)
UPGRADIENT MONITORING WELLS						
SMW-1 (25 feet)	7/21/03	-2	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5/<0.5	7/23/04	1	<0.5
	9/30/03	69	<0.5	9/21/04	61	<0.5
SMW-2 (25 feet)	7/21/03	-2	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	8/26/03	34	0.7/0.7	8/24/04	33	<0.5
	9/30/03	69	<0.5	9/21/04	61	<0.5/<0.5
SMW-3 (25 feet)	7/21/03	-2	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5/<0.5
	9/30/03	69	<0.5/<0.5	9/21/04	61	<0.5
INJECTION WELLS						
IW-1	7/22/03	-1	<0.5/<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	11.0
	8/26/03	34	<0.5	8/24/04	33	<0.5/<0.5
	9/29/03	68	<0.5	9/21/04	61	<0.5
IW-2	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	4.3/4.3	7/23/04	1	38.9
	8/26/03	34	<0.5	8/24/04	33	<0.5
IW-3	7/22/03	-1	<0.5	7/20/04	-2	0.6
	7/24/03	1	193.7	7/23/04	1	278.0/279.7
	8/26/03	34	0.6/0.6	8/24/04	33	24.9
	9/29/03	68	1.0	9/21/04	61	4.5
IW-4	7/22/03	-1	<0.5	7/20/04	-2	1.7/1.7
	7/24/03	1	121.6	7/23/04	1	155.5
	8/26/03	34	1.2	8/24/04	33	10.2
IW-5	7/22/03	-1	<0.5	7/19/04	-3	<0.5/<0.5
	7/24/03	1	2.1	7/23/04	1	<0.5
	8/26/03	34	<0.5	8/24/04	33	<0.5
	9/29/03	68	9.9	9/21/04	61	<0.5/<0.5
IW-6	7/22/03	-1	<0.5/<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	8/26/03	34	<0.5	8/24/04	33	<0.5/<0.5
IW-7	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	9/29/03	68	0.5/0.5	9/21/04	61	0.9
IW-8	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5/<0.5
IW-9	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
IW-10	7/22/03	-1	<0.5	7/20/04	-2	<0.5/<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	9/29/03	68	<0.5	9/21/04	61	1.0

TABLE 4-18
Bromide Tracer Test Results
Perchlorate Site
Elkton, Maryland

Well ID (Distance from Barrier)	Pre-Injection Tracer Test			Post-Injection Tracer Test		
	Sample Date	Days After Tracer Injection	Bromide (mg/L)	Sample Date	Days After Tracer Injection	Bromide (mg/L)
DOWNGRADIENT MONITORING WELLS						
MW-6 (7.5 feet)	7/22/03	-1	<0.5/<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5/<0.5
	8/26/03	34	<0.5/<0.5	8/24/04	33	<0.5
	9/30/03	69	6.6	9/22/04	62	0.7
SMW-4 (12.5 feet)	7/21/03	-2	<0.5	7/19/04	-3	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	8/26/03	34	<0.5	8/24/04	33	<0.5
	9/30/03	69	1.6/1.4	9/22/04	62	<0.5
SMW-5 (20 feet)	7/21/03	-2	<0.5	7/20/04	-2	<0.5
	7/24/03	1	1.4	7/23/04	1	<0.5
	8/26/03	34	2.5	8/24/04	33	6.5
	9/30/03	69	0.5	9/22/04	62	1.6
SMW-6 (20 feet)	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5/<0.5	7/23/04	1	<0.5
	8/26/03	34	<0.5	8/24/04	33	<0.5/<0.5
	9/30/03	69	0.7	9/22/04	62	<0.5/<0.5
SMW-7 (20 feet)	7/21/03	-2	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
	9/30/03	69	0.9	9/22/04	62	0.9/0.9
TRACER TEST WELLS						
TT-1	7/22/03	-1	<0.5	7/20/04	-2	<0.5
	7/24/03	1	<0.5	7/23/04	1	<0.5
TT-2	7/21/03	-2	<0.5	7/20/04	-2	2.3/3.2
	7/24/03	1	Not Sampled	7/23/04	1	470.9
	8/26/03	34	6.4	8/24/04	33	32.4
	9/30/03	69	15.7/15.7	9/21/04	61	3.5

FIGURE 4-27a
Bromide Tracer Test Results
Pre-Emulsion Injection

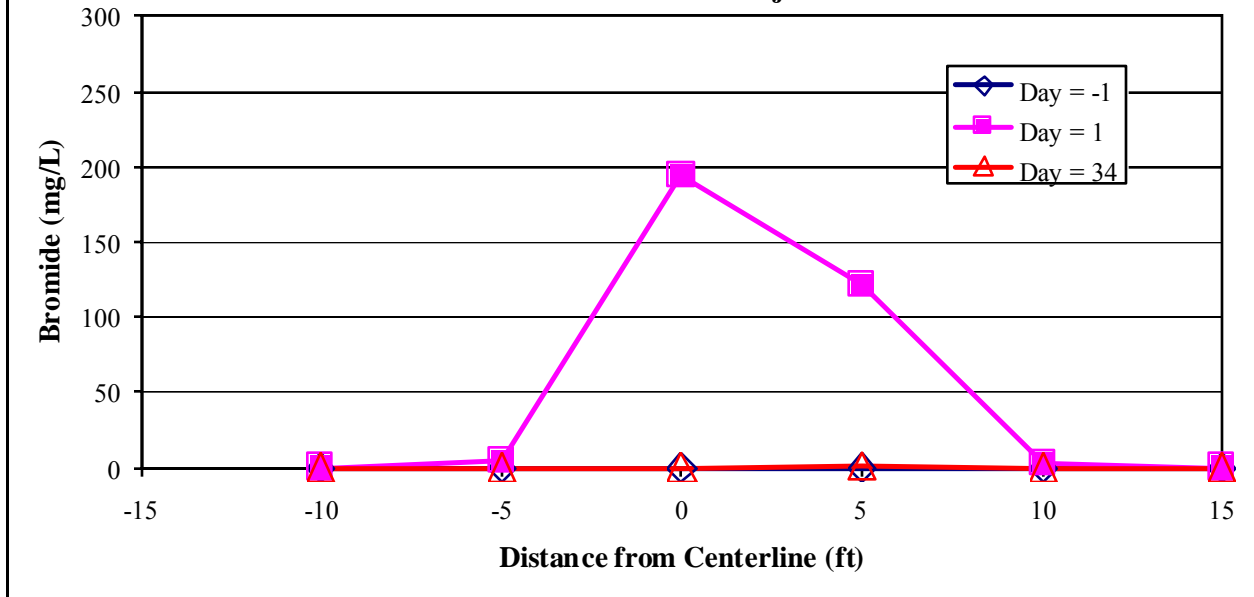
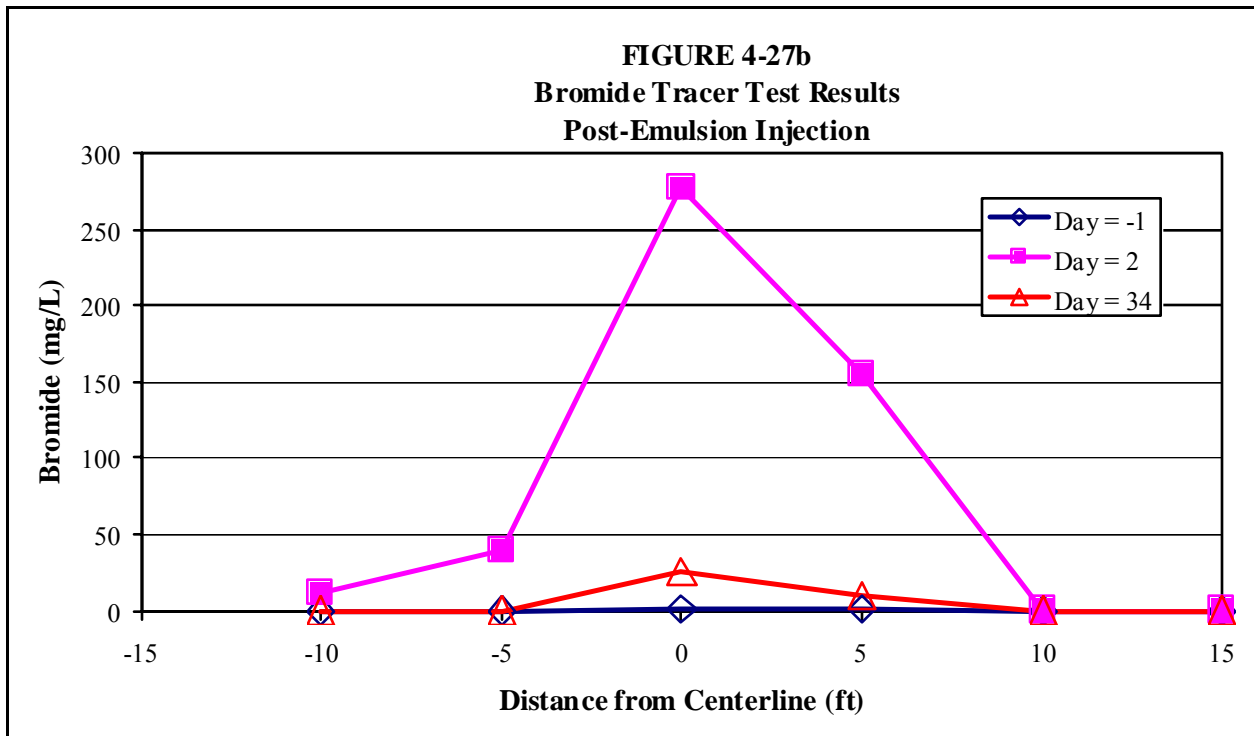


FIGURE 4-27b
Bromide Tracer Test Results
Post-Emulsion Injection



4.3.4 Secondary Water Quality Issues

Secondary water quality issues include changes to color, taste, and odor that could occur as a result of EOS[®] injection. The EOS[®] concentrate contains a faint soybean oil odor. The biological formation of fatty acids from the breakdown of EOS[®] may impart secondary taste and odor to the groundwater. Most of these fatty acids are expected to biodegrade within 25 to 50 ft of the EOS[®] barrier. As shown in Table 4-16, most of the volatile fatty acids at the Maryland site were degraded within 20 feet of the barrier. Other secondary water quality issues include increases in dissolved iron, manganese, and arsenic. As discussed in Section 4.3.1.4, increases in dissolved iron and manganese were observed in the pilot test area. However, these effects dissipated downgradient.

At the Maryland site, the interceptor trench for the air stripper is located less than 50 feet downgradient of the barrier. During the pilot test, increased fouling of the air stripper was observed and the stripper was shut down in early 2005. The increased fouling may have resulted from the increased levels of dissolved iron or from increased biofouling as a result of enhanced microbial activity in the groundwater and/or elevated BOD in the air-stripper influent.

4.3.5 Headspace and Soil Gas

Headspace and soil gas measurements were collected during the pilot test to monitor the potential accumulation of vapors. These data are summarized in Table 4-19. The headspace readings were collected from all of the injection wells and the upgradient and downgradient monitor wells to evaluate the accumulation of vapors due to biological activity. LEL measurements of 100% or greater were observed in all of the injection wells at 18 months post-injection. The elevated LEL readings indicate the accumulation of methane in these wells. Depressed headspace oxygen levels were also observed in all of the injection wells, and about half of these wells also showed some CO ranging from 0.1 to 15 ppm. In contrast, elevated LEL readings were not detected in the headspace of any of the upgradient or downgradient monitor wells. Oxygen readings remained at background levels, and no CO was detected. These results indicate that vapor accumulation was limited to the immediate vicinity of the PRB. Hydrogen sulfide (H₂S) was not detected in the headspace of any of the injection or monitor wells.

The soil gas monitoring points were used to assess the potential for vapors to migrate into the vadose zone and surface soils. As shown in Table 4-19, low LEL readings (less than 5%) and oxygen levels between 17 and 20% were detected in the soil gas monitoring points. These data suggest that the methane is being consumed aerobically in the vadose zone overlying the aquifer before it reaches the surface. Hydrogen sulfide was not detected in any of the soil gas monitoring points, and CO was detected at concentrations <1 ppm.

