

# ESTCP Cost and Performance Report

(ER-0218)



## In Situ Bioremediation of Chlorinated Solvents Source Areas with Enhanced Mass Transfer

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# COST & PERFORMANCE REPORT

Project: ER-0218

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## ACRONYMS AND ABBREVIATIONS

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ARD	anaerobic reductive dechlorination
B.E.T. <sup>TM</sup> bgs	Bioavailability Enhancement Technology <sup>TM</sup> below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
cis-DCE	cis-dichloroethene
CMT	continuous multichannel tubing
COD	chemical oxygen demand
DNAPL	dense nonaqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
DQO	data quality objective
DR	decision rule
EGDY	East Gate Disposal Yard
ERH	electrical resistance heating
ESTCP	Environmental Security Technology Certification Program\
EW	extraction well
FW	flux monitoring well
gpm	gallons per minute
IFT	interfacial tension
INL	Idaho National Laboratory
ISB	in situ bioremediation
ITRC	Interstate Technology & Regulatory Council
IW	injection well
MIP	membrane interface probe
MNA	monitored natural attenuation
msl	mean sea level
MW	monitoring well
NAPL	nonaqueous phase liquid
NWI	North Wind, Inc.
ORP	oxidation reduction potential
PCE	tetrachloroethene

## ACRONYMS AND ABBREVIATIONS (continued)

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QA	quality assurance
qPCR	quantitative polymerase chain reaction
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
TAN	Test Area North
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TDP	Technology Demonstration Plan
UIC	underground injection control
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
VFA	volatile fatty acid
VOC	volatile organic compound
WAC	Waste Administrative Code

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

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## **1.0 EXECUTIVE SUMMARY**

### **1.1 BACKGROUND**

Cleanup of chlorinated solvent sources in groundwater is often considered technically (or economically) impracticable because of their density and hydrophobicity, often compounded by subsurface heterogeneity. As a result, many sites have resorted to pump-and-treat or other containment technologies. Operations and maintenance costs of such systems become very large over time, however, because of the longevity of the subsurface sources, and these costs have become a large proportion of Department of Defense (DoD) environmental budgets.

Bioremediation has the potential to reduce capital costs compared to other technologies for chlorinated solvent source area cleanup. Bioremediation would not generate secondary waste streams, would be nonhazardous to workers and the environment, would destroy contaminants in situ, would be low maintenance, and would minimize disturbance of the site. However, it has traditionally been viewed as very passive with respect to source area remediation, that is, conventional wisdom suggests that bioremediation is limited by the rate at which nonaqueous contaminants dissolve or diffuse to where bacteria can degrade them. Recent advances have shown, however, that mass transfer rates of chlorinated solvents from the nonaqueous phase to the aqueous phase (where they are bioavailable) can be substantially increased during bioremediation.

### **1.2 OBJECTIVES OF THE DEMONSTRATION**

The overall objective of this demonstration was to show that facilitating enhanced mass transfer allows bioremediation to be applied cost-effectively to chlorinated solvent source areas in groundwater. Two hydraulically isolated treatment cells were used to compare different whey powder injection strategies and help quantify their performance. A phased approach ensured experimental control was sufficient to measure with confidence the effects of different whey injection concentrations on mass transfer. This demonstration represents the first time the phenomenon of enhanced mass transfer in chlorinated solvent source areas as a function of whey injection concentration has been thoroughly documented at the field scale. The results far exceeded expectations, and demonstrate the potential impact enhanced mass transfer during bioremediation can have not only on source areas, but also on downgradient plumes.

### **1.3 DEMONSTRATION RESULTS**

Two hydraulically isolated treatment cells, each consisting of a network of monitoring wells, an injection well, and an extraction well, were installed at the site. Two injection strategies were applied to each treatment cell. For Treatment Cell 1, the first injection strategy was high concentration (10%) whey powder injections, and the second strategy was low concentration (1%) whey powder injections. For Treatment Cell 2, the strategies were reversed: low concentration (1%) injections first and high concentration (10%) injections second.

The results allowed quantification of the potential for a high-concentration whey solution to enhance mass transfer and facilitated comparison to that for the lower concentration. The factor of increase in aqueous chloroethene concentrations from baseline to 10% whey injections ranged from 1.8 to 4.2, with only one sampling location showing an increase less than a factor of 2.4,

and four locations were 3.0 or greater. These increases greatly exceeded those during the 1% whey injections, even though the extent of dechlorination was equivalent (i.e., dechlorination was complete to cis-dichloroethene [cis-DCE], with little vinyl chloride [VC] or ethene production). Three statistical comparisons were performed that demonstrated contaminant molar concentrations were increased at the 95% confidence level as a function of electron donor concentration.

The demonstration was aided by the addition of a row of flux monitoring wells installed by the Army downgradient of the treatment cells that revealed the impact of high-concentration whey injections on contaminant flux. Three months after 10% whey injections began in Treatment Cell 1, concentrations downgradient increased by a factor of 3 to 8, while total chloroethene concentrations downgradient of Treatment Cell 2 changed only by a factor of 0.8 to 1.3. The injection concentrations in the two treatment cells were reversed in November 2005. When the downgradient wells were sampled again in January 2006, the highest concentrations were measured downgradient from Treatment Cell 2, and the lowest concentrations were measured downgradient from Treatment Cell 1, including wells FX3-02 and FX3-03, which only 1 month earlier had the highest concentrations in the transect. In fact, chloroethenes concentrations at one well downgradient from Treatment Cell 2 were a factor of 16 higher than baseline. This change in concentrations downgradient from Treatment Cell 2 of a factor almost 3 to greater than 8 from December to January is nearly identical to the change observed downgradient from Treatment Cell 1 in November 2005 compared to the baseline. All of these results are again remarkably similar to the column study results of Macbeth et al. (2006) for 10% whey solutions.

A cost-effectiveness analysis was performed to compare the life-cycle costs of four remediation technologies for treatment of nonaqueous phase liquid (NAPL) Area 3 of the Fort Lewis East Gate Disposal Yard (EGDY). Three of the technologies—bioremediation, pump-and-treat, and electrical resistance heating (ERH)—have actually been applied within or near NAPL Area 3 at EG DY, and so costs developed were based on actual costs of implementing these technologies at the site. Monitored natural attenuation (MNA) was the least expensive at \$1.1 million but would not meet cleanup goals in the 30-year life cycle. Bioremediation was estimated at \$1.6 million, pump-and-treat was \$2.9 million, and ERH was the most expensive at \$3.1 million.

#### **1.4 IMPLEMENTATION ISSUES**

This Bioavailability Enhancement Technology™ (B.E.T.™) (U.S. Patent Numbers 6,783,678; 7,045,339; 7,141,170; 7,449,114) is readily scaled to any size site, as evidenced by deployments at scales ranging from dry cleaner sites to large-scale plumes. The technology as implemented uses a licensed, commercially available electron donor; all other process equipment is non-proprietary and readily commercially available. When using powdered whey as an electron donor, specialized pumping and mixing equipment is helpful. B.E.T.™ was originally developed at the U.S. Department of Energy's (DOE) Idaho National Laboratory (INL). In general, licensed electron donor products can simply be purchased through JRW Bioremediation, and in some cases, no royalty is required for using the technology at government sites.

The Interstate Technology & Regulatory Council (ITRC) has recently developed guidance for bioremediation in chlorinated solvent source areas through the bioremediation of dense nonaqueous phase liquid (DNAPL) technical team. This guidance incorporates many of the

concepts validated in this demonstration (ITRC, 2005; 2008). The guidance documents can be found at [http://www.itrcweb.org/teamresources\\_47.asp](http://www.itrcweb.org/teamresources_47.asp).

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## **2.0 INTRODUCTION**

This report provides the demonstration and cost and performance results for enhanced mass transfer of chloroethenes from DNAPL to groundwater during in situ bioremediation (ISB) at the Fort Lewis EGDY. Enhanced mass transfer from DNAPL to groundwater due to the physicochemical interaction of the electron donor itself and the nonaqueous contaminant(s) is referred to as Bioavailability Enhancement Technology™, or B.E.T.™ (U.S. patents 6,783,678; 7,045,339; 7,141,170; and 7,449,114). This demonstration provided rigorous documentation of concentration-dependent enhanced mass transfer using an electron donor (whey) for chlorinated solvents in a source area for the first time in a field study. It was also observed that anaerobic reductive dechlorination (ARD) occurred concurrently with the enhanced mass transfer and resulted in rapid source strength reduction.

### **2.1 BACKGROUND**

Chlorinated solvents are the most common class of contaminants in groundwater at hazardous waste sites in the United States and are the most common contaminants at DoD sites. The prevalence of chlorinated solvents is due both to their widespread use and to their longevity in the environment. Their longevity is partly due to the hydrophobic nature that makes them such good solvents, their low solubilities, and their relatively oxidized states that prevent them from serving as electron donors for microorganisms.

Cleanup of chlorinated solvent sources, especially those containing DNAPLs, in ground water is often considered technically (or economically) impracticable because of their density and hydrophobicity, often compounded by subsurface heterogeneity. As a result, many sites have resorted to pump-and-treat or other containment technologies. Operations and maintenance costs of such systems become very large over time, however, because of the longevity of the subsurface sources.

While significant progress has been made in addressing solvent source areas, parties responsible for cleaning up sites with chlorinated solvent residual source areas in ground water are still faced with several technologies with significant capital costs, secondary waste streams, the involvement of hazardous materials or energy, and the potential for additional worker or environmental exposure. A more ideal technology would involve lower capital costs, would not generate secondary waste streams, would be nonhazardous to workers and the environment, would destroy contaminants in situ, would be low maintenance, and would minimize disturbance of the site.

While bioremediation satisfies all of the characteristics of an ideal technology described above, it has traditionally been viewed as very passive with respect to source area remediation, that is, conventional wisdom suggests that bioremediation is limited by the rate at which nonaqueous contaminants dissolve or diffuse to where bacteria can degrade them. If that were true, bioremediation would still have all the benefits of an in situ technology regarding low capital cost, lack of secondary waste streams, low maintenance, minimal site disturbance, etc. but would not be much different from pump-and-treat in terms of cleanup times. Recent advances have shown, however, that mass transfer rates of chlorinated solvents from the nonaqueous phase to

the aqueous phase (where they are bioavailable) can be substantially increased during bioremediation through B.E.T.<sup>™</sup> (Sorenson, 2002; Song et al., 2002).

In this demonstration, two hydraulically isolated treatment cells, each consisting of a network of monitoring wells, an injection well, and an extraction well, were installed at the EGDY. One treatment cell was located on the fringe of the DNAPL source area (Treatment Cell 1), and the other was located within the DNAPL source area (Treatment Cell 2). Two injection strategies were applied to each treatment cell. For Treatment Cell 1, the first injection strategy was high concentration (10%) whey powder injections, and the second strategy was low concentration (1%) whey powder injections. For Treatment Cell 2, the first injection strategy was the low concentration (1%) injections, and the second strategy was the high concentration (10%) injections. Comparison of the demonstration results in each treatment cell during injection of low and high whey concentrations facilitated quantification of the relative difference of the enhanced mass transfer mechanisms both within and downgradient of the DNAPL source area.

Three phases of activities were completed for each treatment cell during this demonstration, as follows:

- **Phase 1 – Equilibration.** Hydraulic characterization of the treatment cells was conducted.
- **Phase 2 – Baseline.** ARD performance indicators were collected to evaluate electron donor concentrations, redox conditions, geochemistry, and contaminant concentrations in each treatment cell without electron donor addition.
- **Phase 3 – Biostimulation and enhanced mass transfer demonstration.** ARD performance indicators were monitored under biostimulation conditions during both low and high concentration whey powder injections.

## 2.2 OBJECTIVES OF THE DEMONSTRATION

The overall objective of this demonstration is to show that facilitating enhanced mass transfer allows bioremediation to be applied to chlorinated solvent source areas in groundwater high concentration whey powder injections resulted in greater mass transfer and higher treatment efficiency compared to traditional injection strategies during enhanced ISB for chlorinated solvent source areas. Two hydraulically isolated treatment cells were used to compare two different whey powder injection strategies and help quantify their performance. A phased approach to the demonstration ensured experimental control was sufficient to measure the effects of different whey injection concentrations on mass transfer with confidence.

## 2.3 REGULATORY DRIVERS

Solubilities of the common chlorinated solvents (tetrachloroethene [PCE], trichloroethene [TCE], 1,1,1-trichloroethane [TCA], and carbon tetrachloride) range from about 200 to 1400 mg/L at 25°C (Sale, 1998). These solubilities exceed Federal Safe Drinking Water Act maximum contaminant levels (Table 1) by five to six orders of magnitude. The persistence of chlorinated solvents in groundwater—their prevalence and their solubilities far in excess of health-based levels—drive the need for cost-effective remediation technologies.

**Table 1. Safe Drinking Water Act maximum contaminant levels for Fort Lewis EGDY contaminants of concern.**

<b>Compound</b>	<b>Regulatory Limit (<math>\mu\text{g}/\text{L}^1</math>)</b>
TCE	5
cis-DCE	70
trans-DCE	100
VC	2

<sup>1</sup>40 Code of Federal Regulations (CFR) 141.61

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### **3.0 TECHNOLOGY**

This section provides an overview of the development of the technology for bioremediation of chlorinated solvent source areas, a summary of the development under ESTCP, and the expected applications. Advantages and limitations relative to other technologies are also provided.

#### **3.1 TECHNOLOGY DESCRIPTION**

Enhanced ISB for chlorinated ethene-contaminated groundwater using microbial reductive dechlorination has been well documented in published literature both in the laboratory (Parsons et al., 1984; Vogel and McCarty, 1985; Fathepure and Boyd, 1988; Freedman and Gossett, 1989; DiStefano et al., 1991; deBruin et al., 1992; DiStefano et al., 1992; Ballapragada et al., 1997; Fennell et al., 1997; Carr and Hughes, 1998) and in the field (Major et al., 2002, Song et al., 2002, Rahm et al., 2006; Sharma and McCarty, 1996). Dechlorination-based NAPL source area restoration, however, has not been rigorously evaluated.

Recent research has demonstrated that rapid rates of biological dechlorination in NAPL-containing source areas can dramatically reduce the length of time that a NAPL will continue to be a source of chlorinated solvent contamination (Carr et al., 2000; Cope and Hughes, 2001). A combination of two processes is responsible for this observation in laboratory tests. First, the dechlorinating bacteria are capable of living in close proximity to the NAPL/water interface. Thus, their metabolic activity increases the driving force for mass transfer (i.e., the concentration gradient). Secondly, the metabolic products of dechlorination are less hydrophobic than the parent compounds and they partition more extensively to the aqueous phase. These processes have been attributed to a 14- (Carr et al., 2000) to 16- fold (Cope and Hughes, 2001) increase in removal rates in laboratory reactors and columns. Macbeth et al. (2006) demonstrated a third mechanism for enhanced mass transfer by injecting whey solutions through abiotic columns containing TCE DNAPL. This study showed that the whey solution itself increased mass transfer from the DNAPL by a factor of about 6 relative to deionized water.

Several possible scenarios can be envisioned where enhanced mass transfer during source-zone bioremediation might be advantageous. One is a simple bioremediation system in which electron donor is added to source zones, and mass transfer is enhanced solely due to biological activity. A second is surfactant or cosolvent flushing for NAPL mobilization (Pankow and Cherry, 1996), in which the residual surfactant or cosolvent is a chemical that is later used by dechlorinating bacteria as an electron donor. A third scenario is a combination of the first two in which the electron donor solution for biostimulation also abiotically enhances mass transfer (e.g., Macbeth et al., 2006). In each case, the potential exists for the stimulation of an active anaerobic microbial consortium, including dechlorinators and halo-respiring organisms, within source zones that will influence the time required to completely exhaust the NAPL of chlorinated species. In both the first and third scenarios, all of the cost, safety, land-use and aesthetic advantages of in situ treatment are retained. These two scenarios were the focus of the demonstration.

The ESTCP demonstration was designed specifically for quantifying enhanced mass transfer during bioremediation in a real source zone during whey powder amendment under two injection strategies. The demonstration validated an innovation in bioremediation, specifically injection with high-concentration whey powder, to accelerate the rate of source removal. The

demonstration shows that principles previously shown in the laboratory can be applied in the field. This advancement broadens the applicability of bioremediation for treatment of source-zones such that the benefits of this low cost, low maintenance and in situ treatment will share the advantages of more aggressive and expensive technologies.

### **3.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY**

Significant advantages of this technology compared to alternate technologies—chemical oxidation, thermal treatment and/or pump-and-treat—include low risk to human health and the environment during implementation; low secondary waste generation; minimal impacts during operations; relatively low cost; the potential for complete source cleanup using one technology, without the requirement for separate polishing technologies; and the potential for flexibility of implementation.

