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Cost and Performance Report

(ER-200431)

Emulsified Zero-Valent Nano-Scale Iron Treatment of Chlorinated Solvent DNAPL Source Areas

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TABLE OF CONTENTS

Page

TABLE OF CONTENTS (continued)

Page

LIST OF FIGURES

Page

LIST OF TABLES

Page

ACRONYMS AND ABBREVIATIONS

1,1,1-TCA	1,1,1-trichloroethane
bgs	below ground surface
cDCE	cis-1,2-dichloroethene
CE	chlorinated ethenes
Dem/Val	demonstration/validation
DHG	dissolved hydrocarbon gas
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
EZVI	emulsified zero-valent iron
IPT	integral pump test
ISCO	in situ chemical oxidation
LC34	Launch Complex 34
MCL	maximum contaminant level
MCRD	Marine Corps Recruit Depot
MWR	Morale, Welfare, and Recreation
mV	millivolt
mZVI	micro-scale ZVI
$NaMnO_4$	sodium permanganate
NASA	National Aeronautics and Space Administration
NAVFAC ESC	Naval Facilities Engineering Command's Engineering Service Center
NAVFAC SE	Naval Facilities Engineering Command Southeast
NPV	net present value
nZVI	nano-scale ZVI
O&M	operation and maintenance
ORP	oxidation-reduction potential
P&T	pump-and-treat
PCE	tetrachloroethene
PRB	permeable reactive barrier

RCRA	Resource Conservation and Recovery Act
RI	remedial investigation
RFI	RCRA Facilities Investigation
ROI	radius of influence
SCDHEC	South Carolina Department of Health and Environmental Control
SL	surficial aquifer lower
STTR	Small Business Technology Transfer (Program)
SU	surficial aquifer upper
SWMU	Solid Waste Management Unit
TCE	trichloroethene
TOC	total organic compound
UIC	underground injection control
USEPA	U.S. Environmental Protection Agency
UV	ultraviolet
VC	vinyl chloride
VFA	volatile fatty acid
VOC	volatile organic compound
ZVI	zero-valent iron

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1.0 EXECUTIVE SUMMARY

1.1 BACKGROUND

Chlorinated solvents are present in groundwater at an overwhelming number of Department of Defense (DoD), Department of Energy (DOE), and related contractor sites. A significant number of these sites have volatile organic compounds (VOC) present as free-phase dense non-aqueous phase liquids (DNAPLs) that will act as a long-term source of VOC to groundwater. Due to the slow dissolution of solvents from residual or pooled DNAPL source areas, conventional treatments such as pump-and-treat (P&T) serve solely as containment technologies and require long operational periods (i.e., decades or longer) to satisfy the need for protection of human health and the environment, incurring high operation and maintenance (O&M) costs over that period.

Emulsified zero-valent iron (EZVI) is an innovative remediation technology that can be used to enhance the destruction of chlorinated DNAPL in source zones by creating intimate contact between the DNAPL and the zero-valent iron (ZVI) particles. The EZVI is composed of food-grade surfactant, biodegradable oil, water, and ZVI particles (either nano- or micro-scale iron, nZVI, or mZVI), which form emulsion particles. The ZVI provides rapid abiotic degradation of the DNAPL constituents, and the oil provides an immediate sequestration of the DNAPL constituents as well as a long-term electron donor source to enhance further biodegradation. This report summarizes the work conducted to demonstrate/validate the EZVI technology at Parris Island Marine Corps Recruit Depot (MCRD) in South Carolina.

1.2 OBJECTIVES OF THE DEMONSTRATION

The goal of the program was to evaluate degradation that is occurring due to abiotic and biological components as well as demonstrate the efficacy of EZVI at a scale that is large enough to generate accurate full-scale design and cost information for widespread technology consideration and application at DoD and related sites. The demonstration was designed to evaluate performance objectives, including (1) the reduction in mass flux of VOC in downgradient wells; (2) the reduction in total VOC and DNAPL mass; (3) the radius of influence (ROI) of each injection technology; (4) the ability to inject EZVI without damaging the emulsion structure; (5) the ability to evenly distribute the EZVI; (6) the ease of use of the technology; and (7) the versatility of the technology.

Some complications were encountered during the demonstration as a result of the shallow nature of the target injection interval and preferential flow paths created by previous borings in the area that provided short circuit pathways for the EZVI to surface. Thus objective 5 (ability to evenly distribute EZVI) was partially met. All other performance objectives were met.

1.3 DEMONSTRATION RESULTS

The principal results of the project include:

- Significant reductions in the estimated mass of tetrachloroethene (PCE) DNAPL (~93% reduction) and estimated total mass of target VOC (~86% reduction) in the Pneumatic Injection test plot following EZVI injection.
- Significant reductions in the mass flux of the parent compounds PCE (~85% reduction) and trichloroethene (TCE) (~86% reduction), and of the degradation product cis-1,2-dichloroethene (cDCE) (~71% reduction), and significant increases in the mass flux of the degradation products vinyl chloride (VC) and ethene in the Pneumatic Injection test plot following EZVI injection.
- Degradation of PCE and its daughter products within the Pneumatic Injection test plot was further supported by the compound-specific carbon-13 and chlorine-37 isotope results obtained by the U.S. Environmental Protection Agency (USEPA).
- DNAPL was pumped from some wells where DNAPL was previously absent, indicating that some of the DNAPL is mobile. However, an increase in concentrations of daughter products (VC and ethene) indicated that mass was not just displaced but degraded.
- Equipment and materials for manufacturing and injecting the EZVI were readily available, and the EZVI injection procedure was straightforward. Although there were difficulties with short-circuiting of the EZVI to surface during injection this was believed to be site-specific with the shallow nature of the target treatment interval and the presence of pre-existing short-circuit pathways (old boreholes).
- The cost assessment showed more than 62% cost savings compared to pump-and-treat, and the cost savings for the EZVI injection alternative can be increased if mZVI is used in place of nZVI. The cost for in-situ chemical oxidation (ISCO) falls between the EZVI injection alternatives where mZVI and nZVI are used.

1.4 IMPLEMENTATION ISSUES

At full-scale, an underground injection control (UIC) permit will be required in most jurisdictions for the injection of EZVI and the extraction and re-injection of contaminated groundwater if co-injection of groundwater with the EZVI is being conducted. There is also a potential that the use of nZVI (rather than mZVI) will be a concern to the public and to regulators. Daylighting of EZVI may occur if a vertical pathway connects the injection interval with the surface. Vertical pathways should be plugged with bentonite prior to EZVI injections.

2.0 INTRODUCTION

2.1 BACKGROUND

Chlorinated solvents are present in groundwater at an overwhelming number of DoD, DOE, and related contractor sites. A significant number of these sites have VOC present as free-phase DNAPLs that will act as a long-term source of VOC to groundwater. Due to the slow dissolution of solvents from residual or pooled DNAPL source areas, conventional treatments such as P&T serve solely as containment technologies and require long operational periods (i.e., decades or longer) to satisfy the need for protection of human health and the environment, incurring high O&M costs over that period.