TABLE 4-19
Summary of Headspace and Soil Gas Monitoring Results
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	Headspace CH ₄ %	Headspace CO ₂ %	Headspace O ₂ %	Headspace H ₂ S ppm	Headspace LEL %	Headspace CO ppm
Upgradient Monitoring Wells							
SMW-1 (25 feet)	12/15/2003	0.0	0.7	19.0	NM	NM	NM
	2/17/2004	0.0	NM	19.4	0.0	0.1	0.0
	4/20/2005	NM	NM	20.6	0.0	0.0	0.0
SMW-2 (25 feet)	12/15/2003	0.0	0.7	19.9	NM	NM	NM
	2/17/2004	0.0	NM	19.7	0.0	0.0	0.0
	4/20/2005	NM	NM	20.9	0.0	0.0	0.0
SMW-3 (25 feet)	12/15/2003	0.0	0.3	20.4	NM	NM	NM
	2/17/2004	0.0	NM	19.8	0.0	0.0	0.0
	4/20/2005	NM	NM	20.5	0.0	0.0	0.0
Injection Wells							
IW-1	12/15/2003	0.0	2.4	18.3	NM	NM	NM
	2/17/2004	0.4	NM	20.7	0.0	8.0	0.8
	4/20/2005	NM	NM	16.2	0.0	>100	5.0
IW-2	12/15/2003	0.0	0.9	19.8	NM	NM	NM
	2/17/2004	0.2	NM	20.6	0.0	6.0	0.0
	4/20/2005	NM	NM	3.6	0.0	>100	0.0
IW-3	12/15/2003	0.0	1.9	17.7	NM	NM	NM
	2/17/2004	0.1	NM	20.8	0.0	0.5	0.0
	4/20/2005	NM	NM	11.3	0.0	>100	10.0
IW-4	12/15/2003	0.0	1.5	17.9	NM	NM	NM
	2/17/2004	0.0	NM	18.9	0.0	0.9	0.2
	4/20/2005	NM	NM	15.7	0.0	>100	0.0
IW-5	12/15/2003	0.0	1.7	14.8	NM	NM	NM
	2/17/2004	0.0	NM	15.9	0.0	0.1	0.0
	4/20/2005	NM	NM	3.6	0.0	>100	15.0
IW-6	12/15/2003	0.0	0.7	19.1	NM	NM	NM
	2/17/2004	0.0	NM	19.2	0.0	3.0	0.0
	4/20/2005	NM	NM	18.4	0.0	>100	2.0
IW-7	12/15/2003	0.0	0.6	20.1	NM	NM	NM
	2/17/2004	0.0	NM	19.1	0.0	1.4	0.0
	4/20/2005	NM	NM	13.6	0.0	>100	1.0
IW-8	12/15/2003	0.0	0.9	19.0	NM	NM	NM
	2/17/2004	0.1	NM	18.9	0.0	0.8	0.1
	4/20/2005	NM	NM	16.8	0.0	>100	0.0
IW-9	12/15/2003	0.0	0.3	20.1	NM	NM	NM
	2/17/2004	0.0	NM	19.4	0.0	0.3	0.0
	4/20/2005	NM	NM	7.5	0.0	>100	0.0
IW-10	12/15/2003	0.0	0.2	20.6	NM	NM	NM
	2/17/2004	0.0	NM	19.9	0.0	0.1	0.0
	4/20/2005	NM	NM	17.2	0.0	>100	0.0
Downgradient Monitoring Wells							
MW-6 (7.5 feet)	12/15/2003	NM	NM	NM	NM	NM	NM
	2/17/2004	NM	NM	NM	NM	NM	NM
	4/20/2005	NM	NM	19.0	0.0	0.0	0.0

TABLE 4-19
Summary of Headspace and Soil Gas Monitoring Results
Maryland Perchlorate Site

Well ID (Distance from barrier)	Sample Date	Headspace CH ₄ %	Headspace CO ₂ %	Headspace O ₂ %	Headspace H ₂ S ppm	Headspace LEL %	Headspace CO ppm
SMW-4 (12.5 feet)	12/15/2003	0.0	0.3	20.6	NM	NM	NM
	2/17/2004	0.0	NM	19.3	0.0	0.2	0.0
	4/20/2005	NM	NM	20.5	0.0	0.0	0.0
SMW-5 (20 feet)	12/15/2003	0.0	0.2	20.6	NM	NM	NM
	2/17/2004	0.0	NM	19.9	0.0	0.0	0.0
	4/20/2005	NM	NM	20.9	0.0	0.0	0.0
SMW-6 (20 feet)	12/15/2003	0.0	0.3	20.8	NM	NM	NM
	2/17/2004	0.0	NM	20.2	0.0	0.0	0.0
	4/20/2005	NM	NM	20.5	0.0	0.0	0.0
SMW-7 (20 feet)	12/15/2003	0.0	0.6	20.6	NM	NM	NM
	2/17/2004	0.0	NM	19.8	0.0	0.1	0.0
	4/20/2005	NM	NM	20.4	0.0	0.0	0.0
Soil Gas Monitoring Points							
SG-1	12/15/2003	0.0	0.9	19.3	NM	NM	NM
	2/17/2004	0.2	NM	19.2	0.0	0.2	0.1
	4/20/2005	NM	NM	17.7	0.0	3.0	0.0
SG-2	12/15/2003	0.0	0.5	20.1	NM	NM	NM
	2/17/2004	NM	NM	18.3	0.0	1.0	0.9
	4/20/2005	NM	NM	18.4	0.0	0.0	0.0
SG-3	12/15/2003	0.0	0.3	20.7	NM	NM	NM
	2/17/2004	0.0	NM	17.1	0.0	2.1	0.7
	4/20/2005	NM	NM	18.5	0.0	0.0	0.0
SG-4	12/15/2003	0.0	0.8	20.2	NM	NM	NM
	2/17/2004	0.0	NM	19.5	0.0	0.0	0.0
	4/20/2005	NM	NM	18.8	0.0	0.0	0.0
Tracer Test Wells							
TT-1	2/14/2004	0.0	NM	21.0	0.0	0.0	0.0
	4/20/2005	NM	NM	NM	NM	NM	NM
TT-2	12/15/2003	0.0	0.2	19.1	NM	NM	NM
	2/17/2004	0.0	NM	19.9	0.0	0.1	0.0
	4/20/2005	NM	NM	NM	NM	NM	NM

Note:

NM denotes not measured.

4.3.6 Emulsified Oil Longevity

The longevity of the emulsified oil in the subsurface at the Maryland site was estimated to determine the approximate time required before substrate re-injection. The longevity was calculated in two ways: 1) by developing a mass balance of organic and inorganic carbon entering and discharging from the barrier and 2) by calculating the oil demand based on observed changes in contaminants and biogeochemical parameters.

Changes in total inorganic carbon (TIC) and total organic carbon (TOC) during passage through the barrier were determined by comparing the average TIC and TOC concentrations in wells upgradient and within the barrier. Carbon from methane was also added, since this carbon was likely missed by the TOC analysis due to the volatility of methane. Table 4-20 shows the carbon calculations which indicate that on average 93 mg/L of carbon are being released from the barrier. A time-weighted average was also calculated as 46.84 mg/L of carbon released by the barrier. The time-weighted average is probably more representative due to the high initial release of carbon which skews the average. The time-weighted average value was used in conjunction with the estimated groundwater flow velocity to calculate that the net mass flux of carbon discharging from the barrier is 0.29 pounds of carbon per day.

TABLE 4-20
Carbon Released by Barrier
Perchlorate Site
Elkton, Maryland

Sample Date	Days Since Injection	Average 25 ft Upgradient (mg/L)	Average Injection Well (mg/L)	Carbon Released by Barrier (mg/L)
9/30/03	-9	23.99	23.67	
10/13/03	4	22.75	302.62	279.87
11/13/03	35	20.35	93.79	73.43
12/16/03	68	21.27	97.71	76.45
2/19/04	133	18.31	67.49	49.18
9/21/04	348	20.13	71.77	51.64
4/21/05	560	24.30	52.67	28.37
Average over 18 months (mg/L)				93.16
Time-weighted average over 18 months (mg/L)				46.84

The mass flux of carbon discharging from the barrier was then compared with the amount of carbon injected to develop an approximate substrate life. Accounting for only the carbon from the soybean oil in the EOS[®], approximately 380 pounds of carbon were injected (assuming EOS[®] is 60% soybean oil, and soybean oil is 75% carbon).

Therefore, the carbon should remain in the subsurface for approximately 3.6 years. However, the efficiency of the barrier will degrade over time as the oil is consumed.

The substrate life was also estimated using observed changes in contaminant concentrations and biogeochemical parameters. The average difference between the three upgradient wells and three wells 20 feet downgradient over the course of the 18-month pilot test was determined. These values were then entered into the oil demand spreadsheet (Appendix E). Using these data, the spreadsheet calculated a substrate life of 2.7 years based on injection of 110 gallons of EOS[®] concentrate.

5.0 Cost Assessment

5.1 Cost Reporting

An evaluation of the costs specific to this demonstration are summarized in Table 5-1. A large portion of the costs was associated with site characterization, laboratory studies, and engineering design, modeling and planning. Most of these costs are due to the rigorous evaluation conducted as part of the demonstration project. The primary costs of the technology are associated with the actual injection process including costs for installing the injection wells, purchasing the substrate for injection, mobilizing to the site, and performing the injection. After the injection was completed, subsequent costs were associated with monitoring and evaluating the performance of the barrier.

**TABLE 5-1
Cost Tracking
Maryland Perchlorate Site**

Cost Category	Sub-Total	Total
Capital Costs		
Site Characterization		\$40,300
Laboratory Studies		\$30,000
Engineering design, modeling, planning		\$26,500
Materials (Substrate & Delivery to Site)		\$3,000
Construction of Barrier		\$20,200
- Injection Well Installation	\$10,000	
- Substrate Injection	\$3,000	
- Equipment	\$1,500	
- Mob/demob, set-up, travel	\$5,700	
Monitoring Well Installation		\$12,000
Total Capital Costs		\$132,000
O&M Costs		
Maintenance (over 18 months of operation)		\$0
Monitoring (7 events @ \$12,000/event)		\$84,000
Total O&M Costs		\$84,000
Total Project Costs		\$216,000

5.2 Cost Analysis

5.2.1 Cost Comparison

A detailed cost comparison will be provided in the Cost and Performance Report and will incorporate cost data from both demonstration sites. Emulsified oils will be compared to iron PRBs and to pump-and-treat systems. As discussed in Section 5.2.2 below, we estimated the installation costs of a full-scale emulsified oil PRB at the Maryland site to be approximately \$38,000 which is equivalent to \$19/square foot of barrier or \$0.02/gallon treated. As a rough comparison, construction costs for zero valent iron barriers vary from \$30 to \$500 per square foot of barrier with an average cost of \$200 per square foot (ESTCP, 1999). Since iron barriers are not effective for treatment of perchlorate, we also obtained capital cost estimates from Shaw Environmental for adding an ion exchange unit to the existing pump-and-treat system at the site. The estimated costs for ion exchange are \$50,000 capital cost with \$17,000 annual O&M. A life cycle cost analysis is provided in Section 5.2.4 below.

5.2.2 Cost Basis

The pilot test PRB at the Maryland perchlorate site treats approximately 250 gallons per day. This barrier cost approximately \$23,200 to install. We have estimated the longevity of pilot PRB to be 1.5 to 2.5 years. Assuming a 2-year life, the barrier will treat 182,500 gallons. Therefore, the pilot-scale PRB cost \$0.13/gallon treated or \$46/square foot of barrier. The costs for this PRB are higher than expected given the nature of the demonstration project. A shorter design life and a closer well spacing were used in the design compared to a full-scale system.

Solutions-IES has estimated the costs of a full-scale PRB at the site (Table 5-2). The PRB would be 200 feet long with 10 injection wells spaced 20 feet on center and would be designed with a 5-year life. The estimated costs for installation of this PRB are \$38,000. The full-scale barrier would treat approximately 1,000 gallons per day. Therefore, the costs of the full-scale system are \$0.02/gallon treated or \$19/square foot of barrier.

TABLE 5-2
Estimated Capital Costs Full-Scale PRB
Maryland Perchlorate Site

Cost Category	Sub-Total	Total
Capital Costs		
Materials (Substrate & Delivery to Site)		\$13,000
Construction of Barrier		\$25,000
- Injection Well Installation	\$10,000	
- Substrate Injection	\$6,000	
- Equipment	\$3,000	
- Mob/demob, set-up, travel	\$6,000	
Total Capital Costs		\$38,000

Notes:

Design includes 200-ft long barrier with 10 wells spaced 20-ft on center.

Design life of 5 years.

5.2.3 Cost Drivers

The primary cost drivers associated with this technology are related to the injection process, including the number and spacing of injection wells required, the volume of substrate and chase water needed, and the time required to complete the injection. These costs are primarily influenced by the subsurface lithology and contaminant mass. The potential need for future re-injection of emulsion is also a primary cost driver. In the Cost and Performance Report, a sensitivity analysis will be performed to evaluate how different factors impact costs. Factors that will be considered include contaminant concentrations, presence of co-contaminants, impacted depth, radius of influence, and groundwater velocity.

5.2.4 Life Cycle Costs

The major cost factors associated with emulsified oils are expected to be: (1) initial set-up and injection costs; and (2) required frequency for substrate re-injection. The total net present value (NPV) for implementation of a full-scale emulsified oil PRB was calculated over a 30-year period using an annual discount rate of 3.4%. One of the major uncertainties in determining life cycle costs is the required frequency for substrate re-injection. However, without long-term monitoring data, it is impossible to precisely determine this frequency. For cost estimating purposes, we have assumed that additional oil will be reinjected once every five years. For each re-injection, we have included the following costs: (a) replacement of 25% of the injection wells; and (b) materials and labor for substrate injection.

Table 5-3 shows the 30-year life cycle costs for a full-scale emulsified oil PRB. For comparison purposes, we also calculated the 30-year life cycle costs of adding an ion exchange unit to the existing pump-and-treat system at the Maryland site. As shown in the table, the 30-year life cycle costs for installing an emulsified oil PRB are estimated to be \$161,400 compared to \$383,600 for adding an ion exchange unit to the existing pump-and-treat system.