Challenges for this technology can include any of the site-specific conditions that limit application of many remedial technologies, including complex lithology; low permeability media; high concentrations of competing electron acceptors including oxygen, nitrate, sulfate, and ferric iron; and electron donor distribution factors. A possible disadvantage is the potential for incomplete dechlorination beyond cis-DCE. Bioaugmentation can be used to deal with this issue when it arises. Also, increased volatilization of parent contaminants due to enhanced mass transfer, increased VC in soil gas, and methane generation impacting soil gas are all potential issues that should be considered before implementation. In general these only become problematic at sites with a shallow water table and with buildings or utilities at or near ground surface. In such cases, careful soil vapor monitoring should be a part of implementation, and some means to mitigate contaminants and methane in soil vapor might also be required, depending on site-specific considerations.

## 4.0 PERFORMANCE OBJECTIVES

The overall objective of the demonstration was to show that facilitating enhanced mass transfer allows bioremediation to be applied to chlorinated solvent source areas in groundwater in a manner that realizes many of the benefits of more expensive and hazardous technologies, while retaining its benefits as a low cost, in situ technology. Detailed performance objectives were developed to meet the overall objective. These performance objectives (Table 2) were derived from the decision rules (DR) described in Section 3.1 of the ER-0218 Final Report (NWI, 2003) using the data quality objective (DQO) process (USEPA, 1994). Three decision rules were defined and evaluated:

- **DR 1:** If chloroethene and ethene aqueous concentrations in groundwater measured during biostimulation using low concentration electron donor are significantly greater than those measured during baseline conditions at the 95% confidence level, then biostimulation will be determined to have increased contaminant mass transfer via concentration gradient increases and increased solubility of degradation products. If the DR is not supported by the data, and bioactivity, redox, and dechlorination indicators are favorable (i.e., biostimulation is successful), then the null hypothesis (see below) will be accepted. If the DR is not supported by the data, and if bioactivity, redox, and dechlorination indicators are unfavorable, then further evaluation will be recommended.
- **DR 2:** If chloroethene and ethene aqueous concentrations in groundwater measured during biostimulation using high concentration electron donor, as determined by mass balance calculations, are significantly greater than those measured during baseline conditions at the 95% confidence level, then B.E.T.<sup>TM</sup> will be determined to have increased contaminant mass transfer via some combination of bioavailability enhancement (increased effective solubility) and the mechanisms discussed in DR 1. If the DR is not supported by the data, and if bioactivity and redox indicators are favorable, then the null hypothesis will be accepted. If the DR is not supported by the data, and if bioactivity and redox indicators are unfavorable, then further evaluation will be recommended.
- **DR 3:** If chloroethene and ethene mass flux increase measured during biostimulation using high concentration electron donor, as determined by mass balance calculations, is significantly greater than that measured during low concentration electron donor biostimulation at the 95% confidence level, and if chlorine numbers (i.e., extent of dechlorination) are comparable between the two scenarios, then bioavailability enhancement will be determined to have increased contaminant mass transfer to a greater extent than the DR 1 mechanisms alone. If the DR is not supported by the data, and if bioactivity and redox indicators are favorable, then the null hypothesis will be accepted. If the DR is not supported by the data, and if bioactivity and redox indicators are unfavorable, then further evaluation will be recommended.

**Table 2. Performance objectives for B.E.T.<sup>TM</sup> enhanced mass transfer demonstration.**

<b>Performance Objective</b>	<b>Data Requirements</b>	<b>Success Criteria</b>	<b>Results</b>
<b>Qualitative</b>			
Demonstrate that enhanced mass transfer allows for cost-effective bioremediation of chlorinated solvent source areas.	Sampling of treatment cell multilevel wells and downgradient wells during different phases, analyze for contaminants (PCE, TCE, DCE isomers, VC) and degradation daughter products (ethene).	Demonstrate that high-concentration whey injection strategy accelerated mass removal of source material compared to ambient and low-concentration whey injections.	The high-concentration whey injection strategy substantially accelerated mass removal rates from the residual source area compared to ambient and low-concentration whey injection strategy.
<b>Quantitative</b>			
<b>Phase 1:</b> Determine hydraulic conditions for bioremediation design.	Pre-treatment sampling wells: conduct pumping and tracer tests.	Determination of realistic hydraulic parameters including groundwater conductivity, direction, and residence time to design an effective injection strategy.	Gradient east to west Hydraulic conductivity calculated: Cell 1 - 15.0 ft/d Cell 2 - 24.2 ft/d Significant variability in groundwater velocity within different vertical aquifer zones; data successfully utilized to design injection strategy resulting in acceptable retention time within the treatment cells.
<b>Phase 2: Baseline</b> Determine contaminant distribution and flux under baseline conditions.	Pre-treatment multilevel sampling wells: collect 3 sampling rounds for contaminants (PCE, TCE, DCE isomers, VC) and degradation daughter products (ethene).	Successful determination of contaminant mass distribution to define the target treatment area and determine baseline mass flux within the two treatment cells.	Substantially different contaminant mass concentrations within the volumetric extent of NAPL Area 3, with Treatment Cell 1 containing substantially less mass than Treatment Cell 2.  Found that mass flux in Treatment Cell 2 was substantially greater than Treatment Cell 1.

**Table 2. Performance objectives for B.E.T.<sup>TM</sup> enhanced mass transfer demonstration (continued).**

Performance Objective	Data Requirements	Success Criteria	Results
<p><b>Phase 3: Biostimulation and Enhanced Mass Transfer Demonstration</b></p> <p>Compare contaminant distribution and flux under baseline conditions and biostimulation using low-concentration and high-concentration whey injections.</p>	<p>During and post-treatment multilevel sampling wells: collect 6 rounds of sampling during and 2 rounds of sampling post treatment within the treatment area monitoring wells.</p>	<p>Increase in total volatile organic compound (VOC) and/or ethene mass flux within source area during treatment with high concentration whey powder.</p> <p>Reduction of majority of TCE (&gt;99%) contaminant mass flux within and downgradient from treatment areas.</p>	<p>Factor of 3 and 2 increase in total average VOC and ethene concentrations during 10% whey injections compared to pre- and 1% whey injections within source area (Treatment Cell 2).</p> <p>Factor of 3-16 increase in total VOC concentrations during 10% whey injections compared to pre- and 1% whey injections downgradient of source area.</p> <p>&gt;99.96 reduction in TCE mass and a 33-52% decrease in total VOC mass within treatment areas. Post-treatment samples illustrate conversion to cis-DCE (52-59% of total mass), VC (33-36% of total mass), and ethene (4-10% of total mass) within treatment cells.</p> <p>7 of 8 downgradient monitoring wells observed a 94-98% reduction in total VOC concentrations post bioremediation.</p>

The following null hypotheses were developed based on the results of the field test and the DRs:

- **Hypothesis 1 (DR 1):** The mean total molar VOC concentrations measured in Treatment Cell 2 (located within the DNAPL source zone) during biostimulation with low concentration (1%) electron donor injections is not significantly greater than that measured during Treatment Cell 2 baseline conditions at the 95% confidence level.
- **Hypothesis 2 (DR 2):** The mean of total molar VOC concentrations measured in Treatment Cell 2 during biostimulation with high concentration (10%) electron donor injections is not significantly greater than that measured during Treatment Cell 2 baseline conditions at the 95% confidence level.
- **Hypothesis 3 (DR 3):** The mean of total molar VOC concentrations measured in Treatment Cell 2 during high concentration (10%) electron donor injections is not significantly greater than that measured during biostimulation of Treatment Cell 2 with low concentration (1%) electron donor injections at the 95% confidence level.

## 5.0 SITE DESCRIPTION

This section provides details regarding the site location, geology/hydrogeology, and contaminant distribution.

### 5.1 SITE LOCATION

The EGDY Phase II Remedial Investigation Report (U.S. Army Corps of Engineers [USACE], 2002) summarizes the history and characteristics of the test site, and the following discussion is summarized from that report. The Fort Lewis Logistics Center is located in Pierce County, Washington, approximately 11 miles south of Tacoma and 17 miles northeast of Olympia. The Logistics Center occupies approximately 650 acres of the Fort Lewis Military Reservation, located at Township 19 North, Range 2 East, Sections 21, 22, 26, and 27. It is bounded on the northwest by Interstate 5 and beyond by the town of Tillicum, on the north by the American Lake Gardens Tract, on the west by the Madigan Army Medical Center, and on the southwest by the Madigan Family Housing Area.

The EGDY is located southeast of the Logistics Center in an otherwise undeveloped portion of Fort Lewis (Figure 1). The EGDY is loosely defined as the area southeast of the intersection of Rainier Avenue and East Lincoln Drive in which landfill trenching and disposal activities historically occurred over an area of approximately 35 acres.

The EGDY is located on an extensive upland glacial drift plain, at an elevation of approximately 290 ft above mean sea level (msl). Trees and shrubs have been cleared from the disposal trench areas.

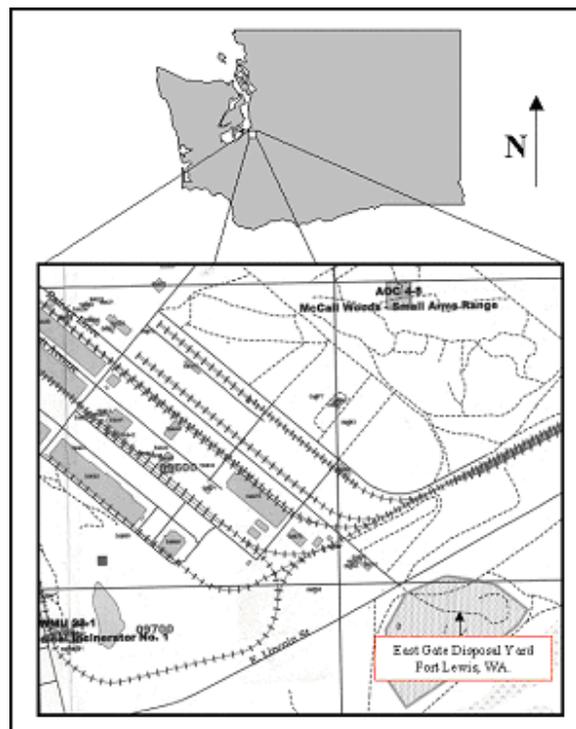


Figure 1. Location of the EGDY (USACE, 2008).

## **5.2 SITE GEOLOGY/HYDROGEOLOGY**

At least three glacial and three non-glacial units have been identified in the sediments occurring above sea level at the EGDY. These units and a brief description are described in the ER-0218 Final Report (Macbeth and Sorenson, 2008). Two primary aquifers and two aquitards are present at EGDY and are described in detail in the ER-0218 Final Report. This demonstration was performed entirely in the upper portion of the Vashon Aquifer, the shallowest aquifer at the site. The geology in this part of the formation consists primarily of interbedded brown to gray sandy gravel and sand with minor silt intervals, as well as loose, well-graded brown to gray, sandy, cobbly gravel. The upper Vashon Aquifer has very high hydraulic conductivity, as well as strong preferential flow evidenced by rapid groundwater velocities, as seen in the results of the tracer testing described in Section 5. The demonstration was performed approximately in the upper 20 ft of the aquifer, from the water table (between 10 and 15 ft below ground surface [bgs]), and about 35 ft bgs.

## **5.3 CONTAMINANT DISTRIBUTION**

NAPL characterization performed as part of the EGDY Phase II Remedial Investigation (RI) was used to locate the treatment cells; this characterization is described in the EGDY Phase II Remedial Investigation Report (USACE, 2002). During this characterization effort, membrane interface probe (MIP) evaluations completed in NAPL Area 3 indicated high concentrations of dissolved phase TCE (up to 125 mg/L) and DCE (up to 140 mg/L) were observed from 3-14 ft bgs. In addition, NAPL contact was observed at one MIP location with concentrations of about 20,000 mg/L observed at approximately 16 ft bgs. High chlorinated contaminant concentrations were believed to be limited approximately to the upper 10 feet of the aquifer. Figure 2 illustrates the inferred NAPL distribution within NAPL Area 3 based on data gathered during the Phase II RI. Figure 2 also illustrates the target areas planned for installation of the two demonstration treatment cells.

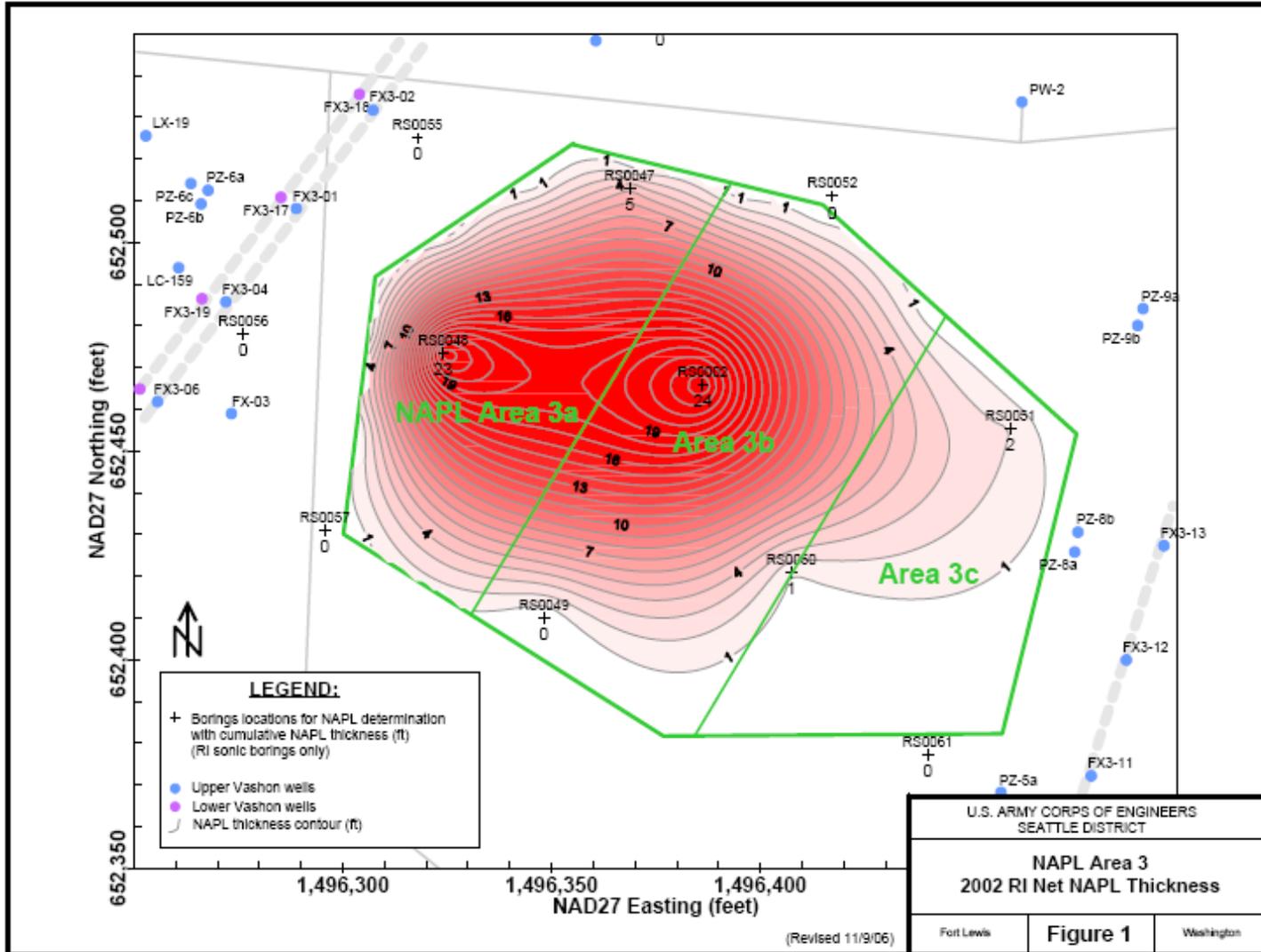


Figure 2. Inference of NAPL distribution within NAPL Area 3 based on data gathered during the Phase 2 RI (2002) (USACE, 2008). Boxes highlighted in blue indicate target treatment cell locations.

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## 6.0 TEST DESIGN

This section provides an overview of the demonstration design, implementation methodology, and results.

### 6.1 CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design for the ER-0218 demonstration included the use of two hydraulically isolated treatment cells within NAPL Area 3 (Figure 2). The objectives of ER-0218 were to evaluate and quantify enhanced mass transfer mechanisms occurring during application of ISB using whey powder under two operational scenarios conducted in series within the two treatment cells. Scenario 1 consisted of low concentration whey powder injections within the treatment area designed to enhance mass transfer from the DNAPL to the aqueous phase by promoting ARD in groundwater surrounding the DNAPL, reducing concentrations in groundwater, and maintaining a high concentration gradient as the driving force for enhanced VOC dissolution. Scenario 2 consisted of relatively high concentration whey powder injections designed to enhance the solubilization of DNAPL in addition to the ARD mass transfer mechanisms described for Scenario 1. Comparison of the two scenarios facilitated quantification, including a statistical analysis, of the different enhanced mass transfer mechanisms.