Significant attention has been devoted in the past few years to research and field applications of source treatment technologies, as they have the potential to lower the overall cost and time required for remediation of contaminated aquifers. Recently, a small-scale field pilot test of EZVI was conducted under the National Aeronautics and Space Administration (NASA) Small Business Technology Transfer (STTR) Program to assess the ability of this technology to treat a TCE DNAPL source zone. The pilot test showed promising results as a method for significantly reducing both mass and flux from DNAPL source zones. However, additional field demonstration research is required to improve the EZVI delivery approach, clarify the relative degradation contributions of the ZVI versus biodegradation promoted by the emulsifying agents (completed laboratory evaluation [Geosyntec Consultants, Inc., 2006]), and validate the technology for widespread use for DNAPL source zone treatment at DoD and related private sectors sites. NASA holds the patent for this technology and, as a U.S. government technology, no fees for the use of EZVI will be levied on any federal facility.

Through funding provided by the DoD's ESTCP, and with support from the USEPA National Risk Management Research Laboratory, Geosyntec Consultants, Inc., and NASA conducted a technology demonstration program evaluating the use of EZVI, an innovative remediation technology, to remediate chlorinated solvent DNAPL source zones. The field demonstration/validation (Dem/Val) was conducted at the Solid Waste Management Unit (SWMU) 45 (Site 45) – former Morale, Welfare, and Recreation (MWR) Dry Cleaning Facility (Building 193), Parris Island MCRD, SC. The goal of the program was to evaluate degradation that is occurring due to abiotic and biological components as well as demonstrate the efficacy of EZVI at a scale that is large enough to generate accurate full-scale design and cost information for widespread technology consideration and application at DoD and related sites. This report provides a summary of the approach, methodology, and results of the EZVI field Dem/Val. A detailed discussion of the field Dem/Val is provided in the Final Report (Geosyntec Consultants, Inc., 2010).

2.2 OBJECTIVES OF THE DEMONSTRATION

The objectives of the field demonstration were to:

- Evaluate the ability of the two most promising injection technologies to evenly distribute the EZVI in a controlled manner
- Evaluate the ability of EZVI to significantly reduce the mass flux of dissolved-phase VOC from a DNAPL source zone and to reduce the DNAPL mass in the source
- Provide reliable technical data relevant to field-scale EZVI trials, including documenting the benefits of the technology in terms of expected reduction in the duration and cost of remediation of DNAPL sites, and develop a Guidance Manual to assist DoD managers and practitioners with appropriate selection and implementation of the EZVI technology
- Provide information to the MCRD Partnering Team for use in the Feasibility Study for Site 45.

The field Dem/Val was conducted at Site 45, Parris Island MCRD, SC. This site has a relatively well-characterized DNAPL source area (primarily PCE), appropriate site conditions, and a suitable on-site support network for execution of the Dem/Val. The rationale for the selection of the site is presented in the Draft Site Selection Memorandum For: Emulsified Zero-Valent Nano-Scale Iron Treatment of Chlorinated Solvent DNAPL Source Areas (Geosyntec Consultants, Inc., 2010).

2.3 REGULATORY DRIVERS

The USEPA maximum contaminant level (MCL) for PCE and TCE in drinking waters is 5 micrograms per liter (µg/L). This concentration is considerably less than the concentrations present in groundwater at many sites throughout the United States. The MCLs for VC and cDCE are 2 µg/L and 70 µg/L, respectively. A significant number of sites have VOC present as free-phase DNAPLs that will act as a long-term source of VOC to groundwater. In situ technologies for treatment of these contaminants often focus on the groundwater plume and not the source of the contamination. Due to the slow dissolution of solvents from residual or pooled DNAPL source areas, conventional treatments serve solely as containment technologies and require long operational periods to remove significant amounts of DNAPL. Therefore, this demonstration seeks to further improve upon a more cost-effective technology that can meet these regulations and remediate DNAPL source areas.

3.0 TECHNOLOGY

The following sections provide a description of the technology (Section 3.1), discuss the technology development (Section 3.2), and outline the advantages and limitations of the technology (Section 3.3).

3.1 TECHNOLOGY DESCRIPTION

Significant laboratory and field research has demonstrated that zero-valent metals will reductively dehalogenate dissolved chlorinated solvents such as PCE and TCE to ethene. Permeable reactive barriers (PRBs) containing ZVI as the reactive material have been shown to be effective in treating plumes of dissolved chlorinated solvents. PRB technology is passive and requires no energy; however, it still relies on DNAPL dissolution and transport of dissolved chlorinated solvents to the barrier for treatment, and therefore PRBs do little to reduce the cleanup time for the site.

EZVI can be used to enhance the destruction of chlorinated DNAPL in source zones by creating intimate contact between the DNAPL and the ZVI particles. The EZVI is composed of food-grade surfactant, biodegradable oil, water, and ZVI particles (either nano- or micro-scale iron, nZVI, or mZVI), which form emulsion particles. Each emulsion particle or droplet contains ZVI particles in water surrounded by an oil-liquid membrane. Since the exterior oil membrane of the emulsion droplet has hydrophobic properties similar to that of DNAPL, the droplets are miscible with DNAPL. It is believed that as the oil emulsion droplets combine with DNAPL TCE, for example, the TCE is sequestered in the oil and then dissolves into the aqueous droplet containing ZVI that was within the oil emulsion droplet. It is also believed that the final degradation by-products from the dechlorination reaction are driven by the increase in concentration inside the aqueous emulsion droplet to diffusion into the non-aqueous phase (oil and TCE), then out into the surrounding aqueous phase. While the ZVI in the aqueous emulsion droplet remains reactive, the chlorinated compounds are continually degraded within the aqueous emulsion droplets, thus maintaining a concentration gradient across the oil membrane and establishing a driving force for additional TCE migration into the aqueous emulsion droplet where additional degradation can occur.

The primary application of the EZVI technology is treatment of DNAPL source zones but it is also capable of treating dissolved-phase chemicals. EZVI that is located near DNAPL will also degrade the dissolved-phase chemicals that it comes in contact with. The reduction in concentration of dissolved-phase chemicals in the vicinity of the DNAPL will enhance mass dissolution from the DNAPL.

In addition to the abiotic degradation associated with the ZVI, the injection of EZVI containing vegetable oil and surfactant will result in sequestration of the chlorinated ethenes into the oil and biodegradation of dissolved chlorinated ethenes. Chlorinated solvents will preferentially dissolve into the oil component of the EZVI, thereby reducing the aqueous phase concentrations. The chlorinated solvents may then be degraded by the ZVI in the EZVI. The vegetable oil and surfactant can also act as electron donors to promote anaerobic biodegradation of the chlorinated solvents. Abiotic degradation resulting from the ZVI in the EZVI was shown to be a very fast process in laboratory studies conducted at the University of Central Florida (Quinn et al., 2005).

If the amount of ZVI is not sufficient to completely degrade the TCE to ethene, then the vegetable oil and surfactant can act as a slow release electron donor for biodegradation processes at the site (Major et al., 2002).

Another potential benefit of EZVI over ZVI for environmental applications is that the hydrophobic membrane surrounding the ZVI protects it from other groundwater constituents, such as some inorganic compounds, that might otherwise react with the ZVI. While the oil membrane of the EZVI will allow organic constituents (TCE and other ethenes) to diffuse through the liquid membrane and contact the ZVI, it may inhibit diffusion of other ionic constituents that may passivate the ZVI surface and limit their contact with the ZVI. This mechanism potentially reduces the mass of ZVI required for treatment relative to unprotected ZVI.