TABLE 5-3
Estimated Life Cycle Costs
Maryland Perchlorate Site

Cost Category	Emulsified Oil PRB	Ion Exchange
Capital Costs	\$38,000	\$50,000
Annual O&M	\$0	\$17,000
Re-Injection Costs (every 5 years)	\$30,000	NA
Present value for 30 years (3.4% discount rate)	\$161,400	\$383,600

Notes:

1. Emulsified oil PRB costs, we assumed re-injection every 5 years. Re-injection costs include replacement of 25% of the injection wells and materials and labor for substrate injection.
2. Ion exchange costs are for adding an ion exchange unit to the existing pump-and-treat system.

6.0 Implementation Issues

6.1 Environmental Checklist

An underground injection permit or similar permit may be required to perform the injection of the emulsion. All materials used in the process are Generally Recognized As Safe (GRAS), food-grade materials (21 CFR 184.1400) to aid in gaining regulatory approval for *in situ* application.

6.2 Other Regulatory Issues

Solutions-IES met with site representatives and regulators before starting the project to address any regulatory concerns. An additional meeting was held approximately 1 year into the project and written progress reports were submitted to update the regulators on the status of the demonstration.

Solutions-IES has attempted to disseminate information about the performance of the technology through presentations at various conferences and several publications, as listed below:

Presentations

- *Enhanced Anaerobic Bioremediation Using Emulsified Edible Oil*, Short Course, The Eighth International In Situ and On-Site Bioremediation Symposium, Baltimore, MD, June 6-9, 2005.
- *Perchlorate and TCA Treatment in an EOS[®] Permeable Reactive Barrier*, The Eighth International In Situ and On-Site Bioremediation Symposium, Baltimore, MD, June 6-9, 2005.
- *Remediation of Perchlorate and Trichloroethane in Ground Water Using Edible Oil Substrate (EOS[®])*, MTBE and Perchlorate: Remediation and Public Policy, Costa Mesa, California June 3-4, 2004.
- *Oil Emulsion Treatment of Perchlorate and Trichloroethane in Groundwater*. Remediation of Chlorinated and Recalcitrant Compounds, The Fourth International Conference, May 24-27, 2004, Monterey, California.
- *Potential for Using Edible Oil Emulsion for Remediation of Chlorinated Solvents in a Source Area*, Partners in Environmental Technology Technical Symposium & Workshop, SERDP and ESTCP, Washington D.C., Dec. 2-4, 2004.
- *Anaerobic Biodegradation of Perchlorate and 1,1,1-Trichloroethane using Edible Oil Emulsion*, Partners in Environmental Technology Technical Symposium & Workshop, SERDP and ESTCP, Washington D.C., Dec. 2-4, 2003.

Publications

- Lieberman, M.T., C. Zawtocki, R.C. Borden and G.M. Birk, 2004. *Remediation of Perchlorate and Trichloroethane in Ground Water Using Edible Oil Substrate (EOS[®])*, MTBE and Perchlorate: Remediation and Public Policy, Costa Mesa, CA, June 3-4.
- Zawtocki, C., M.T. Lieberman, R.C. Borden and G.M. Birk, 2004. *Treatment of Perchlorate and 1,1,1-Trichloroethane in Groundwater Using Edible Oil Substrate*

(EOS[®]). Remediation of Chlorinated and Recalcitrant Compounds – 2004, Proceedings of the Forth International Conference, Monterey, CA, May 24-27, 2004.

- Zawtock, C., M.T. Lieberman, and G.M. Birk, 2004. *A Dash of Oil and Let Marinate*. Pollution Engineering, May 2004, pages 30-34.

6.3 End-User Issues

Potential end users of the technology include a variety of agencies within the federal government (Dept. of Defense, Dept. of Energy, Environmental Protection Agency), state and local governments, and private industry. The site representatives at the Maryland site have been extremely pleased with the demonstration results and are planning to use EOS[®] to treat the source area at the site (the former surface impoundment).

Potential end user concerns may include:

- Possible permeability losses due to injection of the emulsion;
- Potential impact of elevated residual concentrations of daughter products;
- Sorption of the contaminants to the oil versus degradation;
- Secondary water quality issues (e.g., changes to color, taste and odor that might occur); and
- Gas production.

These concerns were addressed during the pilot test demonstration and are discussed in detail in Section 4.3. A brief summary is provided below:

- Some permeability losses are observed in the immediate vicinity of the injection wells. However, at the Maryland site, these changes did not appear to substantially impact groundwater flow through the PRB. Some flow around the PRB was observed along the edges of the treatment area. Permeability losses should be considered when designing emulsified oil projects. Designing barriers to extend 10 to 20 percent beyond the targeted treatment zone can help minimize these effects.
- Daughter products can accumulate if complete biodegradation is not occurring. This is typically not a concern for perchlorate, but can be a potential issue with chlorinated solvents. The contact time needed for complete dechlorination should be considered in the design. Contact times between 30 and 90 days may be needed. In addition, bioaugmentation can be used, if needed, to achieve complete biodegradation.
- Sorption of chlorinated solvents to the oil is typically observed within the injection zone immediately after injection. However, within 1 month of injection, sorption is typically no longer evident and biodegradation is the predominant contaminant reduction pathway. This was observed at the Maryland site as evidenced by the changes in molar concentrations of chlorinated ethanes/ethenes and reductions in chlorine number.

- By-products of emulsified oil injection may include metals mobilized from the solid phase (e.g., iron, manganese), methane, dissolved organic carbon, taste, and odor. Typically, these impacts are limited to the reactive zone. In addition, it is generally believed that dissolved metals will be re-precipitated downgradient when background conditions are reached. During the pilot test, increased fouling of the air stripper was observed. The increased fouling likely resulted from increased levels of dissolved iron and manganese as a result of enhanced microbial activity in the aquifer. These adverse impacts were probably aggravated by the small distance between the EOS[®] barrier and the extraction trench. Enhanced anaerobic bioremediation processes often result in increased levels of dissolved iron, manganese, methane, and organic carbon in the immediate vicinity of the treatment system. Potential adverse impacts on downgradient receptors should be evaluated, especially when the receptor is located within 100 ft of the bioremediation system.
- Gases, such as methane and hydrogen sulfide, may be produced and may potentially migrate into the vadose zone. At the Maryland site, methane accumulation was only observed in the headspace of the injection wells. Vapor accumulation was not detected in the soil gas monitoring points indicating that the methane is being consumed in the vadose zone and does not reach the land surface. At sites where subsurface structures are located in close vicinity to the injection zone, engineering solutions should be used to minimize the potential for vapor accumulation.

7.0 References

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8.0 Points of Contact

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Mr. Stephen Markowski	Maryland Dept. of Environment Hazardous Waste Program Waste Management Administration 1800 Washington Blvd Ste. 645 Baltimore, MD 21230-1719	410-537-3354 410-537-4133 (fax) smarkowski@mde.state.md.us	State Regulatory Contact
Mr. Charles Smyser	Cecil County Health Department Environmental Health Center 401 Bow St Elkton, MD 21921-5515	(410) 996-5160 (410) 996-5153 csmyser@dnhm.state.md.us	County Contact

**APPENDIX A
BORING LOGS**

Log of Soil Boring SMW-6

Project: Maryland Perchlorate Test Site Solutions-IES Project No.: 1130.02A3.ESTC Boring Number: SMW-6
 Client: ESTCP Page: 1 of 1
 Project Location: Maryland City: County:
 Site or Site Area:
 Drilling Method: Geoprobe 3.25" Casing Date Started: 4/22/2003 Date Finished: 4/22/2003
 Sample Type: Soil and Groundwater Initial Water Level: N/R Final Water Level: 4.0' bgs
 Logged By: W. Beckwith Checked By: WJB Total Depth of Boring: 16' bgs Total Depth of Well: 15' bgs

SUBSURFACE PROFILE				SAMPLE				PID Field Screen		Lab Sample	Well Data
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interval	Type	Blows per Foot (N)	Recovery	ppm		
40	0		Ground Surface								
39	0		(ML) Dark Brown SILT (topsoil)								
	1		(ML) Brown Clayey SILT with some fine Mica.	1		MC					
36	3		(SM-GM) Medium Brown Silty SAND with Gravel.								
	4										
	5										
	6			2		MC					
	7										
	8										
	9										
	10			3		MC					
	11										
	12										
	13										
	14										
24	15			4		MC					
24	16		(CL) Yellow Brown Silty CLAY with Gravel.								
	17		16 ft								
	18										

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Log of Soil Boring IW-1

Project: Maryland Perchlorate Test Site Solutions-IES Project No.: 1130.02A3.ESTC Boring Number: IW-1

Client: ESTCP

Page: 1 of 1

Project Location: Maryland

City:

County:

Site or Site Area:

Drilling Method: Geoprobe 3.25" Casing

Date Started: 4/23/2003

Date Finished: 4/23/2003

Sample Type: Soil and Groundwater

Initial Water Level: N/R

Final Water Level: 4.0' bgs

Logged By: W. Beckwith Checked By: WJB

Total Depth of Boring: 16' bgs

Total Depth of Well: 14' bgs

SUBSURFACE PROFILE				SAMPLE				PID Field Screen			Well Data	
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interval	Type	Blows per Foot (N)	Recovery	250 ppm	500 ppm		750 ppm
40	0		Ground Surface									
39	1		<i>(ML)</i> Dark Brown SILT (topsoil)									
36	2		<i>(ML)</i> Brown Clayey SILT with some fine Mica.	1		MC						
	3											
	4		<i>(SM-GM)</i> Light Brown, Silty SAND with Gravel.									▼
	5											
	6			2		MC						
	7											
	8											
	9											
	10			3		MC						
	11											
	12											
	13		Water sample collected with Screen Point Sampler from 10.5 to 14 feet bgs.									▬
25	14			4		MC						
24	15		<i>(GC)</i> Brown Sandy CLAY and Silty SAND									
24	16		<i>(SM)</i> Tan to yellow Brown Silty Fine SAND.									
	17		<i>(ML/CL)</i> Dark Gray Silty Clay									
	18		16 ft									

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Log of Soil Boring IW-5

Project: Maryland Perchlorate Test Site Solutions-IES Project No.: 1130.02A3.ESTC Boring Number: IW-5
 Client: ESTCP Page: 1 of 1
 Project Location: Maryland City: County:
 Site or Site Area:
 Drilling Method: Geoprobe 3.25" Casing Date Started: 4/23/2003 Date Finished: 4/23/2003
 Sample Type: Groundwater Initial Water Level: N/R Final Water Level: 4.0' bgs
 Logged By: W. Beckwith Checked By: WJB Total Depth of Boring: 16' bgs Total Depth of Well: 16' bgs

SUBSURFACE PROFILE				SAMPLE					PID Field Screen		Lab Sample	Well Data
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interval	Type	Blows per Foot (N)	Recovery	250 ppm	500 ppm		
40	0		Ground Surface									
	1		<p>No soil samples collected. No lithology recorded.</p> <p>Screen Point Sampler used to collect water samples. first interval from 8.5 to 12 feet. Second interval from 12.5 to 16 feet.</p>									
	2											
	3											
	4											
	5											
	6											
	7											
	8											
	9											
	10											
	11											
	12											
	13											
	14											
24	15											
	16		16 ft									
	17											
	18											

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Log of Soil Boring IW-10

Project: Maryland Perchlorate Test Site Solutions-IES Project No.: 1130.02A3.ESTC Boring Number: IW-10
 Client: ESTCP Page: 1 of 1
 Project Location: Maryland City: County:
 Site or Site Area:
 Drilling Method: Geoprobe 3.25" Casing Date Started: 4/23/2003 Date Finished: 4/23/2003
 Sample Type: Soil Initial Water Level: N/R Final Water Level: 4.0' bgs
 Logged By: W. Beckwith Checked By: WJB Total Depth of Boring: 16' bgs Total Depth of Well: N/A

SUBSURFACE PROFILE				SAMPLE				PID Field Screen			Lab Sample	Well Data
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interval	Type	Blows per Foot (N)	Recovery	250 ppm	500 ppm		
40	0		Ground Surface									
39	0		(ML)									
	1		Dark Brown SILT (topsoil									
	2		(ML)									
36	2		Brown Clayey SILT with some fine Mica.	1		MC						
	3											
	4		(SM-GM)									
	4		Light Brown, Silty SAND with Gravel.									▼
	5											
	6			2		MC						
	7											
	8											
	9											
	10			3		MC						
	11											
	12											
	13											
26	14		(GC)									
25	14		Orange and Gray Clayey GRAVEL.	4		MC						
	15											
24	15		(CL-ML)									
	16		Gray Clayey SILT, Saprolitic Appearance									
	17											
	18		16 ft									

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Log of Soil Boring Well TT

Project: Maryland Perchlorate Test Site Solutions-IES Project No.: 1130.02A3.ESTC Boring Number: TT
 Client: ESTCP Page: 1 of 1
 Project Location: Maryland City: County:
 Site or Site Area:
 Drilling Method: Geoprobe 3.25" Casing Date Started: 4/22/2003 Date Finished: 4/22/2003
 Sample Type: Soil and Groundwater Initial Water Level: N/R Final Water Level: 4.0' bgs
 Logged By: W. Beckwith Checked By: WJB Total Depth of Boring: 16' bgs Total Depth of Well: 16' bgs