The demonstration was implemented in three Phases (see Figure 3 for the schedule), as follows:

- **Phase 1—Equilibration.** Hydraulic characterization of the treatment cells was conducted. This phase of testing established hydrogeologic baseline parameters within the treatment cells.
- **Phase 2—Baseline.** Performance indicators were collected to evaluate electron donor concentrations, geochemistry, and contaminant and degradation daughter product concentrations in each treatment cell prior to whey injection. This phase of testing established ambient contaminant distribution and flux within the treatment cells.
- **Phase 3—Biostimulation and enhanced mass transfer demonstration.** Performance indicators were collected in two treatment cells during biostimulation with both low- and high- concentration whey powder injections.

Treatment cells were installed within the Fort Lewis EGDY NAPL Area 3 as described in the ESTCP project ER-0218 Final Report (Macbeth and Sorenson, 2008). Each treatment area was configured with four monitoring wells, which were completed using the Solinst™ continuous multichannel tubing (CMT) system to provide multilevel sampling capability. Each CMT well was completed with four sampling ports at discrete depths: Port 1 from 13-14 ft bgs, Port 2 from 17-18 ft bgs, Port 3 from 22-23 ft bgs, and Port 4 from 27-28 ft bgs. Two CMT wells were aligned along the groundwater flow axis between the injection and extraction wells, and two CMT wells were aligned cross gradient from the injection and extraction well axis. The full test cell layout is shown in Figures 4 and 5, including the new injection wells (IW), extraction wells (EW), CMT monitoring wells (MW) and passive flux monitoring wells (FW). The passive flux monitoring wells were placed approximately 3 ft downgradient from CMT monitoring wells A and D, which were aligned along the groundwater flow axis for each treatment cell.

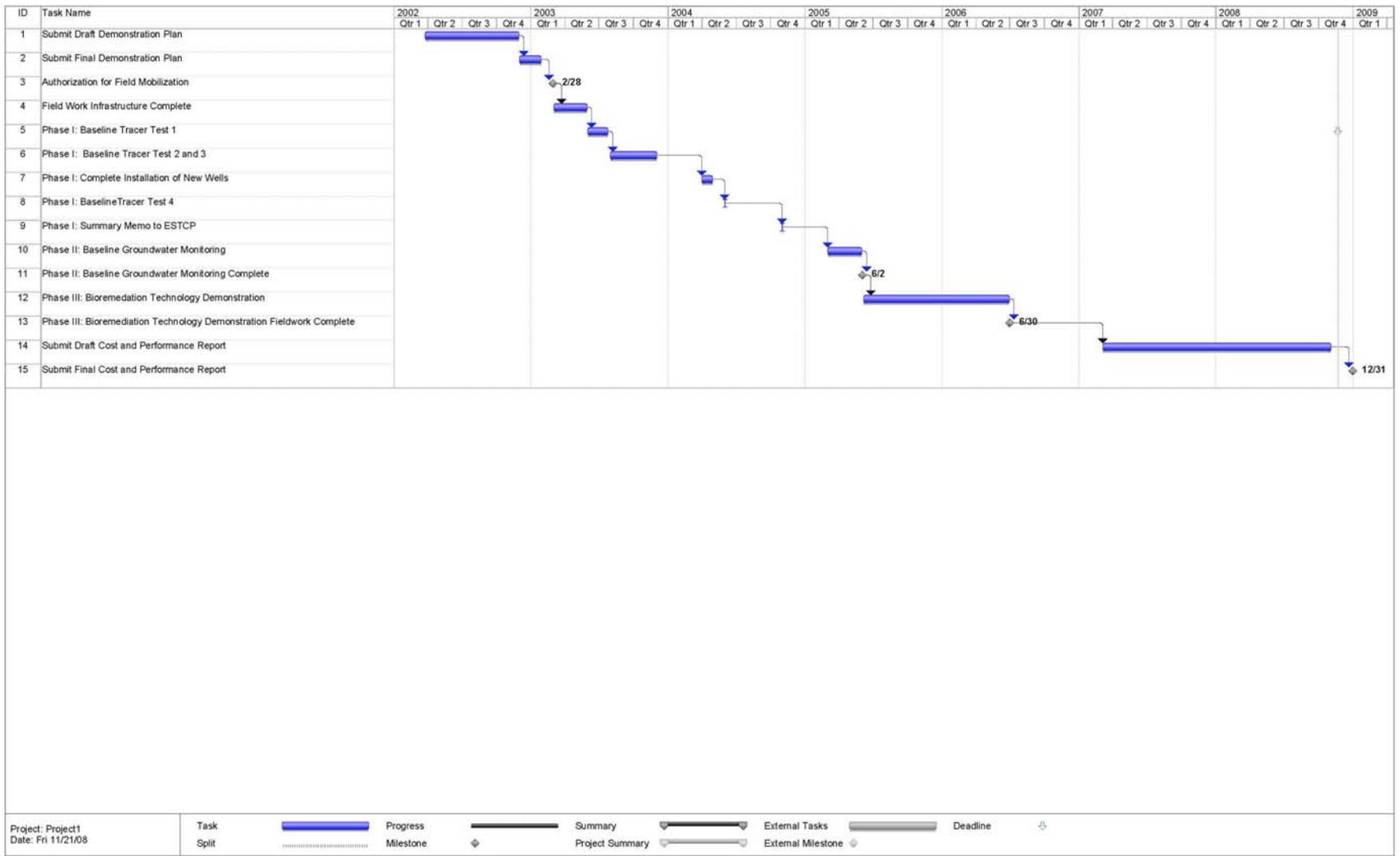


Figure 3. Gantt chart of milestones at Fort Lewis NAPL Area 3.

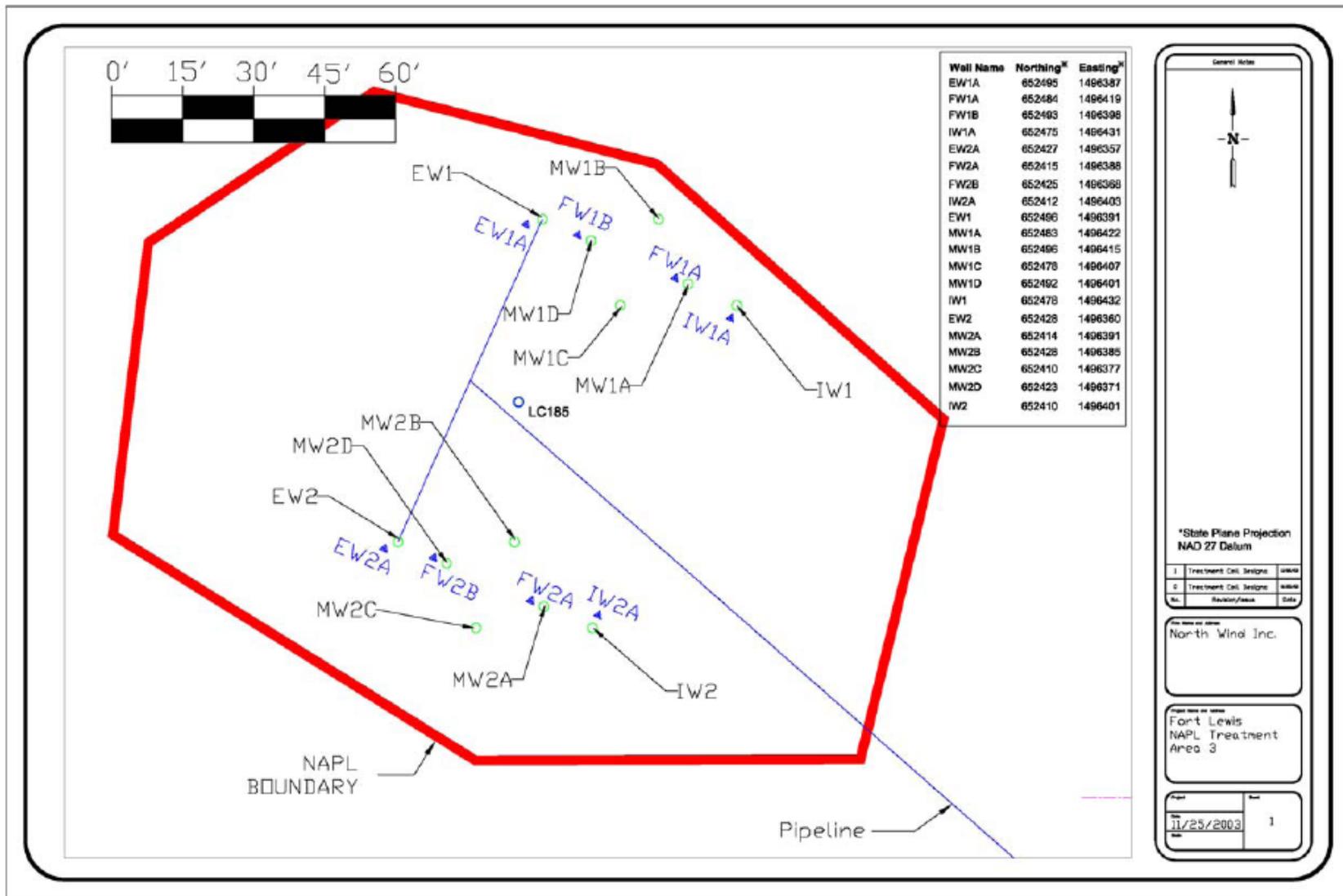


Figure 4. Well locations within treatment cells at Fort Lewis EGDY.



## **6.2 BASELINE CHARACTERIZATION: PHASES 1 AND 2**

Phases 1 and 2 of the demonstration were considered baseline characterization activities. Phase 1 consisted of a series of hydraulic pumping and tracer tests to evaluate the groundwater flow within the two treatment cells. In addition, a round of VOC sampling was conducted to determine contaminant distribution in groundwater.

### **6.2.1 Phase 1-Hydraulic Characterization**

The objective of Phase 1 was to characterize groundwater hydraulic characteristics using pumping and tracer tests within the treatment cells (see ER-0218 Final Report [Macbeth and Sorenson, 2008] for details). Hydraulic parameters were used to design an effective ISB injection strategy to meet the demonstration objectives. Pumping tests evaluated sustainable yield of extraction wells and estimated hydraulic conductivity in the area of the demonstration. Following the pumping tests, tracer studies were conducted to determine the baseline aquifer properties including hydraulic gradient both horizontally and vertically, hydraulic conductivity, residence time, and groundwater velocity and direction. In addition, it was established that the treatment cells were hydraulically isolated from each other.

### **6.2.2 Pumping and Hydraulic Tests**

Following installation of the two treatment cells, the pumping and injection system was tested to determine if it was capable of operating per specifications in the demonstration design. In addition, hydraulic tests, including tracer testing, were conducted to establish the hydraulic properties of the aquifer system. Substantial differences were observed between actual system performance and estimates based on the assumptions stated in the Technology Demonstration Plan (TDP) (NWI, 2003). The most significant issues with the original treatment system were low water yield from the two extraction wells and a substantial vertical gradient within both treatment cells, resulting in transport of the tracer to the lowest depth of the monitored treatment zone and little to no recovery of tracer in the extraction wells. Therefore, system modification, including the installation of new injection and extraction wells, was conducted such that the treatment system could perform per required specifications.

### **6.2.3 Tracer Studies**

Tracer studies were conducted to determine the baseline aquifer properties including hydraulic gradient both horizontally and vertically, hydraulic conductivity, residence time, groundwater velocity and direction, tracer distribution, and to establish that the treatment cells were hydraulically isolated. Initial tracer studies (conducted June, August, and November 2003) revealed groundwater velocities much higher than originally anticipated, a substantial vertical gradient, and no hydraulic connectivity between the treatment cells. Following installation of new injection and extraction wells, the fourth tracer study (June 2004) revealed that distribution of the tracer throughout the monitored treatment zone was substantially improved, allowing the demonstration to proceed to Phase 2. The calculated hydraulic conductivity ranged from about 10 ft/day to 50 ft/day, with Treatment Cell 1 on the low end and Treatment Cell 2 on the high end. Maximum sustainable pumping rates in the new extraction wells were about 10 and 18 gallons per minute (gpm), respectively. Peak breakthrough of the tracers was very fast, generally

reaching the downgradient end of the treatment cell within a few hours, indicative of preferential flow in addition to the high hydraulic conductivity.

#### 6.2.4 Phase 2-Baseline Chemical Characterization

The objectives of Phase 2 were to determine baseline contaminant concentrations and flux under ambient hydrologic conditions, as well as baseline measurements for other analytical parameters. Originally, the baseline testing was planned to consist of monitoring contaminant concentrations and establishing equilibrium in each treatment cell under pumping conditions. As the Phase 1 activities demonstrated that the groundwater velocity and direction was sufficient for distribution of electron donor throughout the treatment cell area without pumping, providing an equilibrium period was unnecessary. Therefore, baseline testing established the contaminant baseline parameters under ambient hydraulic conditions.

Groundwater extraction was used only during injections of whey powder solution. Groundwater was extracted from the extraction wells, pumped through the whey powder injection system, and reinjected into the injection wells. The short-term impacts of injection events on contaminant concentrations were also determined during the baseline phase by conducting an injection without amendment and collecting samples the day of and the day after injection. Groundwater was pumped from extraction wells EW-1A and EW-2A at a rate ranging from 8 to 10 gpm and was reinjected into injection wells IW-1A and IW-2A without the addition of whey. The injections took place during the weeks March 7, March 21, and April 4, 2005. The approximate volume of water recirculated is shown in Table 3.

Phase 2 activities included three rounds of baseline sampling conducted around the three biweekly injection/recirculation events. Each sampling round included collection of samples for VOC and dissolved gas analysis prior to the injection event, immediately following the injection event, and on the day following the injection event for all sample locations. In addition, the groundwater sampling purge parameters of pH, oxidation reduction potential (ORP), specific conductivity, dissolved oxygen (DO), and temperature were measured during each round of sample collection to ensure that representative samples were collected. The field-analyzed parameters, alkalinity and ferrous iron, were analyzed once during the last two baseline sampling events, as were sulfate, nitrate, chloride, and chemical oxygen demand (COD). At the same time, specific compounds expected to be introduced with whey powder were analyzed, including acetate, propionate, isobutyrate, butyrate, isovalerate, and valerate.

**Table 3. Phase 2 recirculation activity summary.**

Month Completed	Volume of Water Recirculated (gal)	
	Treatment Cell 1	Treatment Cell 2
March 2005	1300	1300
March 2005	2000	2000
April 2005	1600	1700

### 6.3 TREATABILITY OR LABORATORY STUDY RESULTS

No treatability studies or laboratory studies were conducted as part of this demonstration.

### 6.4 FIELD TESTING: PHASE 3

Actual field conditions observed during the baseline sampling (Phases 1 and 2) indicated that TCE concentrations within Treatment Cell 1 were much lower than the TCE concentrations in Treatment Cell 2, making the comparison between the cells difficult to implement as envisioned in the ER-0218 Demonstration Plan (NWI, 2003). The original plan was to perform one injection scenario in one cell, and one in the other, and then compare the results. However, to collect data that would ultimately be useable to evaluate mass transfer and dissolution in two cells with dramatically different source characteristics, the injection strategy had to be changed. The revised strategy was to perform both injection scenarios in both treatment cells (Table 4). This operational change allowed for the direct comparison of the effects of enhanced mass transfer as a result of electron donor concentration-dependent effects within each treatment cell. The composition of whey powder used for injections was 70 to 75% w/w lactose and 10 to 13% protein. A similar composition of whey was used in previous column studies that illustrated enhanced effective solubility with increasing concentration (Macbeth et al. 2006).

Phase 3 began with two initial, moderate concentration (~3% w/w), biweekly whey powder injections into each treatment cell in order to stimulate biological activity and reduced conditions prior to attempts to achieve significant enhanced mass transfer. The Phase 3 differential injection strategy, discussed below as Scenarios 1 and 2, began in July 2005.

**Whey Injection: Scenario 1.** The Scenario 1 injection strategy entailed high concentration (10% w/w) whey powder injections into well IW-1A of Treatment Cell 1 on July 19, 2005; September 13, 2005; and October 4, 2005, and in IW-2A of Treatment Cell 2 on November 8, 2005; December 13, 2005; January 15, 2006; and February 22, 2006. Injection flow rates were maintained between 5 and 12 gpm, and injections were performed over a period of several hours. The total target volume injected was approximately 1800 gallons.

**Whey Injection: Scenario 2.** The Scenario 2 injection strategy entailed low concentration (1% w/w) whey powder injections into well IW-2A of Treatment Cell 2 on July 19, 2005; August 16, 2005; September 13, 2005; and October 4, 2005, and in IW-1A of Treatment Cell 1 on November 8, 2005; December 13, 2005; January 15, 2006; and February 22, 2006. Injection flow rates were maintained between 5 and 12 gpm, and injections were performed over a period of several hours. The total target volume injected varied between approximately 1800 and 4000 gallons. The variability in volume was a result of an initial concern that the low concentration whey would be less persistent than the high concentrations whey injections. Once it was demonstrated that whey persisted within the system between injection events with the low concentration whey, the volume was reduced.