3.2 TECHNOLOGY DEVELOPMENT

The first field demonstration of EZVI was conducted between 2001 and 2003 to treat a chlorinated solvent source zone at NASA's Launch Complex 34 (LC34) located on the 45th Space Wing's Cape Canaveral Air Force Station. The demonstration conducted at LC34 demonstrated that the addition of EZVI into a source area containing free-phase DNAPL could reduce the mass flux of dissolved phase TCE from a DNAPL source zone and reduce the amount of free-phase DNAPL mass over time. Although the field demonstration at LC34 was successful in showing a decrease in TCE mass flux and TCE DNAPL mass, there were issues with the EZVI injection techniques and in obtaining a uniform distribution of EZVI in the areas containing DNAPL.

NASA holds the patent on the technology and has successfully licensed the technology to six companies. EZVI has been injected at over 16 sites in the United States from 2004 until present in a range of geologies, including sandy site and fractured rock.

3.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Groundwater remediation approaches at DNAPL sites have historically employed groundwater extraction and ex situ treatment (i.e., P&T). Unfortunately, these approaches have been demonstrated to be ineffective in significantly improving groundwater quality, even after decades of continuous operation (National Research Council, 1994). As a result, remediation technologies such as EZVI have received significant attention, as government and industry struggle to develop remedial approaches for source treatment that are less intrusive, more effective, and less costly. The main advantages of the EZVI technology over other treatment technologies include:

- Potential for lower overall costs than alternative technologies such as groundwater P&T with high O&M costs or thermal technologies with high capital costs
- An effective "one-two punch" of rapid abiotic degradation followed by the slower biological degradation
- Contaminants will be destroyed rather than transferred to another medium

- Ability to treat both DNAPL source zones and dissolved-phase chemicals to contain plume migration.

The main limitations of using the EZVI technology are:

- Difficulty in effectively distributing the viscous EZVI to all areas impacted with DNAPL
- Potential to adversely impact secondary groundwater quality through mobilization of metals and production of sulfides or methane if excess electron donor, in the form of the vegetable oil, is added
- Injection of EZVI may displace DNAPL away from the injection point; however, this limitation can be remedied by strategic placement of the injection points.

Currently, nZVI is being used in environmental remediation and there are no national regulatory restrictions on the use of nZVI for environmental remediation. Nevertheless, nanotechnology use in environmental remediation is still relatively new and there are many unanswered questions about its use in situ. More research is needed to understand the fate and transport of free nano-scale materials in the environment, whether they are persistent and whether they have toxicological effects on various biological systems (USEPA, 2008). Nano-scale ZVI particles range in size from about 10 to 100 nanometers and are larger than many other engineered nano-particles. In addition, nZVI particles used to make up EZVI generally agglomerate and the size of the resulting particles are significantly greater than the nano-scale. This agglomeration reduces the mobility of nZVI in the subsurface. Research is ongoing into methods to treat nZVI with surface coatings to minimize agglomeration and improve the mobility of nZVI materials within aquifers, but it is not anticipated that nZVI treated in this manner would be used in formulations of EZVI.

The fate and transport and potential environmental implications of nZVI used in EZVI will be different than nZVI used directly as an amendment for in situ remediation since (1) the iron is contained within an oil/water droplet; and (2) within the EZVI droplets, the iron is likely to agglomerated to larger, microscale particles. As more information on the fate and transport and potential toxicity of nZVI particles becomes available, it is possible that USEPA or state regulatory agencies will restrict the use of nZVI particles.

It should be noted that EZVI can also be formulated using microscale ZVI, which is lower in cost and could avoid potential environmental concerns regarding the use of nano-scale material.

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4.0 PERFORMANCE OBJECTIVES

The performance objectives are provided in Table 1. Each objective is discussed in detail in the following sections.

Table 1. Performance objectives.

Type of Performance Objective	Primary Performance Criteria	Expected Performance	Actual Performance Objective Met?
Qualitative	1. Ability to inject EZVI without damaging emulsion structure	Injection technologies will be able to deliver the EZVI within the source zone in a way that will not damage the emulsion.	Objective met
	2. Ability to evenly distribute EZVI in controlled manner over an optimum ROI	Injection technologies will be able to deliver the EZVI within the source zone in a way that will allow some control of the direction of EZVI injection so as to evenly distribute the EZVI over the injection interval.	Objective partially met
	3. Implementability	EZVI will be relatively easy to handle and inject in the field with proper operator training.	Objective met
	4. Versatility	Technology can be applied in a variety of geological and hydrogeological settings where DNAPL source areas are present.	Objective met
	5. Duration of remediation	Reduction of total VOC and DNAPL concentrations can be achieved within a short time frame (i.e., <9 months).	Objective met
	6. Scale-up constraints	Technology can be implemented at full scale at larger sites based on performance data from small-scale demonstration.	Objective met
Quantitative	1. Reduction in mass flux of dissolved VOC in downgradient monitoring wells in the Pneumatic Injection test plot; degradation also evaluated in the adjacent Direct Injection test plot, but this is secondary	>75% decrease in mass flux of dissolved chlorinated ethenes based on groundwater samples from multilevel wells over the baseline condition for areas in contact with EZVI.	Objective met
	2. Reduction in the total VOC and DNAPL mass in the Pneumatic Injection test plot	>75% decrease in VOC and DNAPL mass in the Pneumatic Injection test plot over baseline conditions based on groundwater samples and post-demonstration core samples for areas in contact with EZVI.	Objective met
	3. ROI	For the Pneumatic Injection technology a ROI >5 ft. For the Direct Injection technology a ROI of >1 ft.	Objective met

4.1 REDUCTION IN MASS FLUX OF VOC IN DOWNGRADIENT WELLS

A key performance objective is a reduction in mass flux of dissolved VOC in downgradient monitoring wells for areas in contact with EZVI. To evaluate this objective, groundwater and soil samples were collected both before and after EZVI injection and analyzed for VOC. Data from the post-demonstration sampling event are compared to data from the pre-injection (baseline) sampling event. Successful performance will be >75% decrease in mass flux of dissolved VOC based on groundwater samples from multilevel wells over the baseline condition for areas in contact with EZVI.

This objective was met. There were significant reductions in the downgradient groundwater mass flux values for parent compounds PCE (>85%) and TCE (>85%) and a significant increase in the mass flux of ethene. These results are discussed further in Section 7.1.

4.2 REDUCTION IN TOTAL VOC AND DNAPL MASS

The amount of VOC and DNAPL reduction in the Pneumatic Injection test plot is assessed by comparing results of pre-injection (baseline) and post-injection groundwater and soil core samples. A successful performance will be >75% decrease in VOC and DNAPL mass over baseline conditions in the Pneumatic Injection test plot.

This objective was met with a total VOC mass reduction of 86%, an estimated reduction of 63% reduction in the sorbed and dissolved phases, and 93% reduction in the DNAPL mass. Based on the presence of DNAPL in the four wells (ML-2-5, ML-2-7, PMW-4, and PMW-5) post-EZVI injection, it appears that there was more DNAPL present in the plot than the pre-demonstration estimate suggested. Although there is evidence that some DNAPL may have been mobilized outside the plot (DNAPL was observed in PMW-4 and ML-2-7), there is evidence of significant degradation within and downgradient of the plot as evidenced by the increase in concentrations of daughter products (VC and ethene), indicating that mass was not just displaced but degraded.