SUBSURFACE PROFILE				SAMPLE				PID Field Screen			Lab Sample	Well Data
Elevation	Depth in Feet	Symbol	Description	Number	Sample Interval	Type	Blows per Foot (N)	Recovery	• ppm	• ppm		
40	0		Ground Surface									
39	0		(ML) Dark Brown SILT (topsoil)									
36	1		(ML) Brown Clayey SILT with some fine Mica.	1		MC						
34	2		(SM-GM) Medium Brown Silty SAND with Gravel.									
32	3		(SM-GM) Boulders and Cobbles. Geoprobe refusal. Required several offset borings to penetrate beyond 8 feet.	2		MC						
25	4		(SM-GM) Brown Silty SAND and Gravel									
24	5		(SM-GM) Brown Silty SAND and Gravel	3		MC						
24	6		(GC) Orange Silty CLAY with Gravel	4		MC						
24	7		(CL) Gray Green Silty CLAY									
19	8		(CL/GC) Gray CLAY with Gravel									
20	9		(ML) Gray SILT with Saprolite texture.									
21	10		16 ft									

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APPENDIX B
LABORATORY EVALUATION OF
EDIBLE OIL TRANSPORT AND UTILIZATION REPORT

Final Report to

Solutions Industrial & Environmental Services, Inc.
3722 Benson Drive
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919-873-1060
Attn: M. Tony Lieberman

For Research Entitled

Laboratory Evaluation of Edible Oil Transport and Utilization

Department of Civil, Construction and Environmental Engineering
North Carolina State University
Box 7908
Raleigh, NC 27695

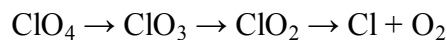
November 1, 2005

1.0 INTRODUCTION

Perchlorate salts are manufactured in large quantities for use as oxidizers in solid rocket propellants, explosives and automobile air bag inflators. Although it reacts energetically when dry, perchlorate in aqueous solution is extremely stable and highly soluble, and therefore difficult to remove with conventional treatment processes. However, in the presence of a suitable electron donor, bacteria can mediate the reduction of perchlorate through the chemical reaction:



In general, perchlorate reduction is very slow even though perchlorate is a strong oxidizing agent. The perchlorate pathway proposed by Rikken (1996) is widely accepted for bacterial respiration, using acetate in each step and forming CO_2 , H_2O and biomass:



Perchlorate is known to occur naturally in only a very few locations (nitrate deposits). However, bacteria capable of degrading perchlorate are surprisingly widespread in nature (Logan, 2001). The ability to use nitrate and chlorate as the electron acceptors is a common characteristic of many heterotrophic perchlorate reducing organisms. Enzymatic reduction of chlorate to chlorite by nitrate reductase occurs as a competitive reaction between nitrate and chlorate in certain denitrifying bacteria (Stouthamer, 1988). Perchlorate and chlorate respiring bacteria contain chlorite dismutase, an enzyme capable of disproportioning chlorite to chloride and oxygen with high efficiency (Van Ginkel, 1988). This is an interesting biological development

because oxygen is a preferred electron acceptor, and under fully aerobic conditions, even bacteria that are capable of carrying out this process do not reduce perchlorate.

1,1,1-Trichloroethane (TCA) is a synthetic organic solvent widely used in industrial processes as a metal degreasing and dry-cleaning solvent and as a feed-stock for production of other organic chemicals. It is a major environmental pollutant commonly found in soil, groundwater, and the atmosphere. Because of TCA's adverse effects on human health, the EPA has set a maximum contaminant level of 200 µg/L in drinking water. TCA is also listed as an ozone-depleting substance by the United Nations Environment Programme. Even when released into soil or leached into groundwater, the primary environmental fate of TCA is volatilization to the atmosphere, where it interacts with ozone and contributes to erosion of the ozone layer. (EPA, 1998).

TCA is relatively resistant to biodegradation. Transformation of TCA to 1,1-dichloroethane (DCA) and chloroethane (CA) occurs through reductive dechlorination. DCA was found as the main product of TCA biotransformation, but conversion to CA and complete dechlorination to CO₂, acetic acid and unknown products was also detected (Vogel and McCarty, 1985).

2.0 APPROACH AND EXPERIMENTAL METHODS

The objective of this project is to evaluate the use of edible oils for enhancing long-term degradation of 1,1,1-trichloroethane (TCA) and perchlorate in laboratory microcosms using

sediment and groundwater from a TCA and perchlorate site in Maryland. Experimental treatments include the following:

1. killed control with emulsified liquid soybean oil, yeast extract and NaOH sufficient to increase the pH>12;
2. live control with no added carbon;
3. emulsified liquid soybean oil, lactate, and yeast extract;
4. emulsified hydrogenated soybean oil, lactate and yeast extract; and
5. emulsified liquid soybean oil, lactate, yeast extract and a bioaugmentation culture enriched from a chlorinated solvent impacted site in Lumberton, NC.

The methods employed in this experiment were designed to mimic groundwater conditions typically seen in contaminated sites. Microcosm and soil column experiments were performed in the NCSU Environmental Engineering Lab with available analytical tools. In all cases, care was taken to ensure the quality of results and the integrity of samples. Duplicate analyses were conducted on approximately 10% of all samples to evaluate the reproducibility of the analytical measurements. The potential for enhancing biodegradation of perchlorate and TCA using liquid soybean oil and hydrogenated soybean oil were evaluated in batch microcosm and intermittent flow columns.

2.1 Analytical Methods

Standard method 4110B: 'Ion chromatograph with chemical suppression of eluent conductivity' was used for analysis of sulfate, nitrate and nitrite ions. Typically, samples were collected from sample ports at the top of the columns and diluted 9:1 with a carbonate eluent

matrix. Samples were allowed to sit 24 hours permitting the dissolved iron to precipitate and settle out of solution, and then filtered using a 0.45 micron syringe filter and frozen until analyzed.

A standard lab analytical pH probe and meter were used for all pH measurements. Perchlorate concentration was monitored using a specific ion electrode. The meters were calibrated before and after every 15-20 samples using pH 4.0 and 7.0 buffers. 5 mL samples were required for effective measurement and analysis occurred immediately after sampling. Standard storage, handling and calibration procedures supplied by the manufacturer were used. Duplicate samples were sent to a commercial laboratory for perchlorate analysis following USEPA approved protocols for perchlorate.

Total organic carbon (TOC) was analyzed using both the DC-190 TOC analyzer manufactured by Dohrman Scientific Products and the Shimadzu TOC analyzer with autosampler. When using the Dohrman DC-190, total carbon (TC) and inorganic carbon (IC) were determined by manual injection of an undiluted sample. TOC was determined as the difference between TC and IC. When using the Shimadzu TOC analyzer, 1:9 dilutions were used in a DI water matrix for analysis. Samples were stored in 2.5 mL serum bottles at 4°C until analyzed.

Dissolved oxygen was measured using Chemet DO ampoules. The detectable range for the Chemet kits was 0-1.0 mg/L of dissolved oxygen. Samples were immediately analyzed and the

ampoules were broken directly into the sampling syringes to limit exposure to atmospheric conditions.

2.2 Experimental Materials

Sediment used for the experiments is from an aquifer in Elkton, MD, sieved before use in microcosms and column experiments using a No. 4 standard size sieve.

The emulsions used for column treatments were prepared according to the procedure outlined by Coulibaly and Borden (2004). They demonstrated that oil-in-water emulsions with small uniform droplets can be prepared by using soybean oil and food grade surfactants that are generally recognized as safe. The emulsions used in this current project were prepared by blending 33% by volume soybean oil, 62% water and 5% premixed surfactant (38% polysorbate 80, 56% glycerol monooleate GMO from Lambent Technologies, and 6% water). The outlined proportions were mixed in a Waring Commercial blender at high speed for five minutes to produce an emulsion with droplets ranging from 1 to 3 μm in diameter. The wax emulsions were prepared similarly by using a fully hydrogenated soybean wax that was first melted in a hot water bath. Hot water was used in the blending process as well, but insignificant separation occurred after mixing.

2.3 Microcosm Procedure

Microcosm experiment was conducted to evaluate the potential of liquid soybean oil and hydrogenated soybean oil to enhance biodegradation and/or immobilization of perchlorate, and

determine whether bioaugmentation was needed to achieve complete conversion of TCA to non-toxic end products. Each microcosm set was prepared in triplicate 245 mL serum bottles containing 175 mL of water from Elkton aquifer, 1.0 μ L of pure 1,1,1-TCA and a bacterial inoculum where necessary. The bioaugmentation culture used in this work was enriched from aquifer material in Lumberton, NC and maintained in the NCSU Environmental laboratory by feeding periodically with nutrient media, lactate, yeast extract and PCE and TCA. Bottles were fitted with thick rubber stoppers and aluminum crimp seals to exclude oxygen. In all the substrate amended treatments, 1 mL of dilute emulsion containing 175 mg oil/mL of liquid or hydrogenated emulsion was added to each bottle. In addition, 100 mg/L of lactate and 50 mg/L of yeast extract were added to each bottle (assuming 175 mL liquid volume). Treatment 3-Killed was titrated with 1.0 M sodium hydroxide to increase the pH to 12 to inhibit biological activity. Experimental conditions for the seven sets of microcosms are shown in Table 3.

A variety of substrates or environmental conditions can be evaluated in this manner to deduce optimal conditions for bacterial growth. Autoclaved, killed controls and live, no added carbon controls were included to observe background reduction. Incubations were monitored over a 7.5 month period for disappearance of the pollutant, pH, dissolved organic carbon and gas production.

Table 3. Basic setup for the seven treatments of microcosms.

TREATMENT	SEDIMENT VOLUME	SUBSTRATE	INOCULATED	ABBREVIATION
1	No	None	No	Water only
2	50 mL	None	No	No carbon
3	50 mL autoclaved	Liquid soybean oil	No	Killed
4	50 mL	Liquid soybean oil	No	Oil only
5	50 mL	Hydrogenated Soybean wax	No	Wax only
6	50 mL	Liquid soybean oil	Yes	Oil-bioaugmented
7	50 mL	Hydrogenated Soybean wax	Yes	Wax-bioaugmented

3.0 MICROCOSM RESULTS

The initial concentration of perchlorate for the seven microcosm treatments was 53 mg/L. After 14 days incubation, perchlorate was depleted to below the analytical detection limit (8 $\mu\text{g/L}$) in all substrate amended treatments, while 40 mg/L remained in the three no-added substrate treatments (water only, no carbon and killed). Measured perchlorate and chloride concentrations in each treatment at 2 and 14 days are shown in Figure 1. Perchlorate degraded rapidly in all substrate amended bottles with no detectable difference in degradation time between the liquid and solid hydrogenated soybean oil. In each substrate amended treatment, the perchlorate concentration declined by approximately 0.5 millimoles/L. At the same time, dissolved chloride increased by approximately 0.5 millimoles per liter, indicating that the

perchlorate was completely mineralized. 5 mL of the bioaugmentation culture for treatments 6 and 7 was added on day 28 with the objective of stimulating TCA degradation. Since the bioaugmentation culture was added after perchlorate was completely degraded, it has no impact on the results presented in Figure 1.

Figure 2 shows the observed variation in dissolved nitrate, sulfate and pH in the different microcosms. Values shown are the average of triplicate incubations. Nitrate remained constant at around 11 mg/L in Treatment 1-Water only and Treatment 3-Killed. However in all substrate amended treatments, nitrate was reduced to below detection (<1 mg/L) by day 2. There was also substantial nitrate loss in Treatment 2-No carbon, presumably due to organic carbon present in the sediment used to construct the microcosm. Sulfate concentration was constant in the 1-Water only treatment and increased slightly in Treatment 2-No carbon and Treatment 3-Killed. Sulfate was below detection (< 0.05 mg/L) in all substrate amended treatments after 30 days. pH remained approximately constant in all live treatments ranging from 5.8 to 7.1. In the Killed Control, pH progressively decreased reaching background levels after 5 months.