**Table 4. Phase 3 whey injection summary.**

	Treatment Cell 1		Treatment Cell 2	
	Volume of Water (gal)	Concentration of Whey (%)	Volume of Water (gal)	Concentration of Whey (%)
June 2005	3200	4	3900	3
June 2005	3200	3	3200	3
July 2005	1700	10	4000	1
August 2005	0 <sup>1</sup>	0 <sup>1</sup>	1800	1
September 2005	1700	10	4000	1
October 2005	1900	10	1800	1
November 2005	1800	1	1800	10
December 2005	1800	1	1800	10
January 2006	1800	1	1800	10
February 2006	1300	1	1800	10

<sup>1</sup> No recirculation or injection of whey due to equipment difficulties.  
 Note: Scenario 2 areas are shaded; Scenario 1 areas are left unshaded.

### 6.4.1 Bioaugmentation

Biological degradation of TCE to ethene requires the presence and activity of microbial populations capable of complete reductive dechlorination. The schedule for the field demonstration was very limited due to the impending implementation of a thermal treatment system in NAPL Area 3. Therefore, bioaugmentation was performed in both treatment cells in order to ensure that a dechlorinating microbial community was quickly established. This was accomplished by injecting a laboratory grown culture that was shown to transform TCE completely to ethene under anaerobic conditions. The culture used was a derivative of the Bachman Road culture and was prepared by the Utah Water Research Laboratory specifically for this purpose. Bioaugmentation entailed injection of approximately 10 liters of culture following the July 2005 whey injection in both test cells (Macbeth and Sorenson, 2008).

### 6.5 SAMPLING METHODS

Table 5 provides a summary of sample locations and analytes collected during Phases 1-3 of the demonstration. Sample containers, volumes, holding times, and analytical methods and are shown in Table 3-4 and Table 3-5 of the ER-0218 Final Report (Macbeth and Sorenson, 2008). In addition to the performance monitoring samples, field blank and field duplicate samples were collected to assess quality assurance (QA) parameters. All sample collection and handling was conducted by trained personnel using standard operating procedures identified in the TDP (NWI 2003, Appendix A). In general, low-flow sampling principles were practiced for all groundwater sampling.

**Sample Collection.** For Phases 2 and 3, samples were collected for (1) contaminant concentrations; (2) purge parameters: pH, ORP, specific conductivity, DO, and temperature; (3) field parameters: alkalinity and ferrous iron; (4) anions: sulfate, nitrate, chloride; and (5) electron donor parameters: COD and volatile fatty acids (VFA). Sample containers, volumes, and holding times are shown in Table 5. Details on sample collection and QA are provided in the

ER-0218 Final Report (Macbeth and Sorenson, 2008). Samples were collected using peristaltic pumps and dedicated tubing.

**Table 5. Summary of samples collected during demonstration phases, sampling locations, and analytes.**

3-D CMT	Phase 1 (Four Tracer Tests)		Analytes
	Sample locations	<i>Treatment Cell 1:</i> IW-1a, EX-1a, MW1A ports 1-4, MW1B ports 1-4, MW1C ports 1-4, MW1D, ports 1-4	Bromide, Fluorescein/ Rhodamine WT, VOCs
		<i>Treatment Cell 2:</i> IW-2a, EX-2a, MW2A ports 1-4, MW2B ports 1-4, MW2C ports 1-4, MW2D ports 1-4	
	<b>Phase 2 (nine sampling rounds for TCE and daughter products and one sampling round for carbon and geochemistry) and Phase 3 (23 sampling rounds for TCE and daughter products, 16 sampling rounds for carbon and 9 sampling rounds for geochemistry)</b>		<b>Analytes</b>
Sample locations	<i>Treatment Cell 1:</i> MW1A ports 1, 2, 4, MW1B port 4, MW1C port 4, MW1D ports 2, 3, 4	VOCs, carbon, and/or geochemistry	
	<i>Treatment Cell 2:</i> MW2A ports 1, 2, 4, MW2B port 4, MW2C port 4, MW2D ports 1, 2, 4		

## 6.6 SAMPLING RESULTS

This section describes the results of the demonstration in terms of the major categories of data collected and analyzed. First is the electron donor distribution. This drives biological activity and associated changes in redox conditions, which are discussed second. Once appropriate redox conditions are established, ARD is expected to become significant, so this is discussed third. The last two topics in the section are the impact of operations on mass flux within and downgradient of the treatment cells, respectively.

### 6.6.1 Electron Donor Distribution and Utilization

Spatial and temporal trends in COD were used to evaluate distribution of whey powder mixtures following 1% and 10% injections to the downgradient and cross-gradient monitoring locations in the treatment cells. Discussion of results is limited to results for Treatment Cell 2 because little or no residual DNAPL saturation was observed in Treatment Cell 1. In addition to COD, VFA analysis was used to evaluate whey powder utilization and fermentation. COD was detected within the treatment cells at relatively low concentrations during Phase 2 sampling. In order to evaluate distribution of whey powder during the Phase 3 injections, COD concentrations were measured prior to whey powder injection and the day following whey powder injection at each of the eight monitoring locations in each treatment cell. In general, COD accumulated in the treatment cell to some extent during the course of injections. Therefore, the change in COD observed the day following whey injection compared to the day prior was calculated (Table 6) and used to evaluate changes in carbon following injections.

During the demonstration, anaerobic fermentation of the whey resulted in the production of the VFAs butyrate, acetate, and propionate at relatively high concentrations, with minor production of lactate, isobutyrate, isovalerate, and valerate. Concentrations of COD and VFAs were generally low or nondetect prior to whey injection (Phase 2) within the treatment cells and dramatically increased following Phase 3 whey powder injections. COD concentrations were generally highest near the injection locations (MWA monitoring locations) and along the axis of the treatment cells (MWA and MWD) and were generally much lower at the cross-gradient locations (MWB and MWC) immediately following injections.

The change in COD observed prior to and following whey injection demonstrated that relatively higher amounts of COD were distributed to the monitoring locations as a result of injection, as shown in Table 6. Over time, however, significantly less change in COD was observed at individual points throughout the treatment cell following the 1% injections. The significant reduction in overall COD change following whey injections can be attributed to COD that had accumulated in the system between injection events. Significant increases in COD were observed with the onset of 10% whey injections relative to the 1% injections, with concentrations again highest along the treatment cell axis. Cross-gradient electron donor distribution was greater with the 10% injections than the 1% injections. As with the 1% injections, significant accumulation of COD was observed between injection events with concentrations ranging between approximately 500 and 7500 mg/L throughout Treatment Cell 2. Therefore, the relative change in COD values by the February 2006 injection event were lower than observed during the December 2005 injection event, but were generally still higher than for the 1% injections.

**Table 6. Whey injection impacts to COD during demonstration.**

COD	Phase 2: Baseline <sup>a</sup>	Phase 3: 1% Whey Powder Injections		Phase 3: 10% Whey Powder Injections		Phase 3: Post-Whey Injection
	Average (mg/L)	Change in COD July 2005 Injection (mg/L) <sup>b</sup>	Change in COD October 2005 Injection (mg/L) <sup>b</sup>	Change in COD December 2005 Injection (mg/L) <sup>b</sup>	Change in COD February 2006 Injection (mg/L) <sup>b</sup>	COD April 2006 (mg/L) <sup>b</sup>
MW2A1	41	6898	3520	16,530	9190	426
MW2A2	53	4617	3540	17,100	1131	405
MW2A4	38	2600	900	25,320	1131	355
MW2B4	37	780	-4480	15,240	8680	799
MW2C4	46	307	330	5180	-10	821
MW2D1	32	7083	1100	13,960	7427	183
MW2D2	35	5936	-110	21,320	947	272
MW2D4	41	1928	260	16,860	270	766

<sup>a</sup> Value represents average concentration of two samples collected March and April 2005.

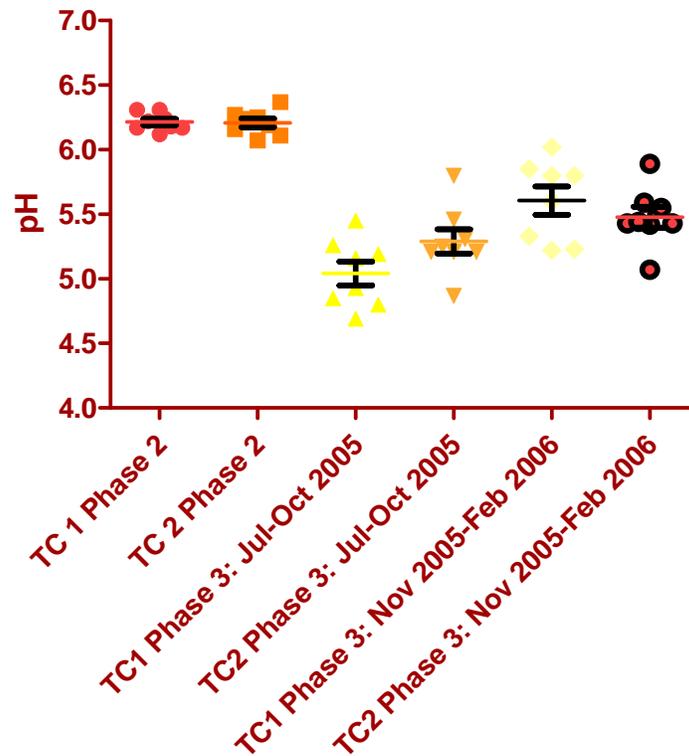
<sup>b</sup> Value represents the difference in COD concentration between samples collected prior to and 1 day following whey powder injection.

### 6.6.2 Bioactivity and Redox Performance Measures

Bioactivity and redox parameters were measured within the treatment cells during Phases 2 and 3 to ensure that whey powder injections resulted in conditions conducive to the growth and activity of dehalogenating bacteria. The changes observed in the bioactivity and redox parameters as a

result of whey injections were nearly identical for both treatment cells, irrespective of the concentration of whey injected.

**pH.** The ambient pH of the groundwater prior to whey injection was 6.1 to 6.4 in Treatment Cell 2. Following the onset of 1% whey injections, pH declined dramatically, ranging from 4.66 to 5.61. The low pH was maintained for approximately 4 months before it began to rebound between injection events (Figure 6). Therefore, the average pH observed during the 10% whey injections was higher (range of 5.1 to 5.9) than observed following the 1% whey injections. The gradual pH increase following 1% w/w whey injections demonstrates the ability of the system to buffer itself naturally over time. In this case, the power of this buffering was especially apparent when the pH was maintained at higher levels during 10% whey injections than during the earlier 1% injections.



**Figure 6. Impact of whey injection on pH in the treatment cells.** Lines represent the mean, and error bars represent one standard deviation from the mean.

**Alkalinity.** In Treatment Cell 2, average alkalinity values ranged from 66 to 78 mg/L as CaCO<sub>3</sub> during baseline. Following the 1% w/w whey injections, average alkalinity concentrations increased to 123 to 370 mg/L as CaCO<sub>3</sub> after approximately 3 months of whey injections. Prior to this, alkalinity measurements could not be reliably measured using the Hach field test kit due to the low pH of the system, which was near the titration endpoint of the method (4.8). The average measured alkalinity was higher during the 10% w/w whey injections, ranging from 107 to 350 mg/L as CaCO<sub>3</sub>. Post-whey injection sampling results showed continued elevated alkalinity concentrations for at least 2 months. These data suggest that increased biological activity over time resulted in increases in the buffering capacity of the aquifer system, which

helped to mitigate reductions in pH observed after initial whey injections. In addition, the enhanced buffering capacity of the system generated during 1% injections resulted in faster recovery of pH during 10% whey powder injections.

**ORP.** ORP values decreased considerably during Phase 3 compared to Phase 2 during the demonstration. For instance, in Treatment Cell 2, average ORP values during Phase 2 ranged from 104 mV to 195 mV, indicative of relatively oxidizing conditions. Following 1% w/w whey injections, ORP values dropped to an average of -137 to -23 mV, and decreased again following 10% w/w whey injections to an average of -155 to -106 mV. After whey injections were complete, post-injection samples revealed that ORP values had increased to an average range of -79 to 81 mV. Similar trends were observed in Treatment Cell 1. The reduction in ORP levels during the whey injection phases indicates reducing conditions were achieved throughout the treatment cells.

**Dissolved Oxygen.** DO concentrations were depleted essentially to zero in Phase 3 relative to Phase 2 of the demonstration.

**Nitrate.** Measurable nitrate concentrations were observed in groundwater within the treatment cells during the baseline sampling, with an average concentration of 1.1 mg/L in Treatment Cell 2. Nitrate concentrations, however, were generally depleted following whey injections, with an average concentration of 0.3 mg/L during 1% and 0.4 mg/L during the 10% whey injections. Nitrate concentrations remained low post-injection, with an average nitrate concentration of 0.5 mg/L 2 months after cessation of whey injections.

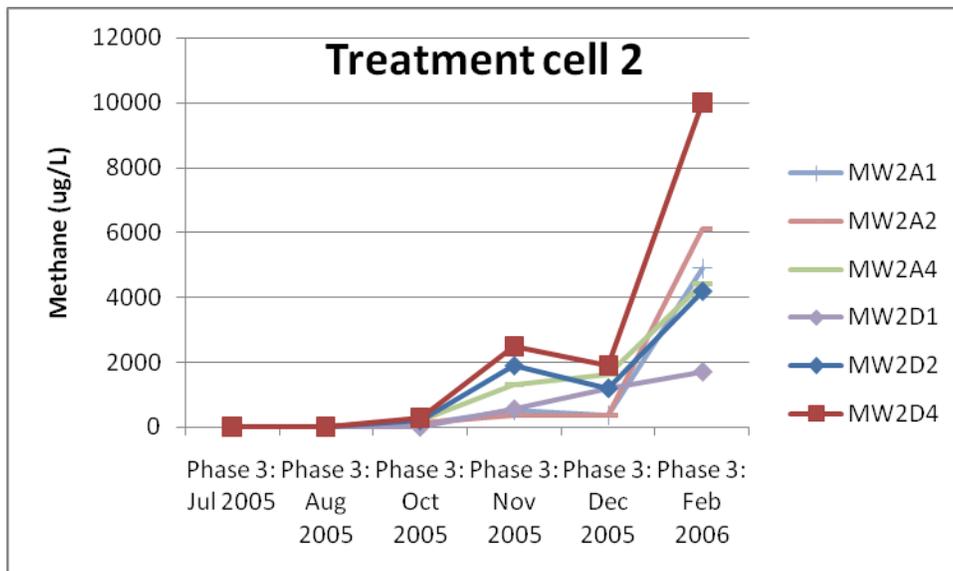
**Ferrous Iron.** Ferrous iron concentrations measured prior to whey injections (Phase 2) were generally nondetect in Treatment Cell 2. Ferrous iron concentrations increased following whey injections and were generally greater than 3.0 mg/L during 1% and 10% whey powder injections, indicative of iron reduction.

**Sulfate.** Sulfate concentrations measured during Phase 2 baseline sampling were generally between 15 and 30 mg/L in the treatment cells, with an average of 19 mg/L in Treatment Cell 2. Sulfate concentrations declined following the 1% w/w whey injections to an average of 7 mg/L. Significant variability in sulfate concentrations was observed during Phase 3, however, which can likely be attributed to sulfate in the whey powder amendment itself. The contribution of the whey injections to sulfate concentrations is supported by the depletion of sulfate concentrations following cessation of whey injections. Sulfate concentrations during the post whey injection samplings were the lowest of all sampling periods with an average value of 5 mg/L.

**Methane.** Methane concentrations were generally nondetect during Phase 2 sampling within the treatment cells. During Phase 3, significant methane production was not observed until approximately 5 months after whey injections in both treatment cells, irrespective of the whey injection strategy (Figure 7). The highest concentrations of methane were observed during the post-injection phase sampling with average concentrations of 6.04 mg/L. The lag in the onset of significant methanogenesis can be attributed to one or more factors, including (1) lag in progression of reducing conditions, (2) slow growth of methanogens, and/or (3) the low pH following the onset of whey injections. In any case, methane-producing conditions were

achieved within both test cells approximately 4 months after whey injections began and continued for at least 2 months following cessation of whey injections.

**Contaminant Distribution.** 3-D CMT sampling was used to determine the distribution of contaminants within the two treatment cells during Phases 2 and 3 of the demonstration. Figure 8 illustrates the change in total molar concentration of TCE and reductive daughter products cis-DCE, VC, and ethene during whey powder injections within the axial MWA and MWD monitoring wells for both treatment cells.