The injection strategy was also designed to minimize mobilizing DNAPLs outside the injection plot. Injections were conducted initially at each of the four corners of the plot such that it was expected that DNAPL within the plot would be pushed further towards the center of the plot and only DNAPL outside the plot would be pushed away from the plot during these injections. Subsequent injections were made along the perimeter of the plot, again pushing DNAPL towards the center of the plot. The final injections were made into the center of the plot, but the volume of the injected fluid would not be sufficient to push mobile DNAPL outside the plot to a significant degree. These results are discussed further in Section 7.2.

4.3 RADIUS OF INFLUENCE

The ROI of each injection technology was assessed through visual inspection of soil cores collected post-injection. For the Pneumatic Injection and Direct Injection test plots, success was marked by the presence of EZVI at distances greater than 5 ft and 1 ft, respectively.

This objective was met with measured ROIs of as much as 7 ft with pneumatic injection and 2.5 ft with direct injection. These results are discussed further in Section 7.3.

4.4 ABILITY TO INJECT EZVI WITHOUT DAMAGING EMULSION STRUCTURE

For this performance criterion, the injection technologies will be able to deliver the EZVI within the source zone without damage to the emulsion structure.

This objective was met with both technologies being able to inject the EZVI without damage to the emulsion structure. These results are discussed in greater detail in Section 7.4.

4.5 ABILITY TO EVENLY DISTRIBUTE EZVI

The ability of each injection technology to evenly distribute EZVI in a controlled manner over an optimum ROI was assessed by collecting groundwater and soil core samples from the test plots. Success was marked by the ability of the injection technology to deliver the EZVI within the source zone in a way that will allow some control of the direction of EZVI injection so as to evenly distribute the EZVI over the injection interval.

This objective was partially met. There were complications with the shallow nature of the target injection interval and preferential flow paths created by previous borings in the area providing short circuit pathways for the EZVI to surface. These results are discussed in greater detail in Section 7.5.

4.6 EASE OF IMPLEMENTATION

The ease of use of this technology was evaluated based on our experience in the field.

This objective was met with respect to both the ease of making the EZVI up on site and with the handling and injection of the EZVI. These results are discussed in greater detail in Section 7.6.

4.7 VERSATILITY

For this performance criterion, the technology was deemed successful if it could be applied in a variety of geological and hydrogeological settings where DNAPL source areas are present.

Given that there are depth and geological settings restrictions for the injection technologies tested but that there are alternative injection approaches that can be used for different geological and hydrogeological settings, the EZVI technology is considered versatile, but the specific injection methods tested are not versatile for all hydrogeological formations. These results are discussed in greater detail in Section 7.7.

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5.0 SITE DESCRIPTION

The field Dem/Val was conducted at Site 45, Parris Island MCRD, SC (the "Site"). The Site location and history, Site geology/hydrogeology, and contaminant distribution are briefly discussed in the following sections. Detailed descriptions of the Site are provided in the Final Report (Geosyntec Consultants, Inc., 2010), and in the Remedial Investigation/Resource Conservation and Recovery Act (RCRA) Facilities Investigation (RI/RFI) for Site/SWMU 45 report (Tetra Tech NUS, 2004a) and the Site/SWMU 45 RI/RFI Addendum Work Plan report (Tetra Tech NUS, 2004b). Information in the following sections is taken directly from these reports.

5.1 SITE LOCATION AND HISTORY

The Site is located in the Main Post area of Parris Island MCRD between Panama Street to the north, Kyushu Street to the south, and Samoa Street to the east. Four aboveground storage tanks (of unknown capacities) were situated along the northern side of former Building 193. These tanks were first put into place in 1988 following the removal of an underground storage system where hydrocarbon-cleaning solvents were previously stored. The location and capacity of the underground storage system are not known. The new storage tanks were positioned within a concrete catch basin used to contain any overflow during tank filling. It was reported that on March 11, 1994, one of the tanks was overfilled with PCE and an unknown amount of the contaminant flowed into the concrete catch basin. The PCE overflow was not collected at that time, and heavy rainfall subsequently washed the contaminant onto the surrounding soil (Tetra Tech NUS, 2004b).

5.2 SITE GEOLOGY/HYDROGEOLOGY

The Dem/Val was conducted within the shallow, unconfined surficial aquifer at the Site. The shallow aquifer generally consists of permeable, fine to medium, Pleistocene age sand, with discontinuous lenses of finer-grained silty clay and clayey sand, to a depth of 17 ft. During the RI/RFI, the surficial aquifer was further divided into an upper (SU) and lower (SL) portion. The shallow aquifer is underlain by a 1- to 3-ft thick layer of peat. The water table generally ranges from 3 to 5 ft below ground surface (bgs), and the general groundwater flow direction in the shallow aquifer is to the southeast. Estimates of the hydraulic gradient, hydraulic conductivity, and groundwater velocity for the shallow aquifer are 0.0023 to 0.0029 ft/ft, 15.3 ft/day, and 0.15 to 0.18 ft/day, respectively. During the RI/RFI, the vertical gradient between wells in a cluster was observed to be negligible, typically less than 0.1 ft.

5.3 CONTAMINANT DISTRIBUTION

Results of previous field investigations indicate chlorinated VOC contamination in the surface and subsurface soil at the Site has impacted the groundwater (i.e., groundwater contaminant concentrations above screening levels) to depths ranging from the upper boundaries of the unconfined aquifer to approximately 19 ft bgs.

In June 2005, Geosyntec Consultants, Inc., NASA, the U.S. Naval Facilities Engineering Command's Engineering Service Center (NAVFAC ESC), and USEPA conducted a field

investigation to collect additional groundwater and soil data from the Site to confirm the results of the membrane interface probe logs collected during prior investigations of the source area (Tetra Tech NUS, 2004b) and to confirm the presence of DNAPL concentrations of PCE or TCE in the subsurface in the area of the former tanks. Results of the field investigation revealed PCE concentrations in soil cores that exceeded the maximum possible dissolved and sorbed phase PCE concentrations (based on site conditions), thereby indicating the presence of PCE DNAPL mass. Furthermore, visual inspection of soil cores indicated the presence of DNAPL.

6.0 TEST DESIGN

The following sections provide an overview of the pre-design investigations and studies, the conceptual experimental design, the design and layout of the technology components, field activities, analytical methods, and test results. A detailed description of these items is provided in the Final Report (Geosyntec Consultants, Inc., 2010).

6.1 PRE-DESIGN SITE INVESTIGATIONS

As discussed in Section 5.3, Geosyntec Consultants, Inc., NASA, NAVFAC ESC, and USEPA conducted a field investigation in June 2005 to confirm the presence of DNAPL at the Site. Results of the field investigation revealed PCE concentrations in some of the soil cores that exceeded the maximum possible dissolved and sorbed phase PCE concentrations (based on site conditions), thereby indicating the presence of PCE DNAPL.

6.2 PRE-DESIGN EVALUATION AND SELECTION OF INJECTION METHODS

A review of possible methods for injecting and distributing EZVI in the subsurface at the Site was conducted to identify the optimal methods for use in the field Dem/Val. The review included an evaluation of data funded by NASA from a field evaluation of four different injection methods for EZVI. Based on the results of the field evaluation, pneumatic injection and direct injection were selected as the optimal technologies for the field Dem/Val.