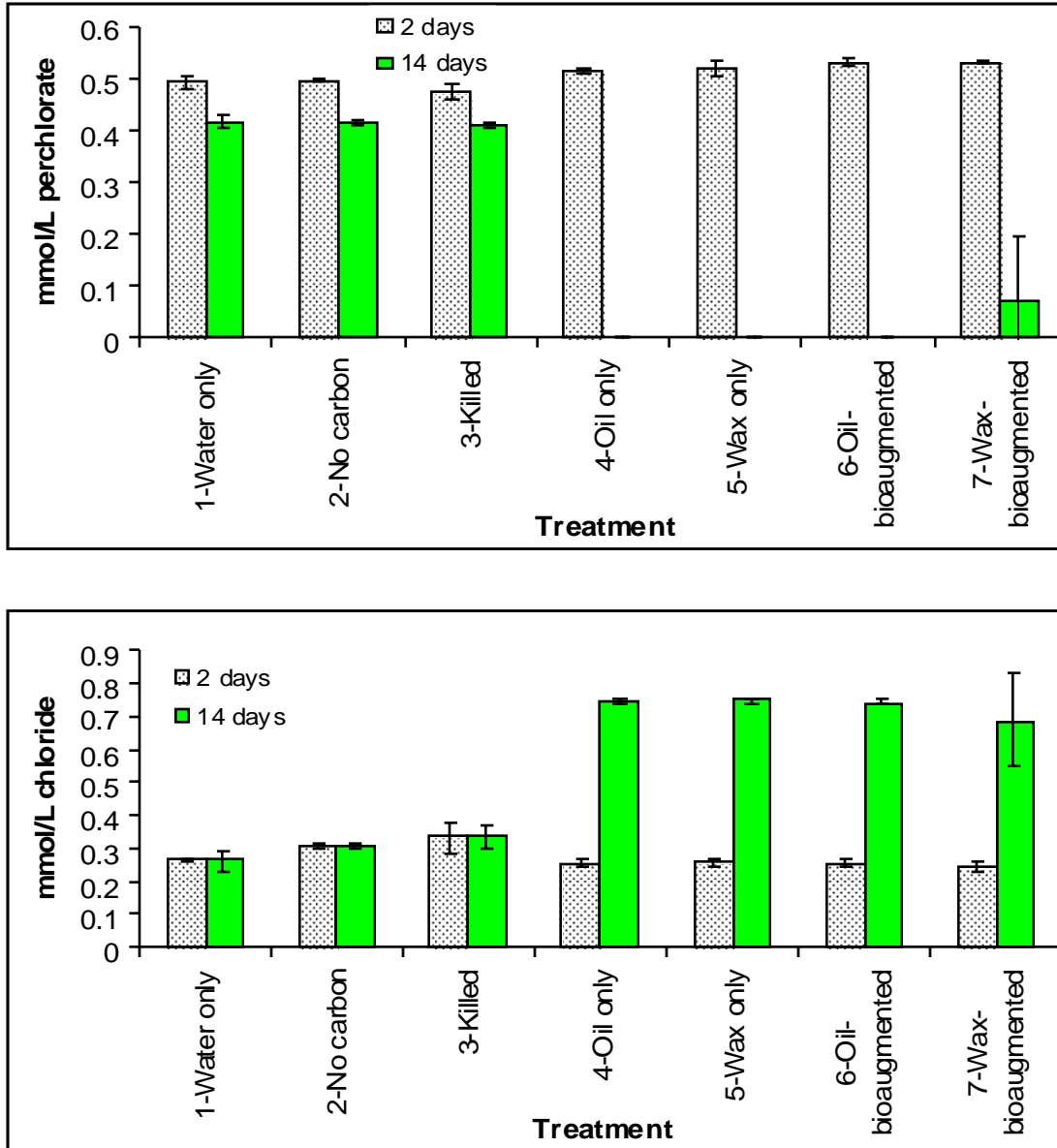


Figure 1 Perchlorate and chloride concentrations in microcosms on days 2 and 14. Errors bars are standard deviation from triplicate incubations.

The microcosm results indicated that both emulsified liquid and solid soybean oil can effectively stimulate perchlorate reduction in aquifer sediment and groundwater from the Elkton, MD site. Bioaugmentation is not necessary for rapid and complete perchlorate biodegradation.

Figure 3 shows analytical results versus time for the treatment 1-Water only. Acetate results are presented as mg/L of carbon. Similar data is shown for the others treatments in Figures 4 to 8.

In Treatment 1-Water only, nitrate and sulfate remained constant throughout the experiment. TOC, acetate and methane concentrations remained low in all incubations. There was a gradual loss of trichloroethane (TCA), presumably due to sorption in the stopper and/or removal of contaminant mass during sampling. Dichloroethane (DCA), 1,1- dichloroethene (1,1-DCE), chloroethane (CA), vinyl chloride (VC) and the sum of ethene and ethane (Eth) were not produced in any incubations indicating very limited biological activity.

In Treatment 2-No carbon (Figure 4), nitrate was removed over the first 36 days. Sulfate and chloride steadily increased with time. The increase in sulfate could be due to dissolution/desorption from the aquifer matrix. The increase in chloride may be due to degradation of perchlorate and reductive dechlorination of TCA. Acetate, TOC and methane concentrations remained low throughout the incubation period. However, there appears to have been some reductive dechlorination activity in these incubations. TCA declined more rapidly in these incubations than in Treatment 1, and significant amounts of DCA were produced.

Treatment 3-Killed was inadvertently amended with very high concentrations of TCA (~1,000 mg/L). As a consequence, these results were not usable.

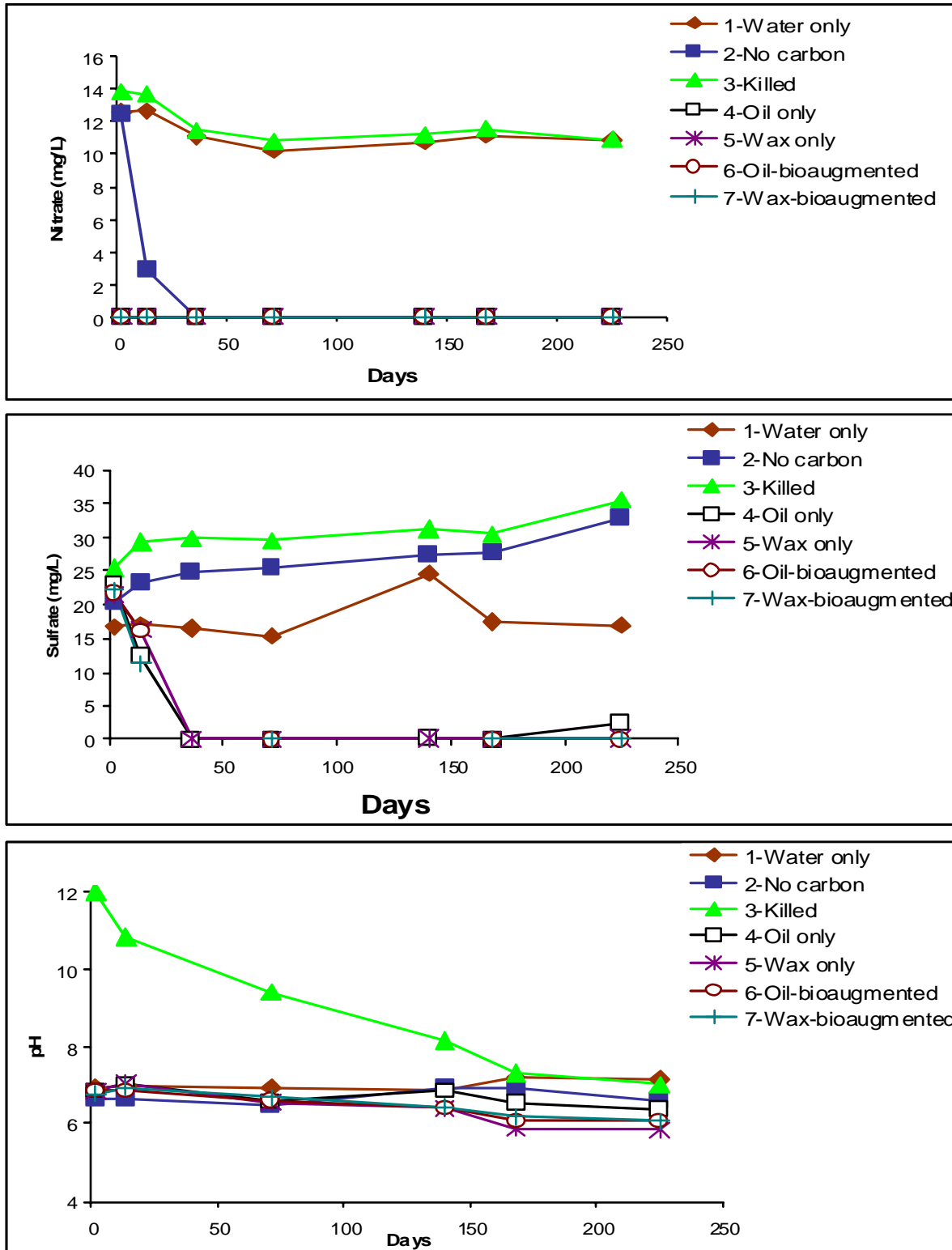


Figure 2 Variation in nitrate, sulfate and pH in microcosm treatments.

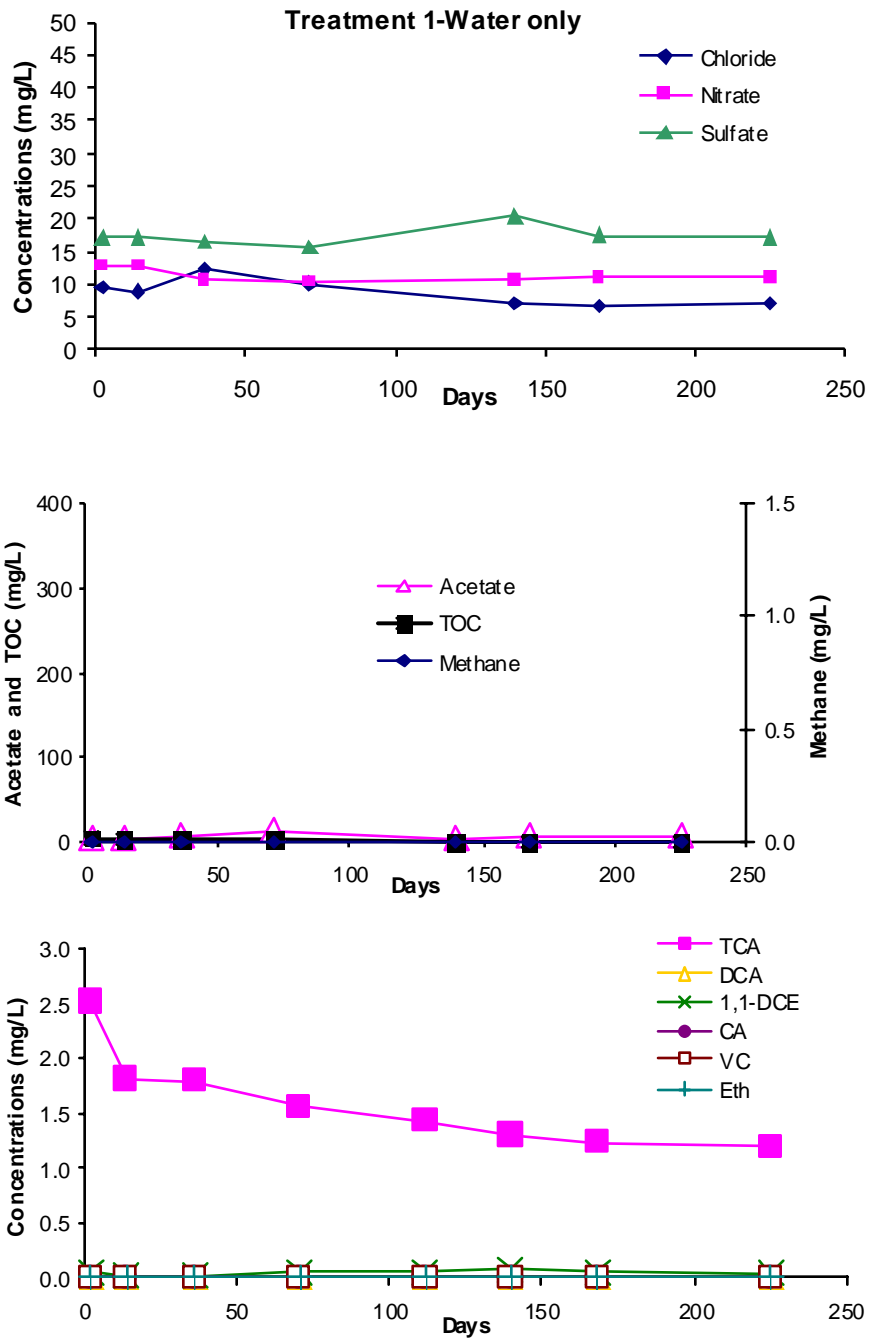


Figure 3 Treatment 1-Water only – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/L of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