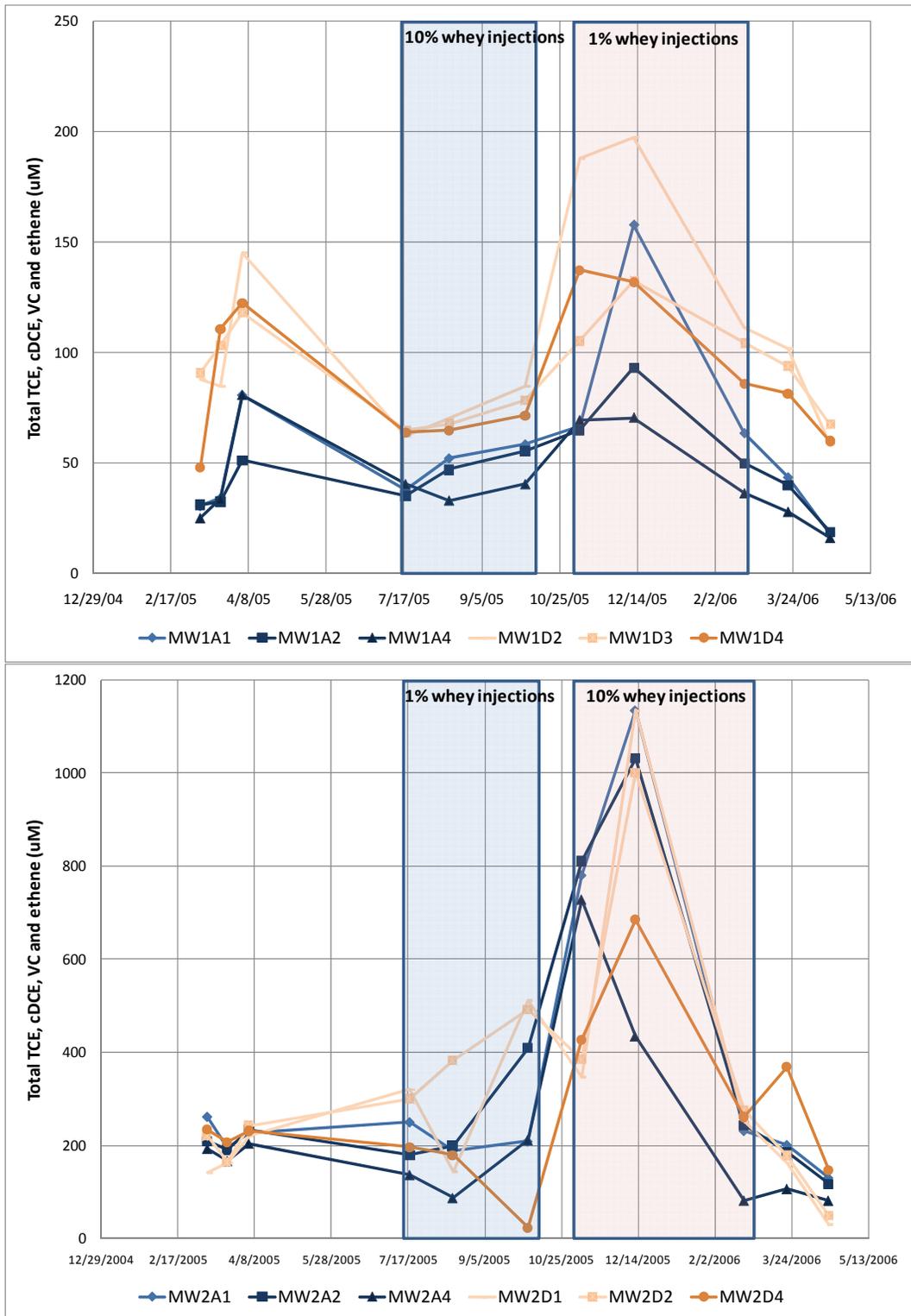


**Figure 7. Methane production observed at discrete vertical depths during Phase 3.**

### 6.6.3 Reductive Dechlorination Performance Measures

Evaluation of the distribution of contaminants and reductive dechlorination processes can be summarized as follows:

- Overall, there was a much greater mass of contaminants in Treatment Cell 2 compared to Treatment Cell 1 (factor of 3-13 times greater in Treatment Cell 2).
- In Treatment Cell 1, no significant change ( $p > 0.05$ ) in contaminant concentrations (defined as total TCE, cis-DCE, VC and ethene molar mass concentrations) was observed between any of the Phase 2 and 3 sampling events (through February 2006).



**Figure 8. Summary of contaminant distribution as total TCE, cis-DCE, VC, and ethene in Treatment Cells 1 and 2 monitoring wells A and D during Phases 2 and 3.**

- In Treatment Cell 2, contaminant concentrations significantly increased ( $p > 0.05$ ) during the November 2005 and December 2005 sampling events conducted during 10% whey injections compared to sampling events during both Phase 2 (baseline) and Phase 3 1% whey injections.
- In Treatment Cell 2, a significant decline in contaminant concentrations was observed during the February 2006 sampling compared to the November and December 2005 sampling events.

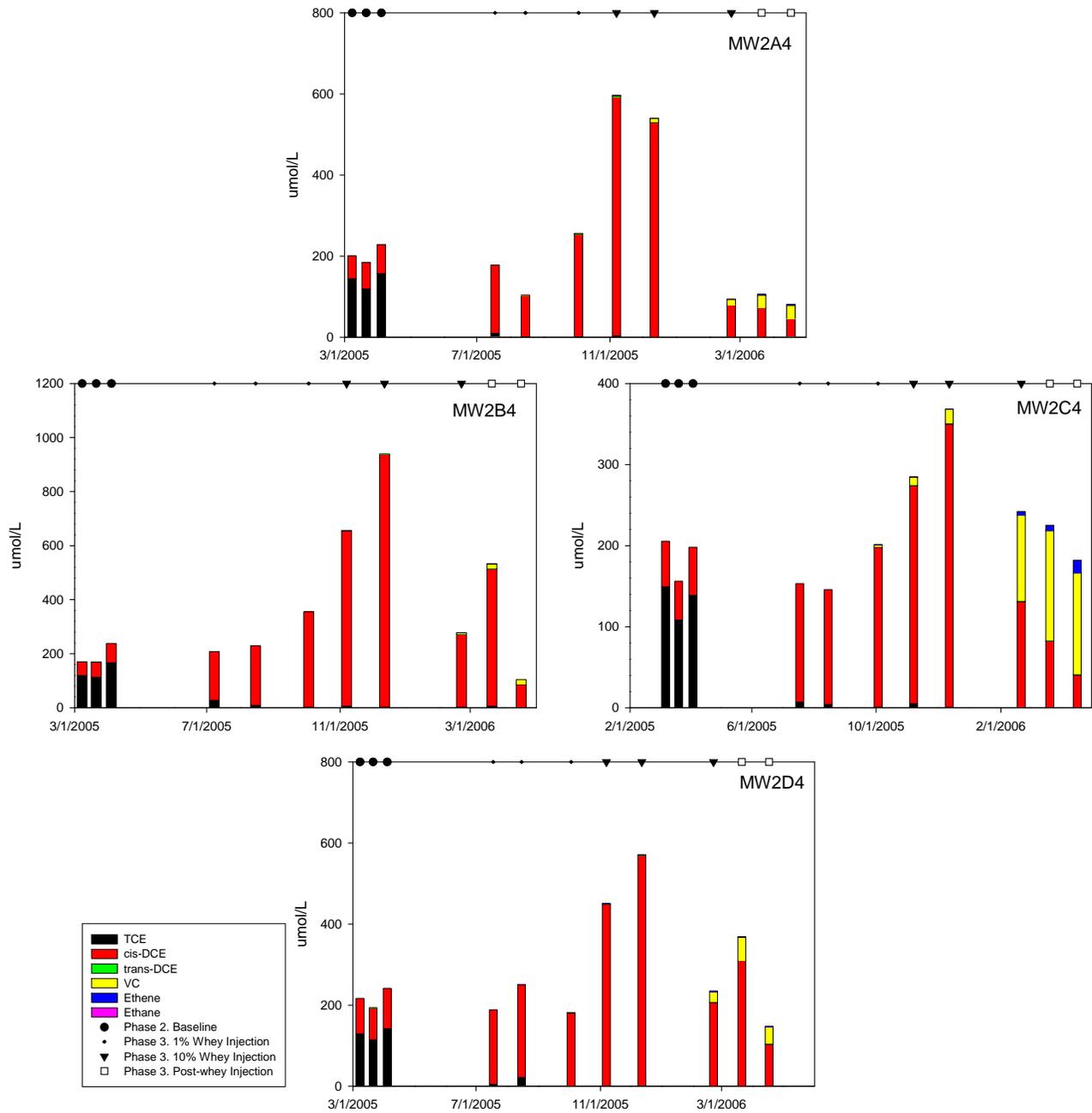
**Contaminant Fate.** Contaminant fate was also evaluated using the 3-D CMT wells in order to determine the impact of whey injections on contaminants. Biodegradation was evaluated by assessing the molar mass balance between parent compounds (TCE) and reductive daughter products (cis-DCE, VC, and ethene). Figure 9 illustrates the total moles of contaminants and reductive daughter products during Phases 2 and 3 in Treatment Cell 2.

Following the onset of whey powder injections, efficient conversion of nearly all aqueous phase TCE to cis-DCE was observed in both treatment cells. Cis-DCE remained the predominant contaminant product by mass throughout the remainder of the demonstration. Concentrations of VC and ethene increased, however, throughout the demonstration with the highest concentrations observed during the two post-injection sampling events conducted at the end of the demonstration.

Molar VOC and ethene concentrations were used to assess the mass balance of the ARD reaction. During Phase 2, TCE was the predominant VOC observed by mass within Treatment Cell 2 (Figure 9). The first sampling event conducted in July 2005, however, was approximately 1 month following the initial 3% whey powder injections. By this time, nearly all VOC mass observed was present as cis-DCE. Cis-DCE remained the predominant ARD product until February 2006, when the concentration of VC and ethene increased significantly. The improvement in overall dechlorination efficiency at the end of the demonstration is consistent with the bioactivity and redox data, showing rebound in pH to more neutral values, increasing alkalinity, and the onset of significant methane production. The mass balance of total VOCs and degradative daughter products, however, was significantly reduced with the onset of more efficient ARD, and specifically once significant VC and ethene production occurred.

Although some of the reduction in total molar mass observed in groundwater between the November 2005 and April 2006 sampling events may have been due to a decline in total residual mass as a result of the bioremediation treatment and contaminant mass removal, soil gas sampling conducted by the USACE Seattle district in August 2006 indicated extremely high concentrations of VC and ethene in the vadose zone within NAPL Area 3, indicating that significant VC and ethene was lost to the vadose zone during ARD. This loss of mass balance once cis-DCE conversion to VC and ethene is robust appears to be common in relatively shallow, thin, contaminated aquifers because of the ease with which dissolved gases are transferred to the vadose zone. Given that an accurate measurement of enhanced mass transfer is dependent on a relatively rigorous mass balance, only the November and December 2005 data sets are used to represent the 10% w/w whey injection results for purposes of estimating enhanced mass transfer in Treatment Cell 2. It was, therefore, fortuitous for this demonstration

that complete transformation to VC and ethene was not widespread until a few months after 10% injections began.



**Figure 9. Trends in Treatment Cell 2 port 4 contaminant molar mass and degradation products during demonstration.**

#### 6.6.4 Evaluation of Enhanced Mass Transfer

The total molar concentration of TCE and reductive daughter products was evaluated during each of the three operational scenarios (baseline, 1%, and 10% whey injections) at Treatment Cell 2. As discussed, the mass balance between parent compound (TCE) and ARD products was substantially affected following the onset of significant VC and ethene production (observed starting in February 2006). Therefore, the evaluation of enhanced mass transfer as a result of the various injection scenarios includes only those data collected during Phase 3 where cis-DCE was the predominant ARD product (November and December 2005).

Two scenarios were statistically evaluated for each decision rule (DR). For DR 1, Scenarios 1 (baseline sample set) and 2 (1% whey injection sample set) were compared; for DR 2, Scenarios 1 and 3 (10% whey injection sample set) were compared; and for DR 3, Scenarios 2 and 3 were compared. Each DR was evaluated to determine whether the scenario sample sets for each monitoring location showed statistically significant differences at a 95% confidence level. The DRs were evaluated for each monitoring location in Treatment Cell 2, as shown in Table 7.

At this point it is important to recall that the hypotheses were framed as null hypotheses, that is, each hypothesis is that no significant difference would be observed for each scenario comparison group at the 95% confidence level. Using Bonferroni's Multiple Comparison Test, the calculated t-Test variable for each comparison group was compared to a significant t-value based on the degrees of freedom and the 95% confidence interval. If the calculated t-Test variable was less than the significant t-statistic, the hypothesis was accepted, meaning the comparison groups were not statistically different at the 95% confidence interval. If the calculated t-Test variable was greater than the significant t-statistic, the hypothesis was rejected, meaning the comparison groups were different at the 95% confidence level.

For each DR, the difference in average total chloroethene and ethene molar concentration was calculated for every sampling port. The average difference and standard deviation were calculated and illustrated in Figure 10. The greatest mean difference occurs between baseline conditions and 10% whey injection conditions at all Treatment Cell 2 monitoring locations. The mean difference between 1% and 10% whey injections was also large, while the mean difference between baseline and 1% whey injections was a factor of about 4 to 6 smaller and was actually exceeded by its own standard deviation at MW2A, MW2B, and MW2C.

Based on the mean difference and standard deviation, t-Test values were calculated for each DR. Based on the comparison of the values with the 95% confidence interval variable, the DR null hypothesis was rejected for DRs 2 and 3 at all monitoring locations. Rejection of each null hypothesis means that increased VOC molar concentrations from 10% electron donor injections relative to baseline conditions and from 10% relative to 1% electron donor injection conditions were statistically significant. For DR 1, the null hypothesis was accepted for all but one monitoring location. This means that average molar VOC concentrations were not increased to a statistically significant extent in seven out of eight locations.

**Table 7. Statistical results from hypothesis testing for Treatment Cell 2 data.**

	MW2A1	MW2A2	MW2A4	MW2B4	MW2C4	MW2D1	MW2D2	MW2D4
Degrees of Freedom	8	8	8	2	2	8	8	8
Factor Difference *	1.4	1.4	1.1	1.6	0.9	1.8	1.8	1.1
t-Test	1.332	1.173	0.1441	1.181	1.452	2.316	3.266	0.2492
Null Hypothesis	Accept	Accept	Accept	Accept	Accept	Accept	Reject	Accept
Conclusion	No statistically significant difference in total chloroethene and ethene concentrations between Scenarios 1 and 2.						Statistically significant difference	No statistically significant difference
Factor Difference *	2.9	3.0	2.6	4.2	1.8	3.5	3.3	2.4
t-Test	5.757	5.844	3.946	6.706	6.003	9.602	8.553	5.309
Null Hypothesis	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Conclusion	Statistically significant difference in total chloroethene and ethene concentrations between Scenarios 1 and 3.							
Factor Difference *	2.1	2.1	2.3	2.5	1.9	2.0	1.8	2.3
t-Test	4.844	4.968	3.898	5.838	7.332	7.421	5.97	5.198
Null Hypothesis	Reject	Reject	Reject	Reject	Reject	Reject	Reject	Reject
Conclusion	Statistically significant difference in total chloroethene and ethene concentrations between Scenarios 2 and 3.							

\*Ratio of the appropriate averages: e.g., DR1 factor difference = average for 1% injections (n=10)/average for the baseline (n=9).

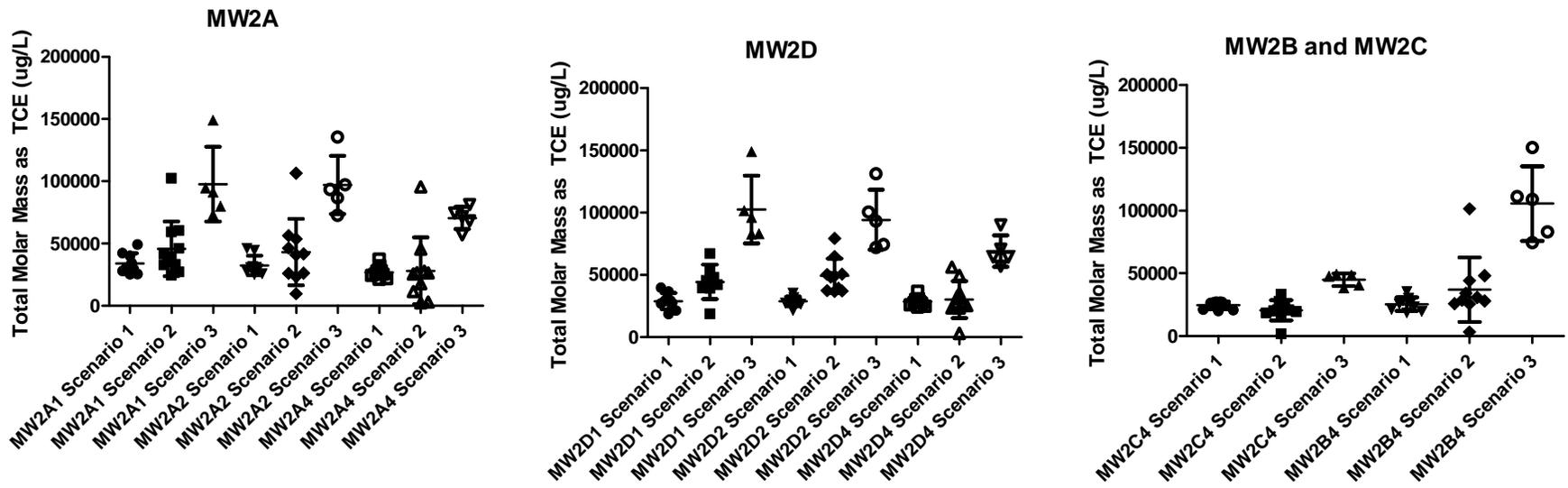


Figure 10. Scenario sample sets evaluated during statistical assessment of DRs illustrating data, mean, and the 95% confidence interval from the mean.