6.3 PRE-DESIGN LABORATORY TREATABILITY STUDY

Laboratory experiments were conducted by SiREM Laboratories (a division of Geosyntec Consultants, Inc.) to evaluate the extent of DNAPL mass destruction that is due to abiotic and biological processes with the application of EZVI. Details of these experiments are presented in the Final Laboratory Treatability Report For: Emulsified Zero Valent Iron Treatment of Chlorinated Solvent DNAPL Source Areas (Geosyntec Consultants, Inc., 2006). The following conclusions were made based on the results of the laboratory experiments:

- Treatment of dissolved phase TCE with nZVI and EZVI can produce significant and rapid decreases in TCE concentrations in the aqueous phase.
- The DNAPL treatment tests demonstrate the advantages of EZVI relative to oil emulsions or nZVI in a situation where a DNAPL is present in the subsurface. The EZVI combines the sequestration of the DNAPL with the degradation of the VOC by the nZVI, resulting in an immediate reduction in the TCE flux from the source area as well as degradation due to the nZVI. The EZVI provides degradation of the TCE to ethene in a similar time frame as the nZVI and also provides sequestration of any potential untreated VOC.
- The EZVI provides oil that should be able to act as an electron donor to promote biodegradation of TCE that is not degraded by the nZVI, but this was not observed to a significant degree in the lab tests because of the lack of microorganisms in the test bottles.

6.4 CONCEPTUAL EXPERIMENTAL DESIGN

For this demonstration the Site was instrumented to create two hydraulically independent pilot test plots (Pneumatic Injection and Direct Injection test plots) in the existing Site DNAPL source area in June 2006 by installing a network of monitoring wells (Figure 1). The Pneumatic Injection test plot consists of five fully screened monitoring wells (PMW-2 through PMW-6) and seven multilevel monitoring wells (ML-1 through ML-7). The fully screened wells are screened between 4 and 19 ft bgs, while the multilevel wells each contain seven 3-inch screened intervals positioned at 2.5-ft intervals from approximately 4 to 19 ft bgs. The Direct Injection test plot consists of a single fully screened monitoring well (PMW-1) screened from 3.5 to 13.5 ft bgs.

6.5 FIELD ACTIVITIES

The field events following the well installations consisted of groundwater sampling for laboratory analysis, pump tests, and EZVI injection. A schedule of the demonstration field activities is provided in Figure 2.

6.5.1 Baseline Sampling

In June 2006, August 2006, and October 2006, prior to EZVI injection, groundwater samples were collected from each of the fully screened and multilevel monitoring wells and analyzed for baseline chemical characterization (see Table 2 for a list of parameters). Eight soil cores (SC-1 through SC-8) were also collected at the Site during the June 2005 Site investigation to evaluate whether there was sufficient VOC mass at the Site to conduct the EZVI field Dem/Val (Figure 1). An additional soil core (SC-9; Figure 1) was collected from within the Pneumatic Injection test plot in June 2006 to complete the baseline mass evaluation. Measurements of soil porosity, bulk density, and fraction of organic carbon were also performed on select soil samples from SC-9 to further refine VOC mass estimates. Samples were collected following sampling protocols established for the Site in the Demonstration Plan.

For both test plots, VOC results from soil cores were used to calculate estimates of VOC mass (as either sorbed or DNAPL), and groundwater VOC results from select wells were used to calculate estimates of dissolved phase VOC. Details of the calculations are provided in Section 5.6.1 of the Final Report (Geosyntec Consultants, Inc., 2010).

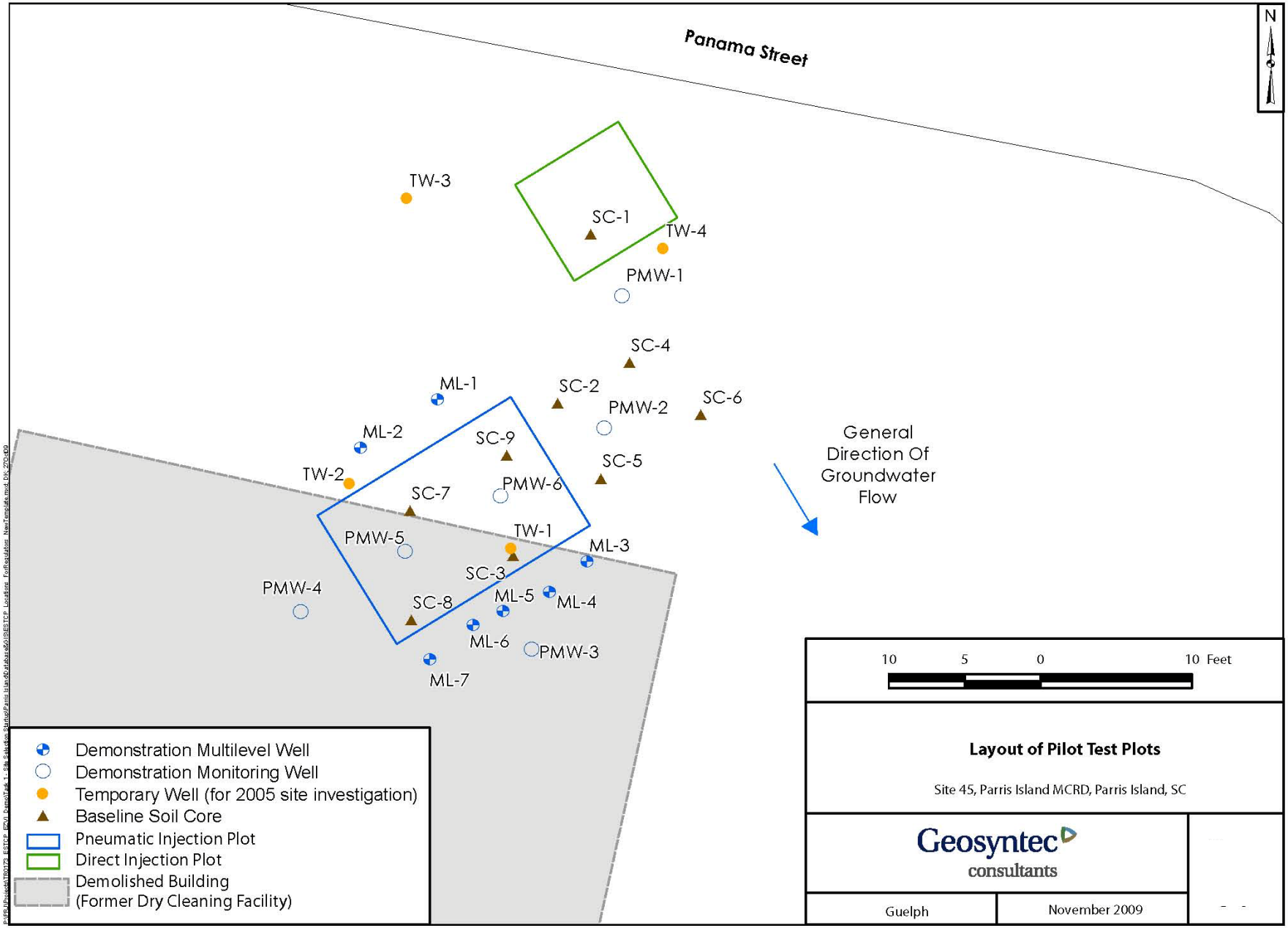

Figure 1. Layout of pilot test plots.