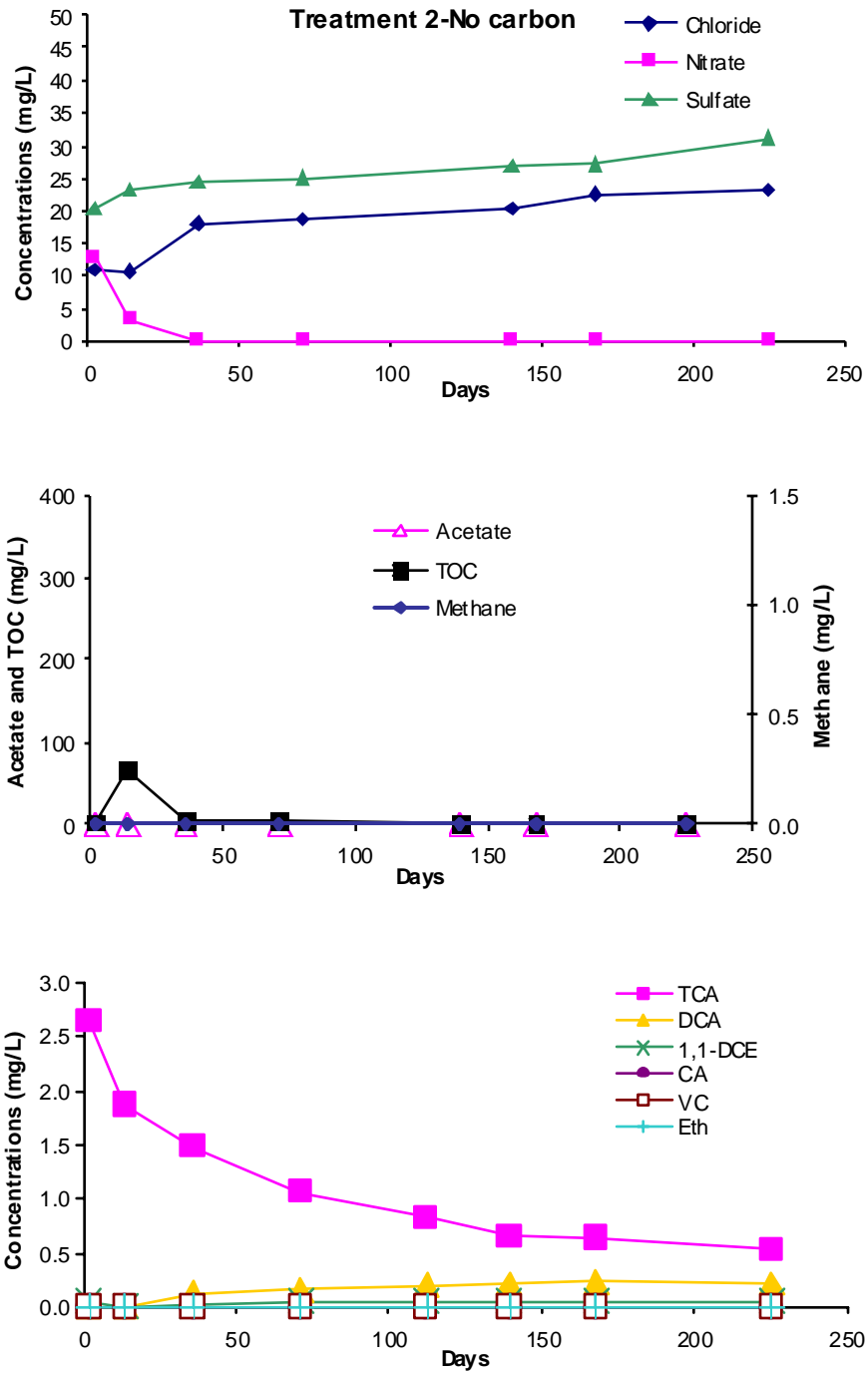


Figure 4 Treatment 2-No carbon – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/L of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

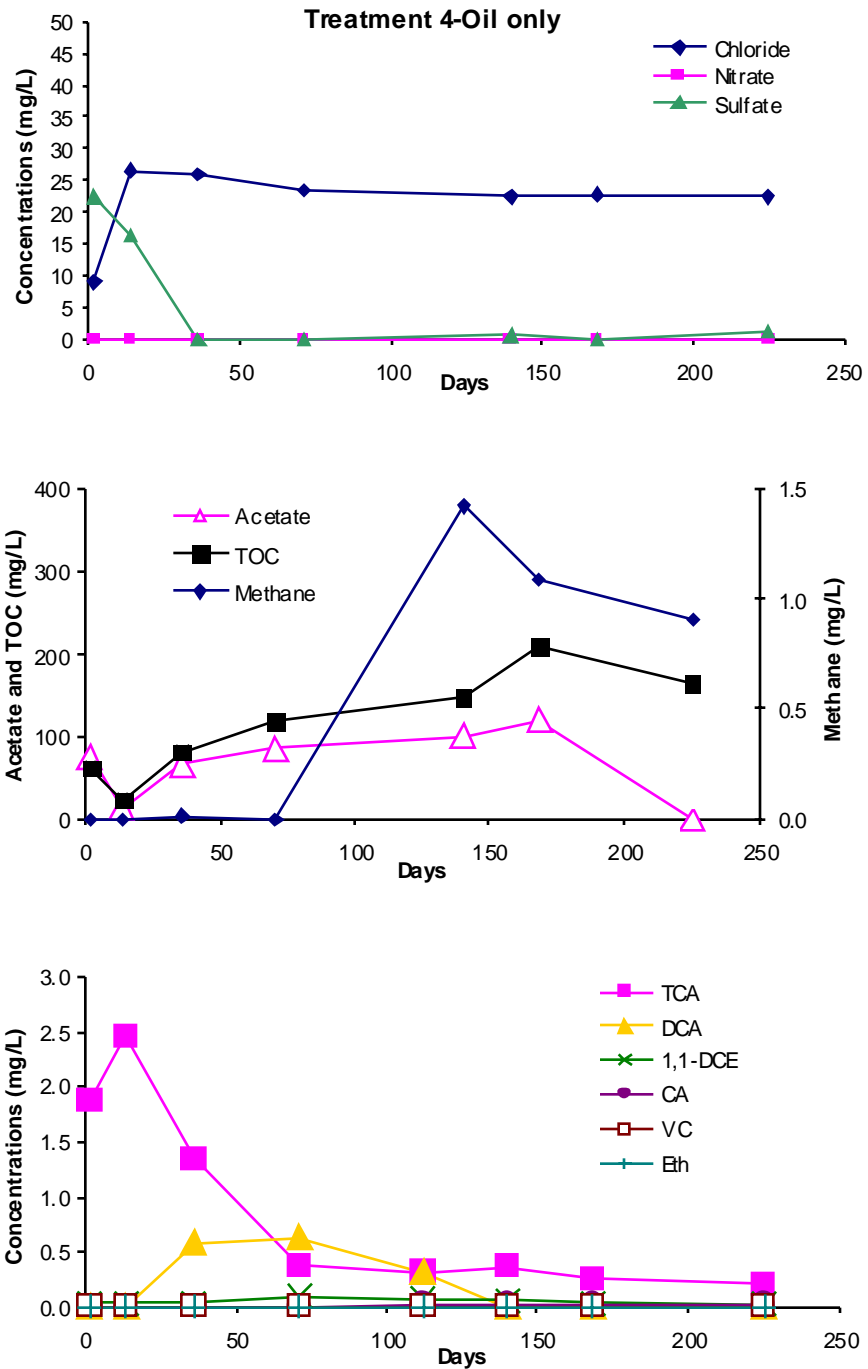


Figure 5 Treatment 4-Oil only – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/L of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

In Treatment 4-Oil only (Figure 5), nitrate was depleted by the first sampling on day 2. Sulfate was removed by day 36. Chloride increased by day 14 and then remained constant throughout the remainder of the experiment. Substantial levels of acetate and TOC were present throughout the incubation period with methane produced after day 71. TCA degraded in all three bottles with concurrent production of DCA. However, TCA degradation rates varied with significantly slower degradation in one of the three replicates. DCA produced through TCA degradation was then reduced to CA. Measured CA concentrations were much lower than the amounts expected based on reaction stoichiometry. This is likely due to release of gaseous CA to the bottle headspace. Significant levels of ethene and ethane were not detected in any of the bottles.

In Treatment 5-Wax only (Figure 6), nitrate was rapidly depleted with somewhat slower removal of sulfate. Acetate and TOC increased gradually over the course of the incubation with methane production after 71 days following the same general pattern observed in the soybean oil incubations. However, maximum methane concentrations in this treatment were about half of those observed in the Treatment 4-Oil only. Reductive dechlorination activity was also variable in this treatment. While TCA degraded to low levels in all three replicates, further degradation of DCA to CA was more variable with accumulation of high levels of DCA in one of three bottles. As in Treatment 4, CA levels remained low (possibly due to volatilization to the headspace) with negligible production of ethene and ethane.

Results from Treatment 6-Oil bioaugmented and Treatment 7-Wax bioaugmented are presented in Figures 7 and 8. In general, experimental results were similar to the previous incubations without bioaugmentation. Nitrate was rapidly depleted followed by sulfate with a concurrent increase in dissolved chloride. TOC and acetate also increased throughout the incubation following the same pattern observed in prior incubations. However, methane production appeared to be somewhat slower than in the prior incubations without bioaugmentation. TCA degraded rapidly in both the oil-bioaugmented and wax-bioaugmented bottles. However, DCA accumulated in all bioaugmented bottles with little or no production of CA, ethene or ethane.

In summary, nitrate was degraded in all live treatments, with the exception of the 1-Water only treatment. Low bacterial activity can be deduced for the behavior of treatments 1-Water only and 2-No carbon. Substantial levels of TOC, acetate and methane were produced in all oil and wax amended bottles. TCA also degraded in all oil and wax amended bottles. However, further conversion of DCA to CA was more variable. Without bioaugmentation, DCA was depleted to below detection in 3 out of 3 oil amended bottles and 1 out of 3 wax amended bottles. In contrast, DCA was not depleted to below detection in any of the bioaugmented bottles (oil or wax).

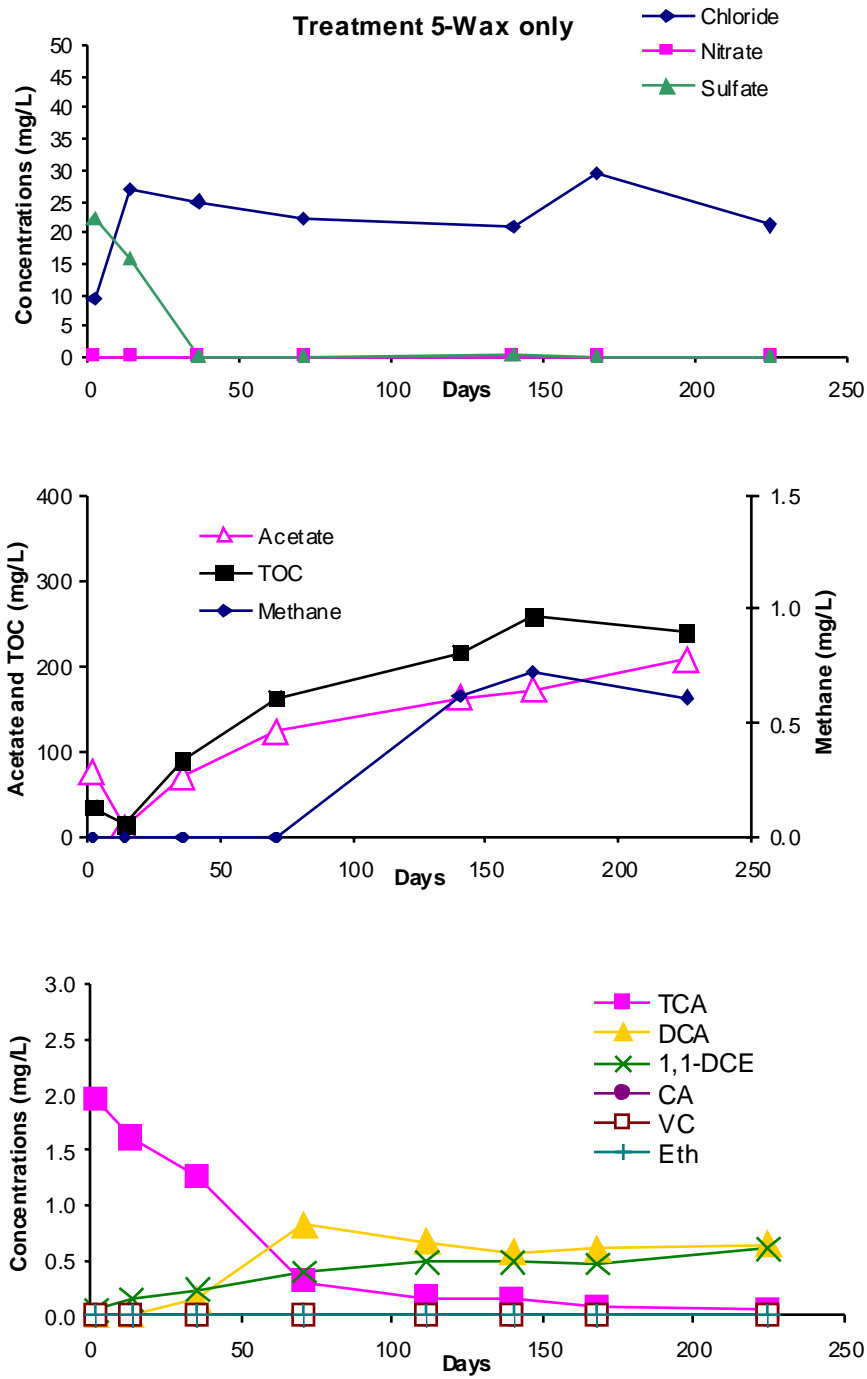


Figure 6 Treatment 5-Wax only – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/l of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