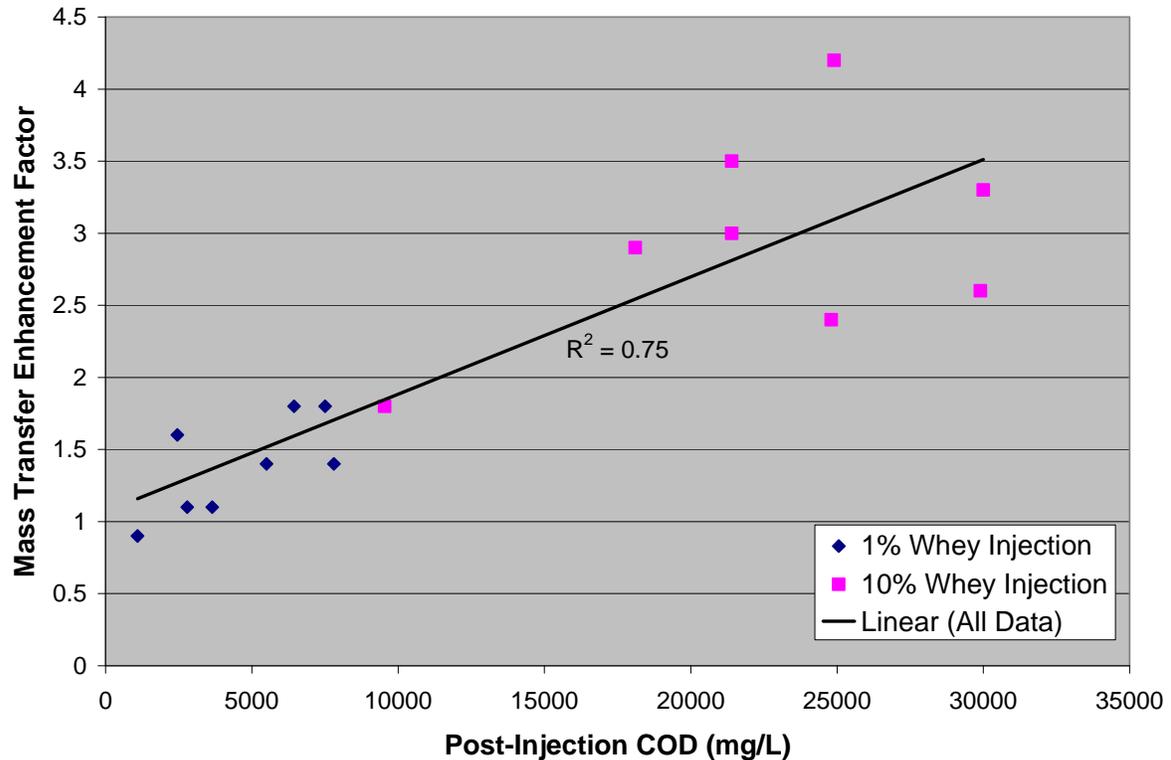
In other words, the Treatment Cell 2 results conclusively demonstrated that the B.E.T.<sup>TM</sup> process significantly enhanced mass transfer during injections of 10% whey. The average factor of increase relative to baseline was 3.0. Furthermore, mass transfer based on aqueous VOC concentrations was at least a factor of 2.1 higher during 10% whey injections than during 1% whey injections.

Unlike the low-concentration whey injection period, which showed slight increases in total average molar concentrations of chloroethenes and ethene (although not statistically significant), high-concentration whey injections significantly enhanced mass transfer of chloroethenes and ethenes in groundwater relative to both baseline and 1% whey injections, as noted above. A detailed evaluation of those data reveals some interesting points. First, the factor of increase in aqueous chloroethene and ethene concentrations from baseline to 10% whey injections ranged from 1.8 to 4.2, with only one sampling location showing an increase less than a factor of 2.0, and four locations were 3.0 or greater. These increases greatly exceeded those observed during the 1% injections, even though the extent of dechlorination was constant for the data used in the analysis (i.e., dechlorination was complete to cis-DCE, but little VC or ethene production had begun yet). In fact, aqueous chloroethene and ethene concentrations during 10% injections increased by factors ranging from 1.8 to 2.5 in Treatment Cell 2 as compared to those during 1% injections.

Second, the correlation between COD concentrations and aqueous chloroethene concentrations was again quite evident. The monitoring point with the lowest chloroethenes increase during 10% injections compared to baseline (a factor of 1.5) was MW2C4, one of the off-axis locations. This location also had the lowest COD concentration during 10% injections relative to baseline, almost a factor of 2 lower than the next lowest. The monitoring locations with higher COD all had much higher enhanced mass transfer factors.

In order to evaluate the correlation between COD concentrations and aqueous chloroethene concentrations, COD concentrations for 1% and 10% whey injections at each monitoring location were plotted against the appropriate enhanced mass transfer factor (Figure 11). The COD values used in Figure 11 are from the day following injection for the July 1% whey injection and the December 10% injection. This figure demonstrates that there is a positive correlation between increasing COD concentration and increased aqueous VOC concentrations. Once the COD exceeds 15,000 mg/L, more variability around the trend is apparent, but the trend is still clear.

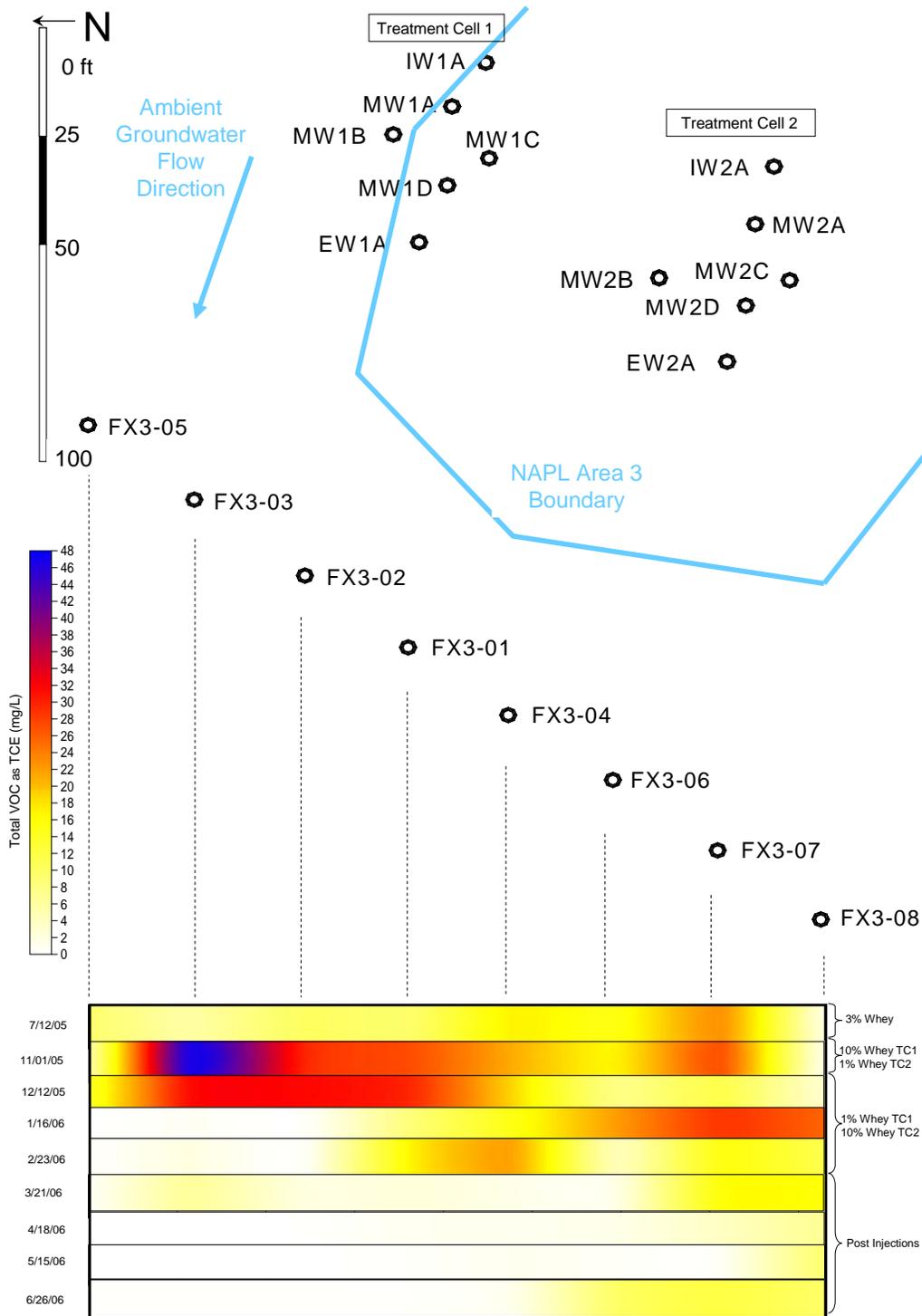
These results clearly demonstrate not only that chloroethene mass transfer to the aqueous phase was enhanced during biostimulation in the Treatment Cell 2 source area but also that the extent of enhanced mass transfer was a strong function of electron donor concentration. This was illustrated by the fact that enhanced mass transfer that occurred due to abiotic interactions of the high concentration electron donor solution with the source material was significantly greater (a factor of 1.8 to 2.5 greater) than that due to the biological ARD process alone. The implications of this accelerated source removal for downgradient flux from a source area are discussed in Section 7.



**Figure 11. Correlation of mass transfer enhancement factors based on aqueous VOC concentration increases with COD concentration at Treatment Cell 2 monitoring locations following 1% and 10% whey injections.**

### 6.6.5 Evaluation of Downgradient Enhanced Mass Flux

The installation of a line of wells downgradient of NAPL Area 3 (and therefore downgradient of the demonstration treatment cells) as part of an Army Environmental Center performance evaluation of the thermal treatment that followed the demonstration fortuitously provided critical information toward meeting project objectives. Figure 12 shows the location of the line of flux wells relative to the treatment cells. Based on the apparent direction of the ambient hydraulic gradient, wells FX3-01, FX3-02, and FX3-03 were downgradient of Treatment Cell 1. FX3-05 was a little north of directly downgradient. Wells FX3-04, FX3-06, and FX3-07 appeared to be directly downgradient from Treatment Cell 2, while FX3-08 may have been a little south of directly downgradient. Samples from all these wells were collected in July 2005, about a month after the initial 3% whey injections in both treatment cells. They were collected again in early November 2005, following the 3 months of 10% whey injections in Treatment Cell 1 and 1% whey injections in Treatment Cell 2. Beginning in December 2005, after the injection strategies were switched to 1% in Treatment Cell 1 and 10% in Treatment Cell 2, the wells were sampled monthly with additional funding provided by ESTCP. This change was due primarily to the results observed at these wells in July and November.



**Figure 12. Total chlorinated ethene concentration contours at select time points.**

The July 2005, chloroethene concentration data were collected about 1 month after the initial 3% whey injections were made in the treatment cells, approximately 150 ft upgradient. Therefore, these concentrations are assumed to represent a baseline condition. A dramatic change occurred in the data collected in November 2005, 3 months after 10% whey injections began in Treatment Cell 1. FX3-03, which had the second lowest total chloroethene concentration in July, had by far the highest total chloroethenes concentration in November, having increased by more than a factor of 8.

The observed response in the downgradient wells in November made it clear that the whey injections in the treatment cells were having a significant effect on chloroethene flux downgradient. The decision was made to switch the 10% whey injections to Treatment Cell 2 and the 1% injections to Treatment Cell 1. The December 12, 2005, monitoring event was about 2 months after the last 10% whey injection in Treatment Cell 1 and 1 month after the first injection of 1% in Treatment Cell 1 and 10% in Treatment Cell 2. At this point, concentrations were still highest downgradient from Treatment Cell 1. When the wells were sampled again in January 2006, however, the distribution of chloroethenes in downgradient wells had undergone a complete reversal from the November 2005 data. The highest concentrations were measured downgradient from Treatment Cell 2, and the lowest concentrations were measured downgradient from Treatment Cell 1. This change in concentrations downgradient from Treatment Cell 2 of a factor almost 3 to greater than 8 from December to January is nearly identical to the change observed downgradient from Treatment Cell 1 in November 2005 compared to the baseline in July. All of these results are again remarkably similar to the column study results of Macbeth et al. (2006) for 10% whey solutions.

As observed within the treatment cells, COD data collected from the downgradient wells confirms the correlation between enhanced mass transfer and electron donor concentration. The highest COD observations downgradient from Treatment Cell 1 occurred in the first 2 months it was analyzed, December 2005 and January 2006, after which it decreased by one to two orders of magnitude with the exception of one measurement in May 2006. In contrast, the COD downgradient from Treatment Cell 2 in December 2005 was still 0 mg/L in FX3-04, FX3-06, and FX3-07, while it had increased to 320 mg/L in FX3-08. This changed along with the chloroethenes concentrations in January 2006, when COD increased to its maximum levels in all four of these wells downgradient of Treatment Cell 2. The COD data not only demonstrated that the enhanced mass transfer in the source area and increased mass flux downgradient was a strong function of the electron donor concentration. They also showed that approximately 2 months was required for the effects of changes in injections in the treatment cells to be fully apparent at the downgradient monitoring wells.

The data collected from the downgradient wells provided a powerful, incontrovertible tool to document the enhanced mass transfer caused by the 10% whey injections compared to the 1% injections. However, they provided an additional benefit never envisioned in the original demonstration plan. These wells provided an additional 4 months of data to document long-term effects on downgradient mass flux due to the enhanced mass transfer and accelerated mass removal that resulted in the source area. The results in Figure 12 demonstrated that flushing the source area with the 10% whey solution for only a few months not only dramatically increased

mass transfer in the short term, it also achieved sufficient mass removal to have a major long-term effect on downgradient flux from the source area. This is further discussed in Section 7.

This demonstration of the B.E.T.<sup>TM</sup> process represents the first time the phenomenon of enhanced mass transfer in chlorinated solvent source areas as a function of the concentration of whey injection solutions has been thoroughly documented at the field scale. These results far exceeded expectations and demonstrate the potential impact the enhanced mass transfer during bioremediation can have not only on source areas but on downgradient plumes as well. It is important to note that the rapid effect on downgradient contaminant flux observed at the Fort Lewis site might be a best-case scenario because of the high ambient groundwater flow rates, but having a similar effect in 1 to 2 years rather than the few months observed here would still be an extremely beneficial result at most sites.

## 7.0 PERFORMANCE ASSESSMENT

***Evaluation of Enhanced Mass Transfer Mechanisms.*** While it is clear that the enhanced mass transfer in this demonstration was a function of the concentration of the whey injection solution, the discussion to this point has made little effort to distinguish between the potential mechanisms occurring during high concentration whey injections that are facilitating the enhancement relative to lower concentrations. From a practical standpoint, it can be argued that differentiating the mechanisms is not nearly as important as documenting that the enhanced mass transfer occurs due to the aggregate effects of the mechanisms. However, if it is possible to identify the mechanisms and even to characterize their relative contributions, the ability to predict performance under different site conditions and for different electron donors would be improved. The mechanisms that are currently understood to have the potential to increase mass transfer during bioremediation of chlorinated solvent source areas include (Sorenson, 2002; ITRC, 2005; ITRC, 2008):

- *Increased concentration gradient.* Biodegradation of aqueous contaminants in the immediate vicinity of a DNAPL-water interface maximizes the concentration gradient, thereby maximizing the driving force for mass transfer.
- *Increased solubility/decreased hydrophobicity of degradation products.* The solubility of less chlorinated compounds is generally significantly higher than the more chlorinated parent compounds such as PCE or TCE, thereby allowing more contaminant mass in solution as reductive dechlorination occurs; in addition, the less chlorinated compounds can result in less sorbed mass due to lower *K<sub>oc</sub>* values than the parent compounds.
- *Abiotic electron donor interactions.* High concentrations of some electron donors either increase effective solubility, increase desorption of sorbed contaminant mass, or both.

The first two mechanisms occur due to transformation of parent compounds in a DNAPL, such as PCE or TCE, to less chlorinated products through ARD. These mechanisms are therefore dependent upon biological activity, specifically the activity of dechlorinating bacteria such as *Dehalococcoides spp.* The third mechanism occurs independent of biological activity because it is a function of the properties of the electron donor solution itself. Three potential mechanisms for the electron donor solution to enhance mass transfer include cosolvency, surfactant partitioning, and dissolved organic matter partitioning (Macbeth, 2008). For purposes of this discussion, the mechanisms for enhancing mass transfer during bioremediation of chlorinated solvent areas will be grouped as biological mechanisms (first two mechanisms above) and abiotic mechanisms (third mechanism above).