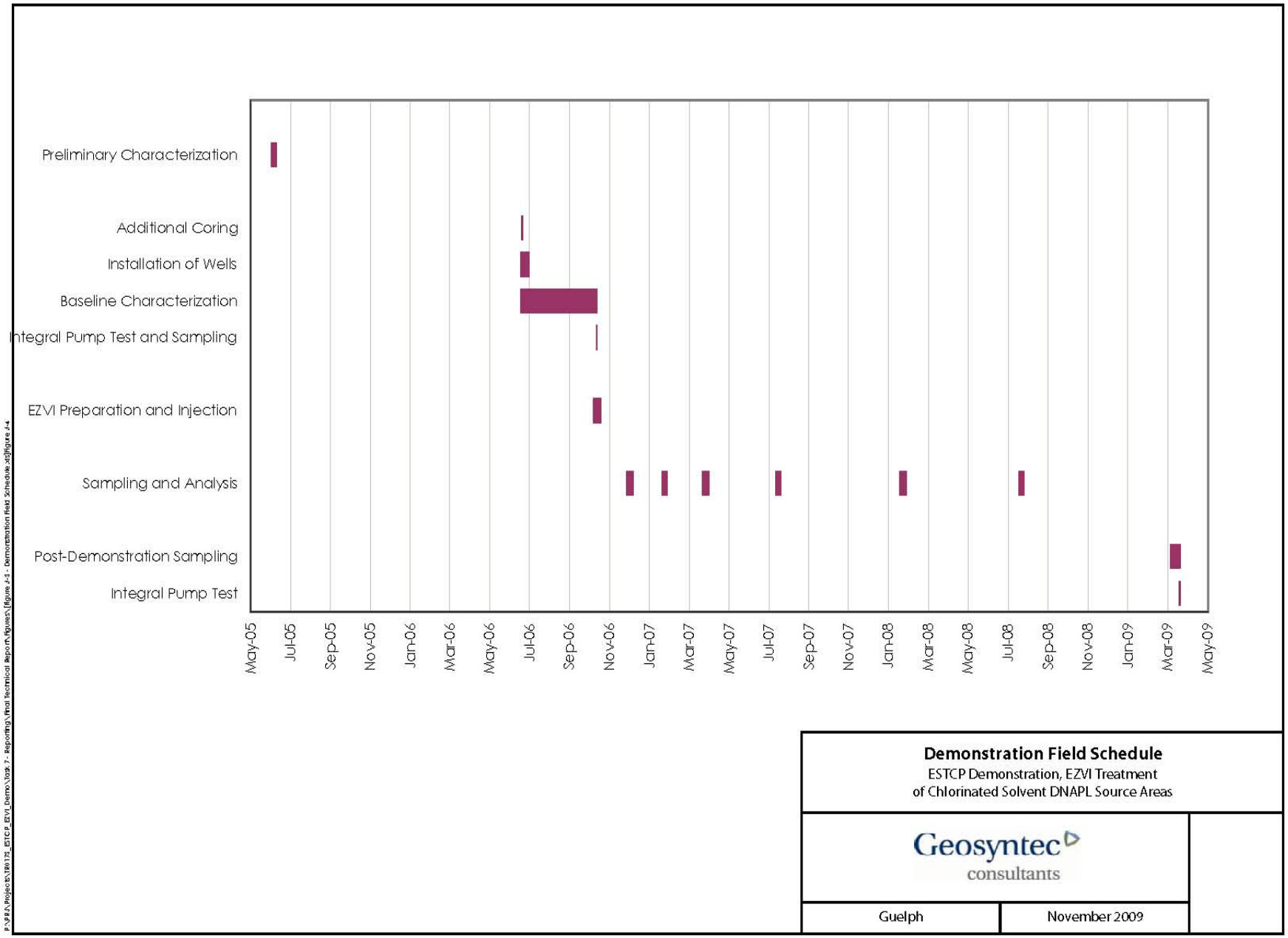

Figure 2. Demonstration field schedule.

Table 2. Summary of sample handling and laboratory analytical results.

	Parameter	Analytical Method	Method Number	Analytical Laboratory	Quantitation Limit	Sample Container	Preservative	Holding Time
	Field parameters (DO, ORP, pH, temperature, conductivity, turbidity)	Multiprobe system	Field	NA	Varies	Flow-through cell	None	NA
GROUNDWATER	Field Parameters (sulfide, ferrous iron, alkalinity)	Field kits	Field	NA	0.01 mg/L for sulfide and Fe(II), 2 mg/L for alkalinity	100 mL plastic (sulfide and ferrous iron)	None	NA
	VOC (PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, 1,1-DCE, vinyl chloride)	Gas Chromatography/ Mass Spectrometry	EPA 8260B	CAS	as low as 1 μg/L	3 x 40 mL VOA	sulfuric acid to pH<2, cool to 4°C	14 days
	Dissolved hydrocarbon gases (methane, ethane, ethane)	Gas Chromatography/ Flame Ionizing Detector	RSK-175	CAS	as low as 1 μg/L	3 x 40 mL VOA	sulfuric acid to pH<2, cool to 4°C	14 days
	Anions (chloride, sulfate, bromide, fluoride, nitrate, nitrite)	Capillary ion electrophoresis	Waters	USEPA	0.2 mg/L for nitrate and nitrite, 1.0 mg/L for the rest	30 mL plastic	cool to 4°C	2 to 28 days
	Anions (nitrate + nitrite)	Flow injection colorimetry	Lachat 10-107-04-2-A	USEPA	0.1 mg/L	30 mL plastic	sulfuric acid to pH<2, cool to 4°C	6 to 13 days
	VFAs	Gas Chromatography/ Flame Ionizing Detector	EPA 8015-Mod	STL/CAS	as low as 0.5 mg/L	3 x 40 mL VOA	cool to 4°C	14 days
	TOC	UV-promoted wet chemical oxidation	EPA 415.1	USEPA	0.5 mg/L	40 mL glas	sulfuric acid to pH<2, cool to 4°C	28 days
	Cations/dissolved metals	Inductively Coupled Plasma-Optical Emission Spectrometry	EPA 6010B	USEPA	4 to 307 μg/L	60 mL plastic	nitric acid to pH<2, cool to 4°C	21 days
SOIL	VOC (PCE, TCE, cis-1,2-DCE, trans-1,2-DCE, 1,1-DCE, vinyl chloride)	Gas Chromatography/ Mass Spectrometry	Mod. EPA 8260B[(a)]	STL	as low as 290 μg/kg	3 x 40 mL VOA	hydrochloric acid to pH<2, cool to 4°C	14 days
	EZVI	Visual/microscopic	NA	NA	NA	Butyrate or acetate sleeve	None	NA
	f_{oc}	Walkley Black	Walkley Black	STL	610-1900 mg/kg	8 oz plastic	cool to 4°C	28 days
	Porosity	Water pyenometer/ drive-cylinder	ASTM D854, ASTM D2937	STL	0.1%	16 oz glass	None	NA

Notes:
NA – Not Applicable
CAS – Columbia Analytical Services, Inc.
STL – Severn Trent Laboratories, Inc.
EPA – EPA GWERD National Risk Management Research Laboratory, Ada, OK
[(a)]Samples extracted using methanol on site. See Appendix B of the Demonstration Plan (Geosyntec Consultants, Inc., 2006b) for the detailed extraction procedure.
DO – dissolved oxygen
ORP – oxidation-reduction potential
VFA – volatile fatty acid
TOC – total organic compound
f_{oc} – fraction of organic carbon
UV – ultraviolet

6.5.2 Pre-Injection Integral Pump Test

Integral pump tests (IPTs) were performed downgradient of the Pneumatic Injection test plot at monitoring well PMW-3 prior to EZVI injection in October 2006 and at the end of the performance monitoring period in March 2009 to aid in evaluating the performance of the EZVI.