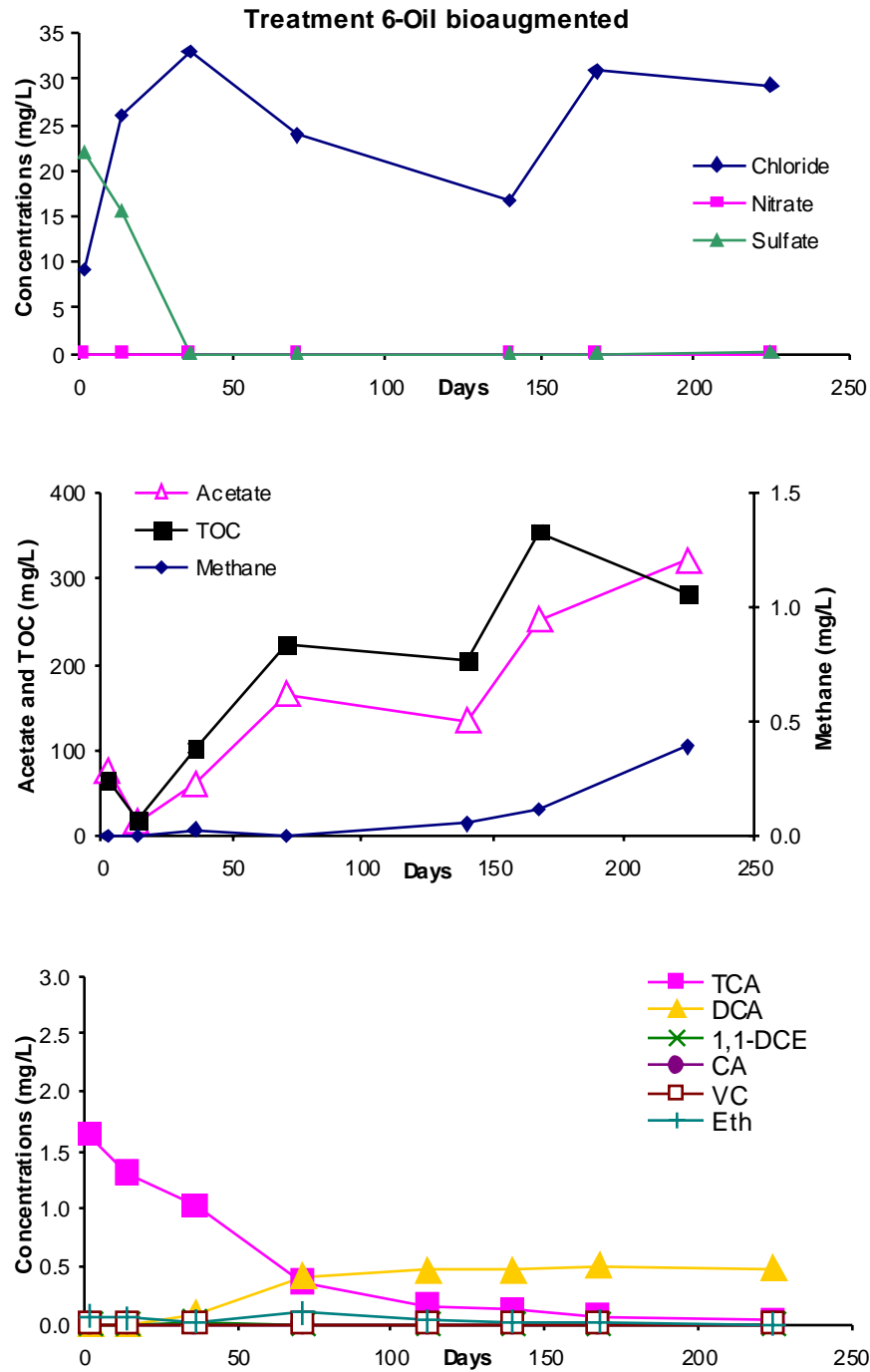


Figure 7 Treatment 6- Oil bioaugmented – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/L of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

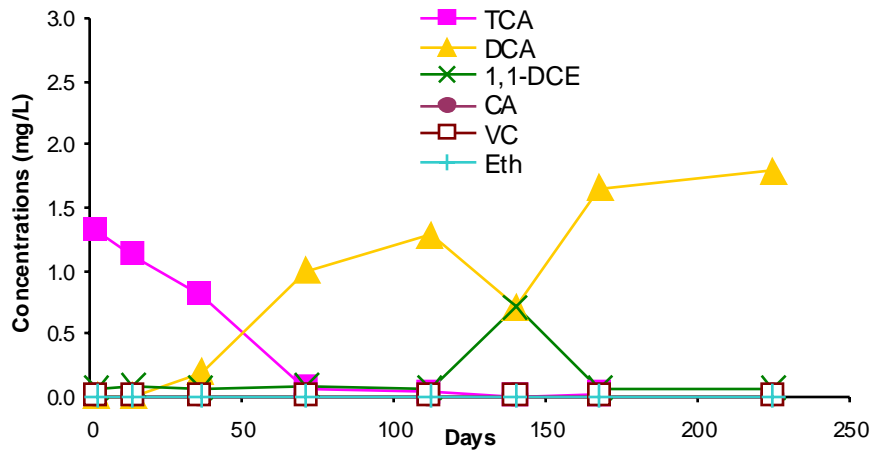
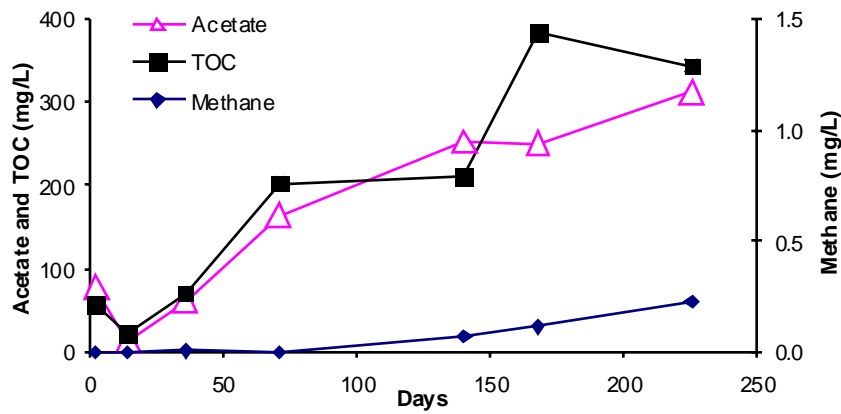
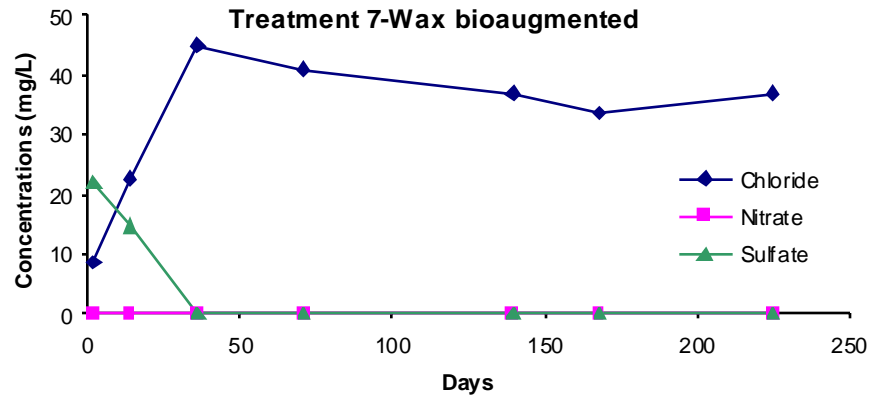


Figure 8 Treatment 7-Wax bioaugmented – analytical results for microcosm concentrations in mg/L: chloride, nitrate and sulfate; acetate (mg/L of carbon), TOC and methane; TCA, DCA, 1,1 DCE, CA, VC and Eth.

4.0 DISCUSSION AND CONCLUSIONS

The microcosm results clearly demonstrated that addition of emulsified soybean oil or hydrogenated soybean oil can be used to stimulate perchlorate and TCA degradation. Perchlorate biodegradation with concurrent chloride production was rapid and complete in every carbon amended bottle. TCA also degraded to DCA in every substrate amended bottle. However, DCA degradation rates were variable between treatments and within each treatment. This illustrates the importance of using triplicates for each experimental treatment, to increase the confidence in the results obtained. Each replicate in the same treatment may present a different behavior due to different initial population of microorganisms, or higher concentration of contaminants in the sediment. Therefore, it is necessary to consider the variability between the samples.

Denitrification and TCA degradation was most rapid in treatments with added substrate. However, some natural attenuation of nitrate and TCA was seen in the treatments with no carbon, presumably due to organic carbon naturally present in the sediment used to construct the microcosms and columns.

Dechlorination was seen, although the observed values for ethene and ethane were low. This may be due to volatilization of these compounds into the bottle headspace, and the liquid samples collected may not accurately represent ethene and ethane production. Higher aqueous concentrations of CA and VC were found, possibly due to the higher solubility of these compounds.

This work successfully demonstrated the potential application of emulsified soybean oil into groundwater systems contaminated with perchlorate. By incorporating liquid soybean oil and solid soybean wax emulsions, the longevity and reducing capabilities of a treatment area can be controlled. The overall benefits include the in-situ approach, low environmental impact, and effective removal of perchlorate.

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APPENDIX C
EOS[®] PRODUCT SHEET MSDS

EOS[®] Concentrate 1.1

Emulsified Edible Oil Substrate

(Licensed under US Patent # 6,398,960)

Benefits	<ul style="list-style-type: none"> ✓ EOS[®] provides simplified product handling and improved subsurface distribution characteristics compared to other <i>in situ</i> products. ✓ EOS[®] provides a long-lasting, natural time-release, organic substrate. ✓ EOS[®] does not require continuous substrate additions. ✓ EOS[®] is supplied as a microemulsion concentrate, making it easier to prepare and inject in the field compared to most other <i>in situ</i> products. ✓ EOS[®] is easily diluted and mixed in the field and pumped into the aquifer, affording immediate impact to greater areas of concern beneath the site. ✓ EOS[®] applications incur no continuing operating and maintenance cost. ✓ EOS[®] is a low cost-effective alternative for aquifer restoration.
Product Uses	<p>Aquifer Remediation EOS[®] accelerates anaerobic biodegradation in aquifers impacted with chlorinated solvents, perchlorate, and nitrate and promotes biotransformations of chromium, radionuclides, and acid mine drainage to less toxic forms.</p>
General Description	<p>EOS[®] Concentrate is a white liquid, food-grade emulsion with a milky appearance and a vegetable oil odor. It is a stable emulsion that is highly miscible in water.</p>
Packaging	<p>EOS[®] Concentrate is packaged in 55-gallon drums. The product can also be packaged in totes or shipped in bulk tankers. Contact your EOS Remediation representative for special packaging requests.</p>
Storage Conditions	<p>EOS[®] Concentrate is stable under normal conditions. Storage in a dry place above freezing is recommended.</p>
Preparation	<p>EOS[®] Concentrate is mixed with 4 parts water prior to injection to achieve the final working concentration. Therefore, each 55-gallon drum of concentrate provides a final mix volume of 275 gallons. Injection can be accomplished with a suitable pump and hoses attached either to wells or direct push points. Contact your EOS Remediation representative for suggestions on injection design.</p>

EOS Remediation, Inc.
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Raleigh, NC 27609
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MATERIAL SAFETY DATA SHEET

EMULSIFIED EDIBLE OIL SUBSTRATE

D.O.T. HAZARD CLASSIFICATION: NONE
0

HEALTH
FLAMMABILITY

----HMIS----
1

REACTIVITY
PERSONAL PROTECTION 0
B

MANUFACTURER'S NAME

**EOS Remediation, Inc
3722 Benson Drive, Suite 101
Raleigh, NC 27609**

DATE OF PREPARATION
01-24-03, Rev. 02-16-04

INFORMATION TELEPHONE NO.
919-873-2204

SECTION I - PRODUCT IDENTIFICATION

PRODUCT NAME **EOS® CONCENTRATE 1.1**
PRODUCT CLASS **VEGETABLE OIL BASED EMULSION**
CAS NUMBER **MIXTURE**

SECTION II - HAZARDOUS INGREDIENTS

COMPONENT(S)

EXPOSURE LIMIT

THIS PRODUCT IS A MIXTURE OF EDIBLE FOOD GRADE ADDITIVES AND CONTAINS NO HAZARDOUS INGREDIENTS.

SECTION III - PHYSICAL DATA

BOILING POINT: **212°F**
SPECIFIC GRAVITY: **.92**
VAPOR PRESSURE: **NOT ESTABLISHED**
PERCENT VOLATILE BY VOLUME (%): **24 (AS WATER)**
VAPOR DENSITY: **HEAVIER THAN AIR**
EVAPORATION RATE: **NOT ESTABLISHED**
SOLUBILITY IN WATER: **SOLUBLE**
APPEARANCE AND ODOR: **OFF WHITE LIQUID WITH VEGETABLE OIL ODOR**

EMULSIFIED EDIBLE OIL SUBSTRATE

SECTION IV - FIRE AND EXPLOSION HAZARD DATA

FLASH POINT: **>300°F**
FLAMMABLE LIMITS: **NOT ESTABLISHED**
EXTINGUISHING MEDIA: **CO₂, FOAM, DRY CHEMICAL**
NOTE: WATER, FOG, AND FOAM MAY CAUSE FROTHING AND SPATTERING.