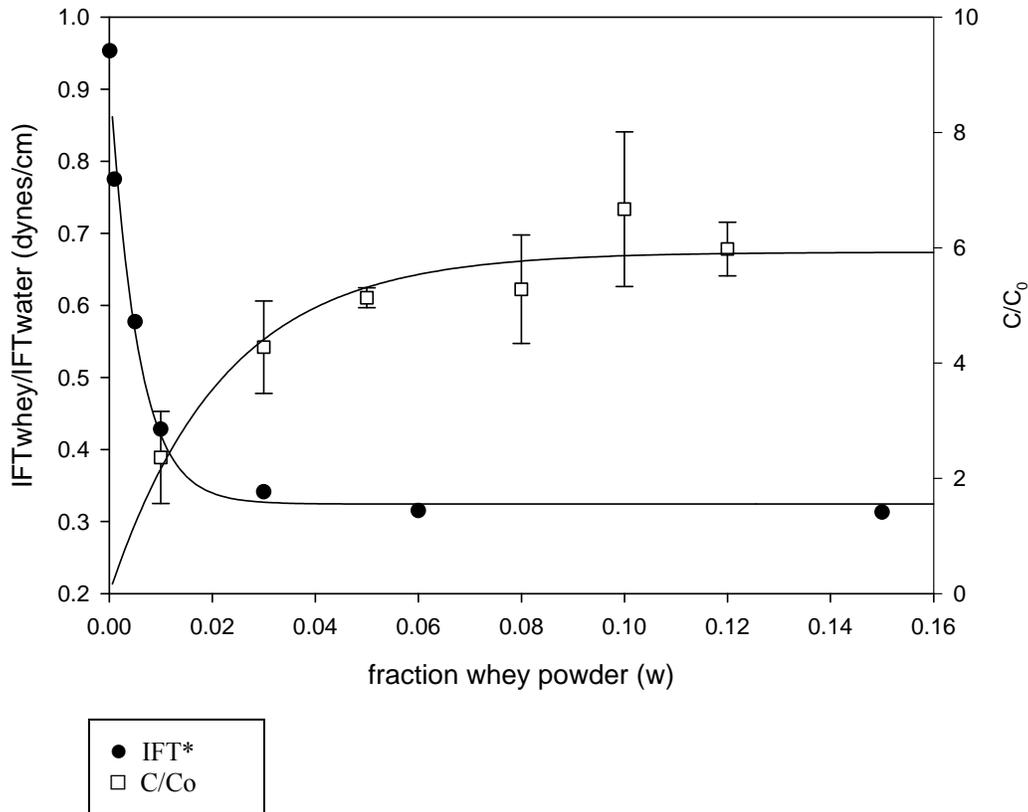
In the evaluation of the potential mechanisms enhancing mass transfer in the demonstration, three major points were considered. First, the pattern of enhanced mass transfer observed following whey injections can be accounted for entirely by previously documented enhanced solubilization of TCE by abiotic whey solutions over a range of concentrations due to its dissolved organic matter (Macbeth 2006, 2008). Second, the extent of reductive dechlorination (complete conversion of TCE to DCE with little vinyl chloride or ethene) was the same for both

1% and 10% whey injections. Third, molecular data collected during the demonstration as part of the ER-0318 project reveal that *Dehalococcoides spp.* DNA and RNA measurements were essentially indistinguishable for the different injection concentrations, suggesting that these bacteria did not grow more, nor were they more active, for the higher whey concentrations. Each of these points is discussed in detail below.

The abiotic impacts of several electron donors on the solubility and mass transfer of TCE in batch and column studies were evaluated by Macbeth (2008), and many of the details of the evaluation of whey were reported by Macbeth et al. (2006). As shown in Figure 13, abiotic whey solutions increased the solubility of TCE by up to a factor of about 6. In particular, it was noted that the interaction of the whey with TCE was consistent with enhanced solubilization by dissolved organic matter partitioning. Specifically, a linear correlation of TCE solubility and whey powder concentration was observed up to whey concentrations of about 6%, along with an exponential decrease in interfacial tension. Above 6% whey concentrations, the increase in TCE solubility was much more gradual. This dissolved organic matter partitioning effect of whey on TCE solubility is attributed to the  $\beta$ -lactoglobulin protein present in whey based on the fact that experiments with lactose alone did not enhance TCE solubility (Macbeth et al., 2006). Thus, the enhanced mass transfer observed in the demonstration, which showed a factor of 3 to greater than 8 increase in chlorinated concentrations downgradient of the treatment cells following 10% whey injections, but not 1% whey injections, could be accounted for solely by the well-documented behavior of abiotic whey solutions shown in Figure 13.

The second consideration in the evaluation of mass transfer mechanisms was the extent of dechlorination. If conversion proceeded further along the dechlorination pathway during 10% whey injections than during 1% whey injections, then it could be concluded that this might account for a significant portion of the enhanced mass transfer. As shown in Figure 9, however, dechlorination only progressed as far as DCE during both 1% and 10% injections in Treatment Cell 2 until the pH increased near the end of and after whey injections. Therefore, no increase in TCE concentration gradients or higher solubility/lower sorption of less chlorinated degradation products can be implicated in the enhanced mass transfer observed.

The third and final consideration for distinguishing between biological and abiotic enhanced mass transfer mechanisms was to evaluate molecular data related to the growth and activity of *Dehalococcoides spp.* bacteria in the treatment cells. Samples were collected to analyze both DNA and RNA from *Dehalococcoides spp.* throughout the demonstration as part of the ESTCP ER-0318 Project. If it could be demonstrated either that growth of these bacteria was greater during 10% injections based on DNA data, or that the activity was greater based on RNA data, then one could conclude that increased dechlorination activity was at least partially responsible for the enhanced mass transfer during 10% injections

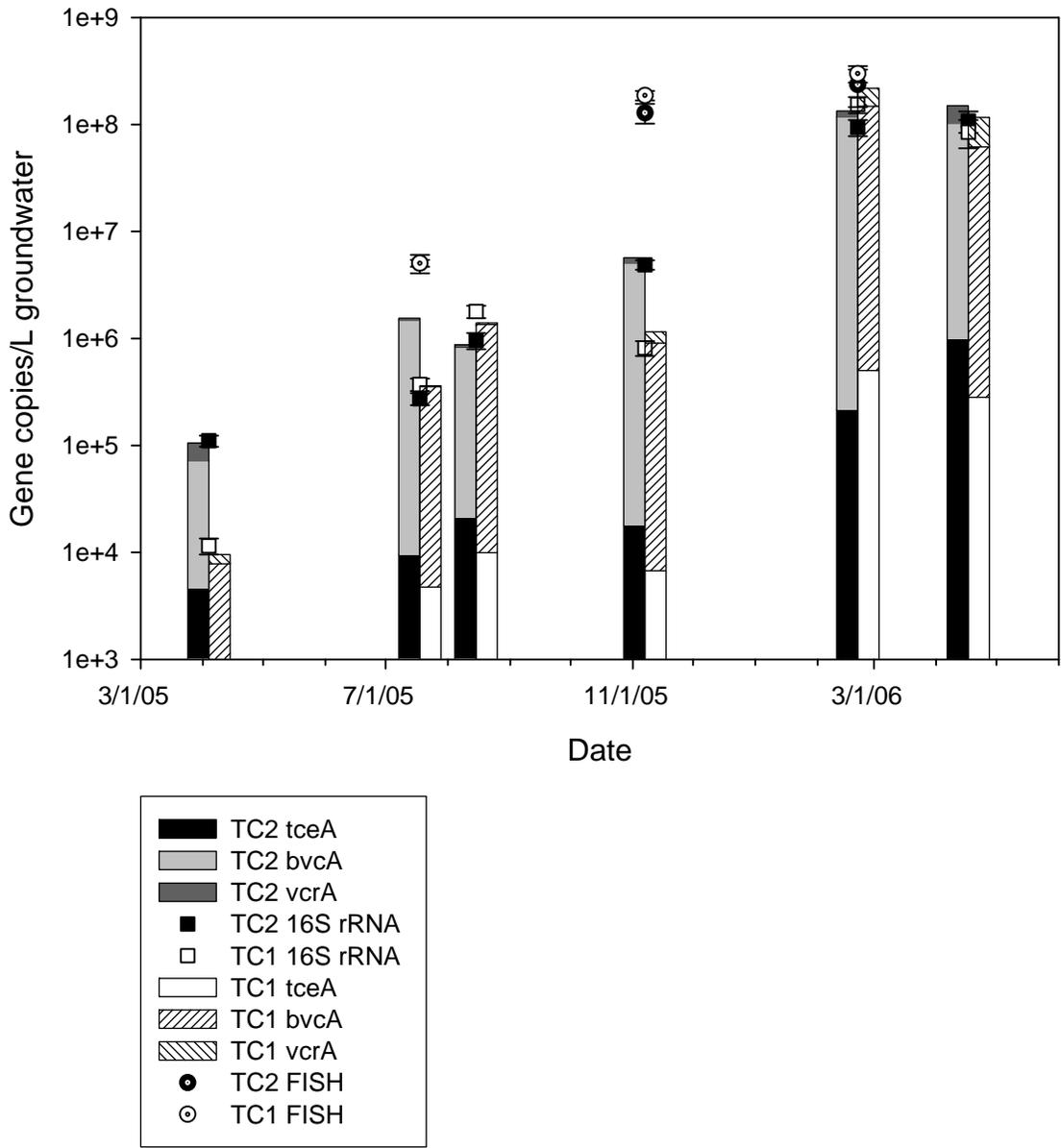


\*IFT = interfacial tension

**Figure 13. Relationship between interfacial tension reduction and enhanced solubility of TCE DNAPL as a function of whey powder concentration (Macbeth, 2008).**

The DNA analysis comprised quantitative polymerase chain reaction for the 16S gene representative of *Dehalococcoides spp.* bacteria, as well as for the *tceA*, *bvcA*, and *vcrA* functional genes that encode for enzymes responsible for various steps in the ARD pathway. Increases in DNA measurements over time indicate growth in *Dehalococcoides spp.* cells, including those with the genes of interest. Figure 14 illustrates the DNA results. The concentrations of both the 16S rRNA gene and the functional genes during baseline sampling were about an order of magnitude higher in Treatment Cell 2 than 1. This is most likely attributable to the higher TCE concentrations in that cell. By September, following 10% whey injections in Treatment Cell 1 and 1% injections in Treatment Cell 2, the 16S rRNA and functional gene concentrations had become about equal, or perhaps slightly higher in Treatment Cell 1. By November, 1 month after switching the injection concentrations, DNA concentrations were again somewhat higher in Treatment Cell 2, though not by as much as during baseline sampling. After the final whey injections in February 2006, DNA concentrations were approximately equal in the two cells. Therefore, from November 2005 to February 2006, after several months of 10% whey injections in Treatment Cell 2 and 1% injections in Treatment Cell 1, DNA concentrations of interest were approximately equal in the two cells, and actually increased more in Treatment Cell 1 during that span.

## qPCR DNA and FISH Results DHC



**Figure 14. Quantitative polymerase chain reaction (qPCR) and fluorescent in situ hybridization results over time in both treatment cells.**

Fluorescent in situ hybridization was used to analyze ribosomal RNA associated with the 16S rRNA gene for *Dehalococcoides spp.* bacteria. This is an indicator of metabolic activity of the bacteria at different time points during the demonstration. This analysis was performed in July and November 2005 and February 2006. As shown in Figure 14, given the error bars representing one standard deviation from the mean of four sampling points per treatment cell, the results indicate that ribosomal RNA production was approximately equal in the two treatment cells at each time point analyzed. Thus, no evidence of an increase in *Dehalococcoides spp.* activity as a function of whey concentration is apparent.

In summary, whey solutions have previously been documented in abiotic batch and column studies to increase TCE solubility by a factor of about 6 due to dissolved organic matter partitioning (Macbeth et al., 2006; Macbeth, 2008). This increase is consistent with the extent of enhanced mass transfer observed in the demonstration. In addition, no difference in the extent the ARD pathway was observed between the treatment cells: both 1% and 10% injections resulted in dechlorination to DCE with little production of VC and ethene. Also, molecular analyses showed that no correlation of growth and activity of *Dehalococcoides spp.* bacteria with whey concentration was apparent. Finally, as shown in Table 7, although 1% injections (which dramatically increased biological activity) appeared to increase mass flux to some extent, that difference was not found to be statistically significant relative to baseline. In contrast, the mass transfer increases from baseline to 10% whey injections and from 1% to 10% whey injections were found to be statistically significant. Based on these lines of evidence, it appears that the mechanism most responsible for the factor of 3 to greater than 8 total mass discharge enhancement from the treatment cells undergoing 10% whey injections was the abiotic enhanced solubilization of TCE due to interaction with the dissolved organic matter in the whey.

***Impact of B.E.T.<sup>TM</sup> on Downgradient Mass Flux Post-Treatment.*** The data collected from the downgradient wells provided a powerful, incontrovertible tool to document the enhanced mass transfer caused by the 10% whey injections compared to the 1% injections. However, they provided an additional benefit never envisioned in the original demonstration plan. These wells provided an additional 4 months of data to document long-term effects on downgradient mass flux due to the enhanced mass transfer and accelerated mass removal that resulted in the source area. The results in Figure 12 demonstrated that flushing the source area with the 10% whey solution for only a few months not only dramatically increased mass transfer in the short term, it also achieved sufficient mass removal to have a major long-term effect on downgradient flux from the source area. In fact, just 2 months after the highest aqueous concentrations of chloroethenes for the entire demonstration were observed at FX3-03, concentrations were observed to decrease to just 14% of baseline concentrations in that location.

Furthermore, concentrations in FX3-03 in the last three sampling events (April, May, and June 2005) ranged from just 2 to 6% of baseline concentrations. In other words, downgradient mass flux from Treatment Cell 1 was decreased by 94 to 98% after only 8 months of whey injections. Even more impressive is that in seven of the eight downgradient wells, downgradient mass flux based on total chloroethenes concentrations had decreased by a factor of 94 to 99% in May 2006.

The only well where this was not observed was FX3-08, which was at the far southern end of the downgradient wells, and might have been influenced by chloroethene concentrations from the

greater plume surrounding NAPL Area 3 in addition to what was happening in Treatment Cell 2. Some increase in concentrations was observed in the other wells downgradient from Treatment Cell 2 in June, but it is not clear whether this was due to rebound in that part of the source area, or a similar influence from the greater contaminant plume to the south of NAPL Area 3.

This demonstration of the B.E.T.<sup>TM</sup> process represents the first time the phenomenon of enhanced mass transfer in chlorinated solvent source areas as a function of the concentration of whey injection solutions has been thoroughly documented at the field scale. These results far exceeded expectations and demonstrate the potential impact the enhanced mass transfer during bioremediation can have not only on source areas but on downgradient plumes as well. It is important to note that the rapid effect on downgradient contaminant flux observed at the Fort Lewis site might be a best-case scenario because of the high ambient groundwater flow rates, but having a similar effect in 1 to 2 years rather than the few months observed here would still be an extremely beneficial result at most sites.

## **8.0 COST ASSESSMENT**

A critical evaluation criterion for any cleanup technology is cost. In this section, implementation costs for various treatment technologies were evaluated for cleanup of chlorinated solvent source areas. Four treatment technologies were evaluated: (1) MNA, (2) in-situ bioremediation (ISB), (3) pump-and-treat and (4) thermal remediation using ERH. The three active remediation technologies (2-4) were selected based on availability of information on implementation of these technologies at Fort Lewis EGDY. The costs for ISB were based on the ER-0218 demonstration. Pump-and-treat using an air stripper system and thermal ERH heating are based on actual costs of implementing these technologies at or near NAPL Area 3 of the EGDY (USACE, 2008). This allowed for a more realistic cost comparison than is possible for most sites. It is important to note that the costs presented are the costs that would be expected if the technology were implemented for cleanup of NAPL Area 3 at Fort Lewis EGDY as a model. This assessment was designed to estimate the life-cycle costs of implementing the technologies. Assumptions for the cost model are presented in Section 8.1; cost drivers are discussed in Section 8.2; and actual and annualized costs are presented in Section 8.3.

### **8.1 COST MODEL**

A simple cost model was generated for each technology to develop an estimate of actual costs. Table 8 illustrates the operational phases and assumptions for each treatment technology evaluated. The implementation costs estimated in Section 8.3 assume B.E.T.<sup>TM</sup> bioremediation is applied to the entire NAPL Area 3 source area at Fort Lewis (Table 9). For ISB, the costs collected during the demonstration were used as the basis for the estimate. For pump-and-treat and thermal treatment, the costs were estimated based on the actual implementation of these technologies at NAPL Area 3. The costs for all three active treatments, however, were modified to reflect both the size of the treatment area and the purpose (see ER-0218 Final Report, Macbeth and Sorenson [2008]). The MNA cost model was developed based on actual costs to conduct monitoring and hydraulic evaluations at the site during the demonstration.