During the pre-injection IPT, groundwater was extracted from well PMW-3, located immediately downgradient of the Pneumatic Injection test plot, for 16 hours using a submersible pump. Samples of the extracted groundwater were collected from the pump discharge at predetermined times for analysis of VOC and dissolved hydrocarbon gases (DHGs). Results were then used to calculate the total mass flux across the Pneumatic Injection test plot as described in Section 5.6.2 of the Final Report (Geosyntec Consultants, Inc., 2010). This calculation was also performed for the post-demonstration IPT (see Section 6.5.7) in order to assess the change in contaminant mass flux from the Pneumatic Injection test plot over the test period. Results were also compared to mass flux estimates calculated using data collected from the multilevel transects located downgradient of the Pneumatic Injection test plot.

6.5.3 Injection Permitting

Approval was obtained from the South Carolina Department of Health and Environmental Control (SCDHEC) for the injection of EZVI at the Site.

6.5.4 EZVI Manufacturing

The EZVI used in the Dem/Val was the same formulation that was used in the laboratory treatability tests, and was composed of nZVI from Toda (RNIP-10DS), water, corn oil, and surfactant (Span 85) in the following proportions by weight: 10%, 51%, 38%, and 1%, respectively. The EZVI was manufactured on site in the same 55 gal drums that the nZVI was shipped in from Japan. The EZVI manufacturing process is described in detail in Section 5.6.4 of the Final Report (Geosyntec Consultants, Inc., 2010). Once all EZVI had been made and the drums moved to the staging area, the EZVI was transferred from the drums to holding tanks on the injection rigs using industrial pumps.

6.5.5 EZVI Injection

EZVI was injected into the test plots in October 2006. The technology demonstration was designed to inject a maximum of 850 gal of EZVI into the Pneumatic Injection test plot and 50 gal into the Direct Injection test plot. However, due to daylighting of EZVI (EZVI migrating up former investigation borings to ground surface) in the Pneumatic Injection test plot it is estimated that 576 gal of EZVI was injected into 8 locations within the Pneumatic Injection test plot between 7 and 18.5 ft bgs (two injection locations were performed using Direct Injection technology), and an estimated 32 gal of EZVI came to surface. A total of 151 gal of EZVI was injected into 4 locations within the Direct Injection test plot between 6 and 12 ft bgs and an estimated 5 gal of EZVI came to surface. Figure 3 depicts the injection locations. A detailed discussion of the injection procedures is provided in Section 5.6.5 of the Final Report (Geosyntec Consultants, Inc., 2010).

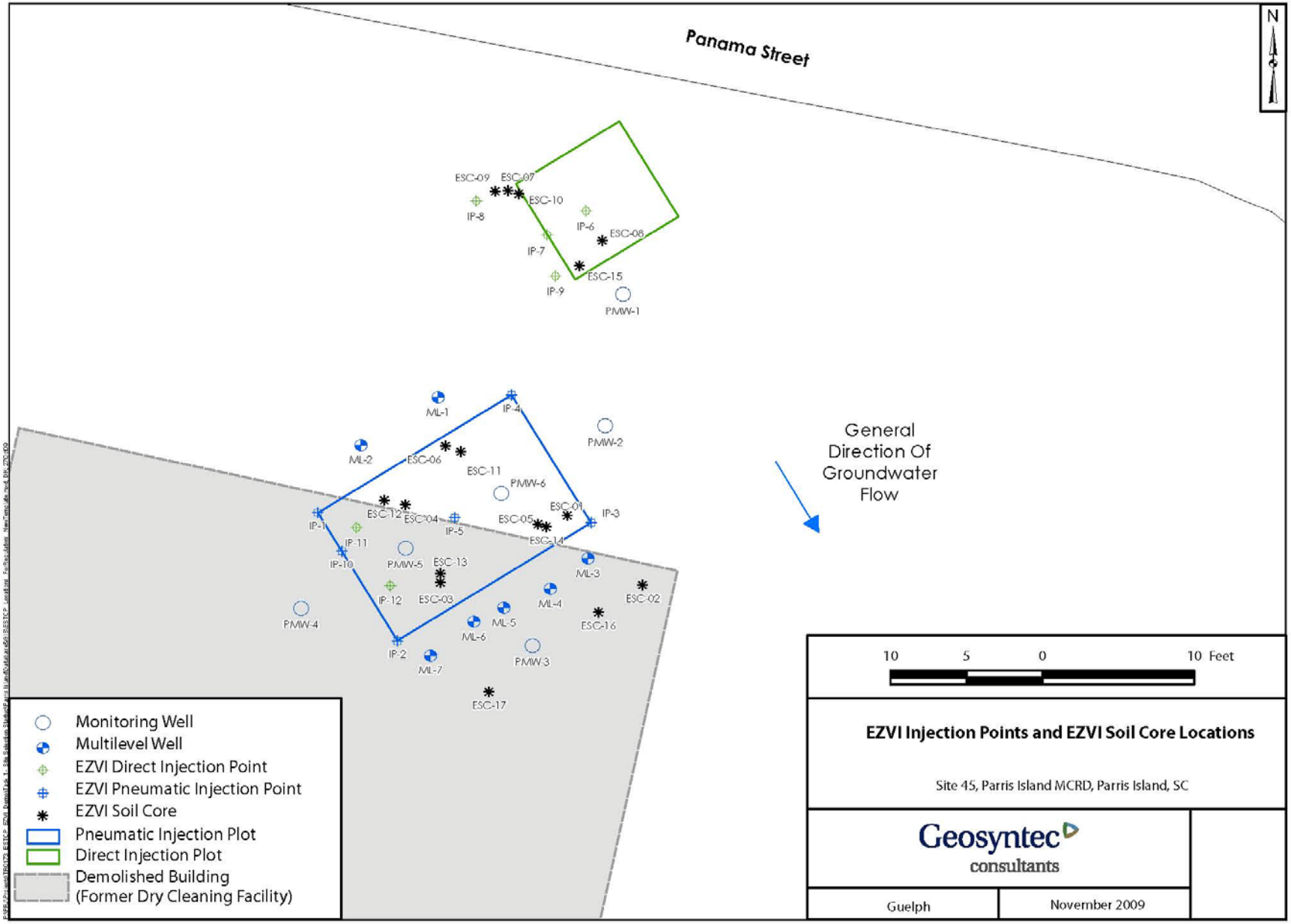

Figure 3. EZVI injection points and EZVI soil core locations.

Following EZVI injection, soil cores were collected from 10 locations (ESC-1 through ESC-10) around the injection points to evaluate the ability of the two injection technologies to provide effective distribution of the EZVI within the source zones (Figure 3). Soil cores were collected after all EZVI injections were complete to reduce the likelihood of providing short-circuit pathways through boreholes. As a result, it was not possible to determine which direction the EZVI observed in each soil boring came from. However, inspection of soil cores suggested good lateral distribution of EZVI within the test plot. The cores did indicate that the EZVI was not as evenly distributed throughout the target treatment interval as expected and that there was strong indication of fingering or preferential flow paths.