UNUSUAL FIRE AND EXPLOSION HAZARDS: **BURNING WILL CAUSE OXIDES OF CARBON.**

SPECIAL FIRE FIGHTING PROCEDURES: **WEAR SELF CONTAINED BREATHING APPARATUS AND CHEMICAL RESISTANT CLOTHING. USE WATER SPRAY TO COOL FIRE EXPOSED CONTAINERS.**

SECTION V - PHYSICAL HAZARDS

STABILITY: **STABLE**
CONDITIONS TO AVOID: **NONE**

INCOMPATIBILITY: **STRONG ACIDS AND OXIDIZERS.**

HAZARDOUS DECOMPOSITION PRODUCTS: **THERMAL DECOMPOSITION MAY PRODUCT OXIDES OF CARBON.**

HAZARDOUS POLYMERIZATION: **WILL NOT OCCUR**

SECTION VI - HEALTH HAZARDS

SIGNS AND SYMPTOMS OF EXPOSURE:
1. Acute Overexposure - **NONE**
2. Chronic Overexposure - **NONE**

MEDICAL CONDITIONS GENERALLY AGGRAVATED BY EXPOSURE: **NONE KNOWN**

CHEMICAL LISTED AS CARCINOGEN OR POTENTIAL CARCINOGEN:
N.T.P. - **NO** I.A.R.C. - **NO** OSHA - **NO**

EMERGENCY AND FIRST AID PROCEDURES:
1.) Inhalation- **REMOVE TO FRESH AIR.**
2.) Eyes- **FLUSH WITH WATER FOR 15 MINUTES, IF IRRITATION PERSISTS SEE PHYSICIAN.**
3.) Skin- **WASH WITH MILD SOAP AND WATER.**
4.) Ingestion- **PRODUCT IS NON-TOXIC. IF NAUSEA OCCURS, INDUCE VOMITING AND SEEK MEDICAL ATTENTION.**

EMULSIFIED EDIBLE OIL SUBSTRATE

SECTION VII - SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION: **NOT NORMALLY REQUIRED**
VENTILATION: **LOCAL EXHAUST**
PROTECTIVE GLOVES: **NOT NORMALLY REQUIRED**
EYE PROTECTION: **NOT NORMALLY REQUIRED**
OTHER PROTECTIVE CLOTHING
OR EQUIPMENT: **NONE**

SECTION VIII - SPECIAL PRECAUTIONS AND SPILL/LEAK PROCEDURES

PRECAUTIONS TO BE TAKEN **DO NOT STORE NEAR EXCESSIVE HEAT OR**
IN HANDLING AND STORAGE: **OXIDIZERS.**

OTHER PRECAUTIONS: **NONE**

STEPS TO BE TAKEN IN CASE **SOAK UP WITH DRY ABSORBENT AND FLUSH AREA**
MATERIAL IS SPILLED: **WITH LARGE AMOUNTS OF WATER.**

WASTE DISPOSAL METHODS: **DISPOSE OF ACCORDING TO FEDERAL, STATE, AND**
LOCAL REGULATIONS.

SECTION IX - ADDITIONAL REGULATORY INFORMATION

SARA TITLE III

UNDER THE PROVISIONS OF TITLE 111, SECTION 311/312 OF THE SUPERFUND
AMENDMENTS AND REAUTHORIZATIONS ACT, THIS PRODUCT IS CLASSIFIED
INTO THE FOLLOWING HAZARD CATEGORIES: **NONE**

THIS PRODUCT DOES **NOT** CONTAIN SECTION 313 REPORTABLE INGREDIENTS.

THE INFORMATION CONTAINED HEREIN IS BASED ON AVAILABLE DATA AND IS BELIEVED TO BE
CORRECT. HOWEVER, EOS REMEDIATION, INC. MAKES NO WARRANTY, EXPRESSED OR IMPLIED,
REGARDING THE ACCURACY OF THIS DATA OR THE RESULTS TO BE OBTAINED THEREOF. THIS
INFORMATION AND PRODUCT ARE FURNISHED ON THE CONDITION THAT THE PERSON RECEIVING
THEM SHALL MAKE HIS/HER OWN DETERMINATION AS TO THE SUITABILITY OF THE PRODUCT FOR
HIS/HER PARTICULAR PURPOSE.

APPENDIX D
OIL DEMAND SPREADSHEET
PILOT TEST DESIGN

Section A: Barrier Dimensions

Width of proposed barrier perpendicular to groundwater flow	50	ft	15.2	m
Minimum depth to contamination	5	ft	1.5	m
Maximum depth of contamination	15	ft	4.6	m
Barrier thickness parallel to groundwater flow	5.0	ft	1.5	m
Treatment thickness	10	ft	3.0	m
Surface area of barrier face	500	ft ²	46	m ²

Section B: Site Hydrogeologic Data

Total Porosity		(decimal)		
Effective Porosity	0.30	(decimal)		
Hydraulic Conductivity	22	ft/day	7.8E-03	cm/sec
Hydraulic Gradient	0.003	ft/ft		
Seepage velocity (V _s)	0.2200	ft/day	0.0671	m/day
Groundwater flowrate through barrier (Q)	247	gal/day	934	L/day

Section C: Barrier Design Lifespan For One Application

Total groundwater volume treated over design life	3	year(s)	typical values 5 to 10 years
	270,290	gallons	1,023,276 L

Section D: Electron Acceptors

Inputs	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e ⁻ equiv./mole	Stoichiometry Contaminant/H ₂ (wt/wt H ₂)	Hydrogen Demand (g H ₂)
Dissolved Oxygen (DO)	0 to 8	5.78	32.0	4	7.94	745.185242
Nitrate Nitrogen (NO ₃ ⁻ - N)	1 to 10	14.42	62.0	5	12.30	1199.2766
Sulfate (SO ₄ ²⁻)	10 to 50	28.56	96.1	8	11.91	2453.1639
Tetrachloroethene (PCE), C ₂ Cl ₄		0.086	165.8	8	20.57	4.27882938
Trichloroethene (TCE), CHCl:CCl ₂		0.131	131.4	6	21.73	6.16984107
cis-1,2-dichloroethene (c-DCE), C ₂ H ₂ Cl ₂			96.9	4	24.05	
Vinyl Chloride (VC), CH ₂ =CCl ₂			62.5	2	31.00	
Carbon tetrachloride, CCl ₄			153.8	8	19.08	
Chloroform, CHCl ₃			119.4	6	19.74	
sym-tetrachloroethane, C ₂ H ₂ Cl ₄			167.8	8	20.82	
1,1,1-Trichloroethane (TCA), CH ₃ CCl ₃		22.7	133.4	6	22.06	1052.97021
1,1-Dichloroethane (DCA), CH ₃ CHCl ₂		0.093	99.0	4	24.55	3.87699389
Chloroethane, C ₂ H ₅ Cl			64.9	2	32.18	
Perchlorate, ClO ₄ ⁻		12	99.4	8	12.33	995.791165
Hexavalent Chromium, Cr(VI)			52.0	3	17.20	
User added 1,1-DCE		0.62	96.9	4	24.04	26.3959934
User added						
User added						

Section E: Additional Hydrogen Demand and Carbon Losses

Generation (Potential Amount Formed)	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e ⁻ equiv./mole	Stoichiometry Contaminant/H ₂ (wt/wt H ₂)	Hydrogen Demand (g H ₂)	DOC Flux (moles)
Estimated Amount of Fe ²⁺ Formed	10 to 100	50	55.8	1	55.41	923.412643	
Estimated Amount of Manganese (Mn ²⁺) Formed			54.9	2	27.25		
Estimated Amount of CH ₄ Formed	5 to 20	10	16.0	8	1.99	5143.10439	
Target Amount of DOC to Release	60 to 100	60	12.0				5111.69

Note:

- Calculations assume:
 - all reactions go to completion during passage through emulsified edible oil treated zone; and,
 - perfect reaction stoichiometry.

Section F: Substrate Requirement Calculations Based on Hydrogen Demand and Carbon Losses

Stoichiometric Hydrogen Demand	28	pounds
DOC Released	176	pounds
Pounds Hydrogen Produced per Pound Substrate	0.11	pounds H ₂ /pound substrate
Soybean Oil = 0.18		
Soybean Oil Emulsion Concentrate = 0.11		
Substrate Density	7.66	pounds substrate/gallon
Soybean Oil = 7.7 lbs/gal		
Soybean Oil Emulsion Concentrate = 7.66 lbs/gal		

Substrate Requirement Based on Stoichiometric Hydrogen Demand and Carbon Losses

	427	pounds
	56	gallons

Section G: Substrate Requirement Calculations Based on Adsorptive Capacity of Soil

Adsorptive Capacity of Soil	0.0020	lbs oil/lbs soil
Typical Values = 0.001 to 0.004		
Bulk density of soil	120	lbs/ft ³
Weight of sediment to be treated	300,000	lbs

Substrate Requirement Based on Adsorptive Capacity of Soil

	600	pounds
	78	gallons

APPENDIX E
OIL DEMAND SPREADSHEET
PILOT TEST LONGEVITY

Section A: Barrier Dimensions

Width of proposed barrier perpendicular to groundwater flow	50	ft	15.2	m
Minimum depth to contamination	5	ft	1.5	m
Maximum depth of contamination	15	ft	4.6	m
Barrier thickness parallel to groundwater flow	5.0	ft	1.5	m
Treatment thickness	10	ft	3.0	m
Surface area of barrier face	500	ft ²	46	m ²

Section B: Site Hydrogeologic Data

Total Porosity		(decimal)		
Effective Porosity	0.18	(decimal)		
Hydraulic Conductivity	22	ft/day	7.8E-03	cm/sec
Hydraulic Gradient	0.009	ft/ft		
Seepage velocity (V _s)	1.1000	ft/day	0.3353	m/day
Groundwater flowrate through barrier (Q)	741	gal/day	2803	L/day

Section C: Barrier Design Lifespan For One Application

Total groundwater volume treated over design life	2.7	year(s)	typical values 5 to 10 years
	729,782	gallons	2,762,765 L

Section D: Electron Acceptors

Inputs	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e ⁻ equiv./mole	Stoichiometry Contaminant/H ₂ (wt/wt H ₂)	Hydrogen Demand (g H ₂)
Dissolved Oxygen (DO)	0 to 8	1.6	32.0	4	7.94	556.939141
Nitrate Nitrogen (NO ₃ ⁻ - N)	1 to 10	8.58	62.0	5	12.30	1926.60525
Sulfate (SO ₄ ²⁻)	10 to 500	17.01	96.1	8	11.91	3944.79126
Tetrachloroethene (PCE), C ₂ Cl ₄		0.02	165.8	8	20.57	2.68663003
Trichloroethene (TCE), CHCl:CCl ₂		0.14	131.4	6	21.73	17.802544
cis-1,2-dichloroethene (c-DCE), C ₂ H ₂ Cl ₂		-0.06	96.9	4	24.05	-6.8937045
Vinyl Chloride (VC), CH ₂ =CCl ₂		-0.021	62.5	2	31.00	-1.8712843
Carbon tetrachloride, CCl ₄			153.8	8		19.08
Chloroform, CHCl ₃		0.016	119.4	6	19.74	2.23928183
sym-tetrachloroethane, C ₂ H ₂ Cl ₄			167.8	8		20.82
1,1,1-Trichloroethane (TCA), CH ₃ CCl ₃		3.6	133.4	6	22.06	450.862463
1,1-Dichloroethane (DCA), CH ₃ CHCl ₂		-1.3	99.0	4	24.55	-146.32107
Chloroethane, C ₂ H ₅ Cl		-1.1	64.9	2	32.18	-94.436578
Perchlorate, ClO ₄ ⁻		11.3	99.4	8	12.33	2531.72667
Hexavalent Chromium, Cr[VI]			52.0	3		17.20
User added						
User added						
User added						

Section E: Additional Hydrogen Demand and Carbon Losses

Generation (Potential Amount Formed)	Typical Value	GW Conc. (mg/L)	MW (g/mole)	e ⁻ equiv./mole	Stoichiometry Contaminant/H ₂ (wt/wt H ₂)	Hydrogen Demand (g H ₂)	DOC Flux (moles)
Estimated Amount of Fe ²⁺ Formed	10 to 100	3.6	55.8	1	55.41	179.506287	
Estimated Amount of Manganese (Mn ²⁺) Formed		4.2	54.9	2	27.25	425.762983	
Estimated Amount of CH ₄ Formed	5 to 20	1.2	16.0	8	1.99	1666.31819	
Target Amount of DOC to Release	60 to 100	78	12.0				17941.53

Note:

- Calculations assume:
 - all reactions go to completion during passage through emulsified edible oil treated zone; and,
 - perfect reaction stoichiometry.

Section F: Substrate Requirement Calculations Based on Hydrogen Demand and Carbon Losses

Stoichiometric Hydrogen Demand	25	pounds
DOC Released	616	pounds
Pounds Hydrogen Produced per Pound Substrate	0.11	pounds H ₂ /pound substrate
Soybean Oil = 0.18		
Soybean Oil Emulsion Concentrate = 0.11		
Substrate Density	7.66	pounds substrate/gallon
Soybean Oil = 7.7 lbs/gal		
Soybean Oil Emulsion Concentrate = 7.66 lbs/gal		

Substrate Requirement Based on Stoichiometric Hydrogen Demand and Carbon Losses

845	pounds
110	gallons

Section G: Substrate Requirement Calculations Based on Adsorptive Capacity of Soil

Adsorptive Capacity of Soil	0.0018	lbs oil/lbs soil
Typical Values = 0.001 to 0.004		
Bulk density of soil	135	lbs/ft ³
Weight of sediment to be treated	338,445	lbs

Substrate Requirement Based on Adsorptive Capacity of Soil

609	pounds
80	gallons