### **8.2 COST DRIVERS**

As with most in situ remediation technologies, the most important aspect of implementing bioremediation in chlorinated solvent source areas is delivery and distribution, that is, the electron donor must be distributed throughout the target treatment zone to stimulate the desired degradation and enhanced mass transfer. Therefore, the major cost drivers are likely to be the hydraulic conductivity and the degree of heterogeneity. The “bulk” hydraulic conductivity of the treatment zone will determine the spacing of injection wells and will have a strong influence on the required treatment duration. The heterogeneity will mostly impact the treatment duration because a high degree of heterogeneity will increase the potential for preferential flow. A high degree of preferential flow will result in a cleanup time frame that is dependent upon diffusion more than advection, which will increase treatment duration, thereby increasing costs.

**Table 8. Summary of 30-year life-cycle cost assumptions for treatment technology implementation at Fort Lewis NAPL Area.**

<b>Assumed Operational Phases</b>	<b>Monitored Natural Attenuation</b>	<b>In Situ Bioremediation</b>	<b>Pump-and-Treat</b>	<b>Electrical Resistance Heating</b>
Active treatment duration (years)	NA <sup>1</sup>	3	30	1
Performance monitoring (years)	10	3	NA	1
Long-term monitoring (years)	20 <sup>2</sup>	27 <sup>3</sup>	30 <sup>2</sup>	4 <sup>3</sup>
Assumptions	<ul style="list-style-type: none"> <li>Initial hydraulic characterization and modeling required to demonstrate natural attenuation</li> <li>10 monitoring wells</li> <li>Semi-annual sampling years 1-10</li> <li>Annual sampling years 20-30</li> <li>30 annual reports</li> <li>Seven 5-yr reviews</li> </ul>	<ul style="list-style-type: none"> <li>3 injection wells, 30 ft deep, with quarterly amendment injections</li> <li>8 treatment area and 8 downgradient monitoring wells</li> <li>Monthly sampling for 6 months and quarterly sampling for 3-year operational period.</li> <li>Semiannual sampling years 4-10</li> <li>Annual sampling years 10-30</li> <li>26 annual reports</li> <li>Six 5-yr reviews</li> </ul>	<ul style="list-style-type: none"> <li>4 extraction wells 50 ft deep</li> <li>Electricity drop available</li> <li>Air stripping for above-ground treatment only</li> <li>Performance monitoring for extracted and treated water only</li> </ul>	<ul style="list-style-type: none"> <li>Assume that RI characterization is sufficient for thermal treatment design and that minimal additional characterizatoin during installation is used to finalize the design</li> <li>10 treatment area monitoring wells</li> <li>Annual sampling years 1-5</li> <li>5 annual reports</li> <li>One 5-yr review</li> </ul>

<sup>1</sup> Not applicable

<sup>2</sup> Indicates that the treatment time frame will likely be longer than the 30 years assumed to develop a life-cycle cost in this evaluation.

<sup>3</sup> Assume that ISB will achieve closure in 30 years and ERH-treated area will achieve closure in 5 years.

**Table 9. Parameters used as the basis of the model used for treatment of NAPL Area 3 and costing of treatment technologies.**

Parameter	Value
Site area	0.5 acre
Contaminated thickness treated	20 ft
Treatment volume	16,000 yd <sup>3</sup>

Similarly, the sheer mass of contamination can be a cost driver. As long as the source consists primarily of solvents at residual saturation or sorbed to the soil, mass removal can be fairly rapid as observed in the demonstration (subject to the potential constraints of hydraulic conductivity and heterogeneity discussed above). However, if DNAPL is present in pools, cleanup time frame becomes limited by dissolution rates. While B.E.T.<sup>TM</sup> can enhance the mass transfer by a factor of more than 2.5 to even 10 or higher, large pools of DNAPL could still require decades to dissolve, driving costs up significantly.

Another potential cost driver is hydraulic containment. If a sufficient downgradient buffer zone is not available at a site and extraction of groundwater is required to prevent the temporary increase in mass flux caused by B.E.T.<sup>TM</sup> from impacting some nearby downgradient receptor, costs would increase. This is especially true if, for some reason, the extracted water cannot simply be reinjected in the source area.

A fourth potential cost driver is vapor intrusion. Bioremediation of chlorinated solvents via ARD generates VC and methane. For shallow, unconfined groundwater sites, this creates the potential for these gases to reach fairly high concentrations in the unsaturated zone above the water table. If potential receptors were present above the treatment zone and soil vapor extraction were required, this would also increase technology costs.

### 8.3 COST ANALYSIS

A cost-effectiveness analysis was performed as outlined in Circular A-94 (OMB, 2008) to compare the life-cycle costs of four remediation technologies for treatment of NAPL Area 3 of the Fort Lewis EGDY. The technologies evaluated include MNA, ISB, pump-and-treat using air stripping, and thermal remediation using ERH for treatment of chlorinated solvent contamination in groundwater.

A cost model was developed for each treatment technology based on assumptions described in Section 8.1. Three of the technologies—ISB, pump-and-treat, and ERH—have actually been applied within or near NAPL Area 3 at EGDY, so costs developed were based on actual costs of implementing these technologies at the site. Cost elements were identified for each technology for comparison of overall implementation costs (Table 10) and included:

- Start-up
- Capital
- Operation and maintenance
- Demobilization
- Waste disposal
- Long-tem monitoring.

**Table 10. Summary of estimated costs for implementing MNA, ISB, Pump-and-Treat, and ERH treatment strategies for NAPL Area 3 of the Fort Lewis EGDY.**

Cost Element	Sub-Category	Data Tracked During Demonstration	Subcategory Estimated Costs	Total Estimated Cost
<b>MNA Treatment Strategy</b>				
Start-up	Mobilization	Work plan (design, field sampling plan, health and safety plan) Field preparation (drilling)	\$55,000 \$142,100	\$289,700
	Preliminary site characterization	Hydraulic testing (pumping test, tracer tests, labor, equipment, supplies) Modeling	\$55,228 \$37,372	
	Capital	NA	NA	
Operation and maintenance	NA	NA	NA	NA
Demobilization	NA	NA	NA	NA
Waste disposal	NA	NA	NA	NA
Long-term monitoring	Semi-annual sampling (Years: 1-10)	Sampling MNA parameters	\$232,167	\$1,166,684
	Annual report (Years: 1-30)	Results of sampling	\$232,167	
	Annual sampling (Years: 11-30)	Sampling MNA parameters	\$503,148	
	5-year review (Years: 1-30)		\$199,202	
<b>Total</b>				<b>\$1,456,384</b>
<b>ISB Treatment Strategy</b>				
Start-up	Mobilization	Work plan (design, field sampling plan, health and safety plan) Field preparation (drilling)	\$55,000 \$142,100	\$289,700
	Preliminary site characterization	Hydraulic test (pump tests, tracer tests, labor, equipment, supplies)	\$92,600	
	Capital	Well pumps and electrical	Equipment and installation of equipment	
Operation and maintenance	Capital equipment rental	Injection system	\$23,000	\$633,200
	Ancillary equipment rental	Tanks	\$10,000	
	Supervision	Project management, routine reporting, regulatory interface, technical oversight	\$180,400	
	Injection	Assume 3 wells and 4 injections per year for 3 years	\$180,000	
	Sampling and analysis	VOC, bioactivity, carbon, and redox for 12 events	\$239,800	

**Table 10. Summary of estimated costs for implementing MNA, ISB, Pump-and-Treat, and ERH treatment strategies for NAPL Area 3 of the Fort Lewis EGDY (continued).**

<b>Cost Element</b>	<b>Sub-Category</b>	<b>Data Tracked During Demonstration</b>	<b>Subcategory Estimated Costs</b>	<b>Total Estimated Cost</b>
Demobilization	Well abandonment		\$26,000	\$26,000
Waste disposal	NA	NA	NA	NA
Long-term monitoring	Biannual sampling (Years: 4-10)	Sample MNA parameters	\$162,517	\$1,001,489
	Annual report (Years: 1-30)	Results of sampling	\$436,062	
	Annual sampling (Years: 11-30)	Sample MNA parameters	\$232,167	
	5-year reviews (Years: 4-30)		\$170,744	
			<b>Total</b>	<b>\$1,976,390</b>
<b>Pump-and-Treat Treatment Strategy</b>				
Start-up	NA	NA	NA	NA
Capital	Well pumps and electrical	Extraction well pumps and equipment	\$700,000	\$700,000
Operation and maintenance	Operation and maintenance	Operation and maintenance, monitoring	\$1,800,00	\$1,800,000
Demobilization	Well abandonment		\$26,000	\$26,000
Waste disposal	NA	NA	NA	NA
Long-term monitoring	Annual report (Years: 1-30)		\$503,148	\$702,350
	5-year review (Years: 1-30)		\$199,202	
			<b>Total</b>	<b>\$3,228,350</b>
<b>Thermal Treatment Strategy</b>				
Start-up	NA	NA	NA	NA
Capital costs	Equipment	All equipment and installation	\$335,000	\$335,000
Operation and maintenance costs	Operating costs		\$2,360,000	\$2,680,000
	Electricity		\$245,000	
	Oversight		\$75,000	
Demobilization				
Waste disposal	NA	NA	NA	NA
Long-term monitoring	Annual sampling (Years: 1-5)	Sample for contaminants of concern	\$21,750	\$134,065
	Annual reports (Years: 1-5)	Results of sampling	\$83,858	
	5-year review (Years: 1-5)		\$28,457	
			<b>Total</b>	<b>\$3,149,065</b>

A 30-year life-cycle cost was evaluated for three of the technologies—MNA, ISB, and pump-and-treat—and a 5-year life-cycle cost was evaluated for thermal treatment. The assumptions for the cost elements were as follows:

- Costs were assumed to occur at the end of each year
- Costs were real values
- Discount rate of 2.7% (as indicated in Appendix C of Circular A-94 [2008]) was used for MNA, ISB, and pump-and-treat
- Discount rate of 1.6% (as indicated in Appendix C of Circular A-94 [2008]) was used for thermal treatment.

Table 11 presents the actual and net present value costs of each treatment technology for comparison. Overall, thermal treatment using ERH was the most expensive treatment technology based on the net present value, although the remedial time frame was much shorter than the other technologies evaluated. Pump-and-treat was the second most expensive treatment technology. In addition, it is unlikely, based on the mass of residual DNAPL present within NAPL Area 3, that 30 years would be long enough to remove sufficient residual mass to achieve site closure. Therefore, the actual remedial time frame is likely much longer.

MNA was the least expensive treatment option. Again, however, it is unlikely that a 30-year time frame would be sufficient to achieve site remedial objectives. In addition, it is also unlikely that this option would gain regulatory acceptance due to the risk to receptors as a result of a nearly 5-mile-long contaminant plume from the residual source at the EGDY.

ISB was more expensive than MNA but less expensive than pump-and-treat. The implementation of ISB assumed 3 years of active treatment and then 27 years of MNA/long-term monitoring. One of the uncertainties with ISB in a source area like NAPL Area 3, however, is that the amount of DNAPL mass present was unknown, making estimates regarding remedial time frame difficult. One of the greatest uncertainties of B.E.T.<sup>TM</sup>, and with in situ remedial technologies in general, is an understanding of the remedial time frame required to clean up DNAPL contamination. Factors such as the quantity and architecture of DNAPL within a given aquifer volume are often unknowns at DNAPL-contaminated sites. While B.E.T.<sup>TM</sup> can substantially enhance mass removal rates, the duration required to remove sufficient residual mass to meet site remedial objectives cannot be easily determined. In comparing the cost-effectiveness of B.E.T.<sup>TM</sup> with the alternate technologies, however, it should also be noted that ERH is the only technology where DNAPL mass and architecture is less important, and there is less uncertainty about removal rates. Although ERH may have a much shorter operational duration (e.g., 4 to 5 months at NAPL Area 3), the cost was approximately \$3 million over 3 years. ISB could be actively operated using B.E.T.<sup>TM</sup> for an additional 12 years (total active treatment time frame of 15 years) with long-term monitoring for 15 years for approximately the same cost. Therefore, even using conservative estimates regarding required remedial time frame, the life-cycle cost of B.E.T.<sup>TM</sup> will likely be less expensive than ERH technology. In addition, contaminant mass flux can also be effectively reduced during the entire period of treatment, and therefore, application of B.E.T.<sup>TM</sup> would also likely reduce the size of the dissolved-phase plume over the treatment duration.

**Table 11. Net present value of alternative technologies evaluated for Fort Lewis NAPL Area 3.**

<b>Cost Element</b>	<b>MNA</b>	<b>MNA Net Present Value</b>	<b>ISB</b>	<b>ISB Net Present Value</b>	<b>Pump-and-Treat</b>	<b>Pump-and-Treat Net Present Value</b>	<b>Thermal</b>	<b>Thermal Net Present Value</b>
Start-up	\$327,072.00	\$318,473.22	\$289,700.00	\$282,083.74				
Capital costs			\$52,000.00	\$48,688.22	\$726,000.00	\$706,913.34	\$335,000.00	\$329,724.41
Operation and maintenance			\$633,200.00	\$605,900.79	\$1,800,000.00	\$1,752,677.70	\$2,680,000.00	\$2,637,795.28
Long-term monitoring	\$1,166,684.00	\$807,249.58	\$1,001,490.00	\$664,270.08	\$702,350.00	\$470,083.05	\$134,065.00	\$127,007.94
<b>Total</b>	<b>\$1,493,756.00</b>	<b>\$1,125,722.80</b>	<b>\$1,976,390.00</b>	<b>\$1,600,942.83</b>	<b>\$3,228,350.00</b>	<b>\$2,929,674.09</b>	<b>\$3,149,065.00</b>	<b>\$3,094,527.63</b>

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## **9.0 IMPLEMENTATION ISSUES**

### **9.1 ENVIRONMENTAL CHECKLIST**

North Wind, Inc. (NWI) did not have to prepare a State of Washington underground injection control (UIC) permit application to inject whey and make up water extracted from the area of contamination into the aquifer at the Fort Lewis EGDY due to interpretation of the applicable sections of the Washington Administrative Code Chapter 173-218 Waste Administrative Code (WAC) Underground Injection Control Program.

Resource Conservation and Recovery Act (RCRA) regulations (specifically 3020(b)) specifically allow for both injection of treatment agents and reinjection of extracted water amended with bioremediation treatment agents if certain conditions are met: “Specifically, the groundwater must be treated prior to reinjection; the treatment must be intended to substantially reduce hazardous constituents in the ground water – either before or after reinjection; the cleanup must be protective of human health and the environment; and the injection must be part of a response action under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Section 104 or 106, or a RCRA corrective action intended to clean up the contamination.”

The State of Washington classifies injection wells into classes based on construction and function. The state requires that all wells be registered, and most wells must be rule authorized. The demonstration wells were registered with the Washington Department of Ecology, and the injection well was rule authorized for the life of the well because it is authorized under the Resource Conservation Recovery Act, 40 CFR 144.23(c).

### **9.2 OTHER REGULATORY ISSUES**

RCRA provides opportunities for public involvement throughout the remedial action process to expand public access to information about the facility and its activities. Since the small-scale ISB demonstration was supplemental to the permitted remedial activities, the actions were not subject to formal public involvement. All activities were performed within the previously disturbed, contaminated area. Generally, ISB is regarded by the public as a safe, effective, low-risk remedial alternative.

### **9.3 END-USER ISSUES**

End users for this technology are contractors, potentially responsible parties, and state and federal agencies responsible for mitigating risks to human health and the environment posed by DNAPL in groundwater. This technology is readily scaled to any size site, as evidenced by deployments at scales ranging from dry cleaner sites to large-scale plumes such as the INL Test Area North. All or most of the previously identified design elements must be addressed during design and implementation, requiring the services of hydrogeologists and engineers.

As noted in Section 8, bioremediation of chlorinated solvents via ARD generates VC and methane. For shallow, unconfined groundwater sites, this creates the potential for these gases to reach fairly high concentrations in the unsaturated zone above the water table. If potential

receptors were present above the treatment zone, this could pose a vapor intrusion risk. In such cases, careful monitoring of soil gas would be required as a minimum, and vapor intrusion mitigation might ultimately be required. Accumulation of methane in the shallow subsurface could also pose an explosion hazard if concentrations were between the lower and upper explosive limits and a source of sparks or flames were present. For shallow site with impervious surface covers, soil gas monitoring should be performed routinely to ensure that VC and methane do not create hazards in the shallow subsurface or in indoor air. While the Fort Lewis EGDY did have a shallow water table and VC and methane were present in soil gas, the site land surface is essentially undeveloped, and no risk was posed.

This technology as implemented uses a licensed, commercially available electron donor; all other process equipment is nonproprietary and readily commercially available. When using powdered whey as an electron donor, however, specialized pumping and mixing equipment is helpful. Deployment of this technology is tailored to the specific site.

B.E.T.<sup>™</sup> (U.S. Patent Numbers 6,783,678; 7,045,339; 7,141,170; 7,449,114) was originally developed at the DOE's INL and commercialized through a technology transfer program. In general, licensed electron donor products can simply be purchased through JRW Bioremediation. In some cases, no royalty is required for using the technology at government sites.

## 10.0 REFERENCES

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## APPENDIX A

### POINTS OF CONTACT

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