During the post-demonstration sampling event, soil cores from an additional seven locations (ESC-11 through ESC-17) were collected to further evaluate the distribution of the EZVI within the source zones (Figure 3). Results suggest an ROI of ~5 ft for the pneumatic injection technology and a minimum ROI of ~2.8 ft for the direct injection technology. The most conservative estimate was used by selecting the closest injection points as the assumed point of origin.

6.5.6 Performance Monitoring Groundwater Sampling

The field sampling events following EZVI injection consisted of groundwater sampling for laboratory analysis. The Gantt Chart in Figure 2 presents the groundwater sampling schedule used during the demonstration. For each event, groundwater samples were collected from select fully screened and multilevel monitoring wells and analyzed for either some or all of the parameters initially tested during baseline sampling activities.

6.5.7 Post-Demonstration Sampling and Integral Pump Test

In March 2009, a final set of post-demonstration groundwater samples was collected from each of the fully screened and multilevel monitoring wells and was analyzed for the parameters initially tested during baseline sampling activities. A set of post-demonstration soil cores (SC-10 through SC-13) was also collected in the Pneumatic Injection test plot from locations adjacent to the baseline soil cores (Figure 4), and cores were analyzed for VOC concentrations to determine post-demonstration VOC mass estimates. As was done during baseline sampling, post-demonstration VOC results from soil cores were used to calculate estimates of VOC mass (as either sorbed or DNAPL), and groundwater VOC results from select wells were used to calculate estimates of dissolved phase VOC. Following groundwater and soil core collection, a post-demonstration IPT was conducted in order to evaluate the change in contaminant mass flux from the Pneumatic Injection test plot over the treatment duration. The post-demonstration IPT was conducted using the same method as the pre-injection IPT, and results from the mass flux estimate calculations were also compared to estimates calculated using the multilevel well data.

6.6 ANALYTICAL METHODS

The analytical methods used to analyze groundwater and soil samples are presented in Table 2. Information pertaining to calibration of analytical equipment, quality assurance, decontamination, and sample documentation can be found in Appendix D of the Final Report (Geosyntec Consultants, Inc., 2010).

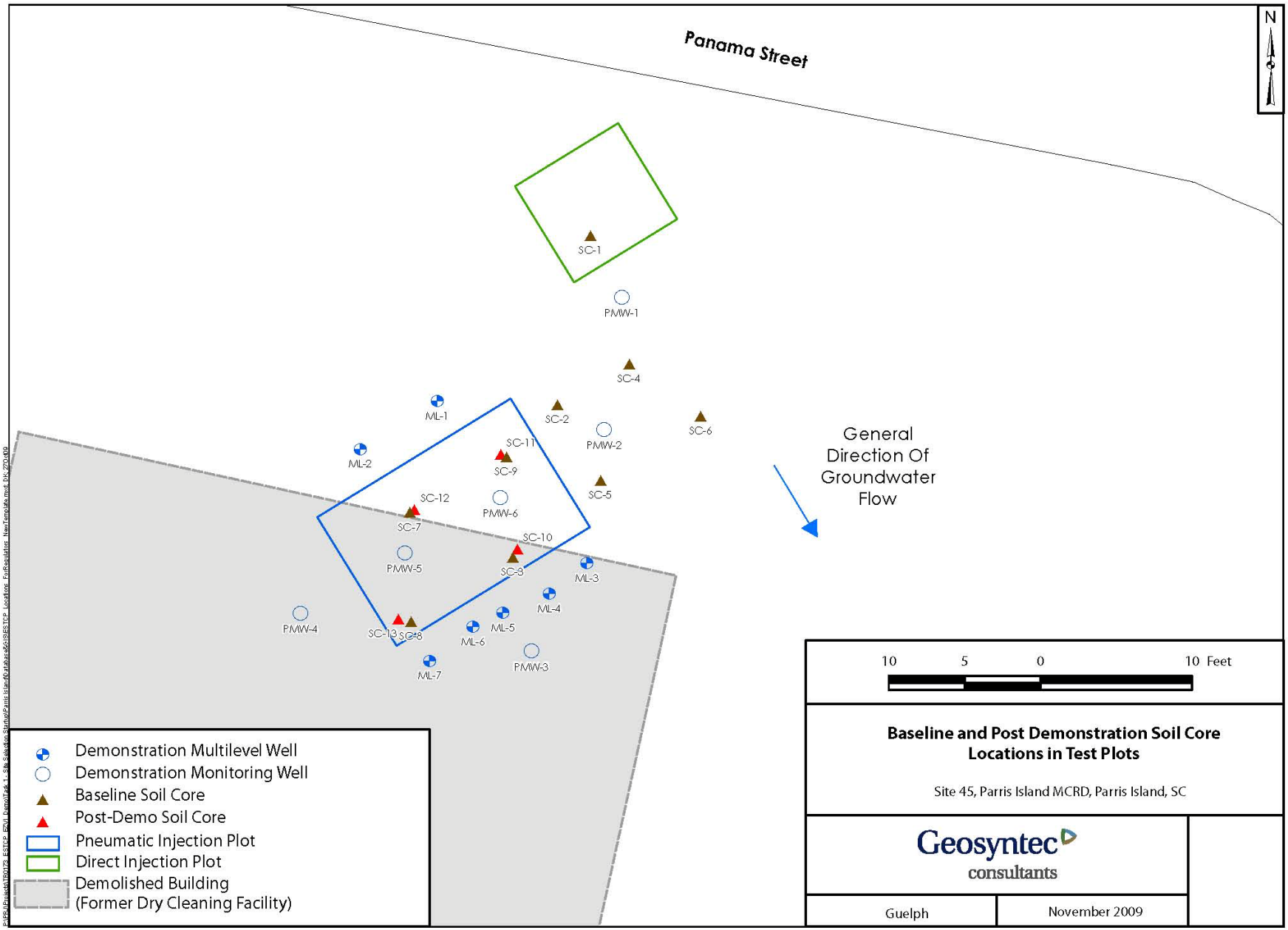

Figure 4. Baseline and post-demonstration soil core locations in test plots.

6.7 SAMPLING RESULTS

In the following sections, the analytical results are summarized. Water level elevation data can be found in Section 6.7.1, field parameters in Section 6.7.2, geochemical parameters in Section 6.7.3, and VOC data in Section 6.7.4. A complete compilation of the analytical data can be found in Appendix E of the Final Report (Geosyntec Consultants, Inc., 2010). All VOC, DHG, and VFA data were validated using USEPA data qualifiers for organic and inorganic data (USEPA 540-R-08-01 and 540-R-04-004). A summary of the data validation results and findings is presented in Appendix G of the Final Report (Geosyntec Consultants, Inc., 2010).

6.7.1 Water Level Elevation Data

During select sampling events at the Site, groundwater elevations were measured at select wells to assess groundwater velocities and flow directions. The groundwater velocities were used to calculate the mass flux estimates for the baseline, post-injection, performance monitoring and post-demonstration sampling events. The gradient at the Site is very flat and there was little change in gradient over the duration of the investigation. A complete compilation of measured water level elevations is presented in Appendix C of the Final Report (Geosyntec Consultants, Inc., 2010). It is possible that the gradient may have reversed for short periods of time through the plot during the demonstration. However, with the gradient as flat as it is, the changes in water levels measured in the wells within the plot were very small and often within the margin of measurement error. The estimated gradient used in the mass flux calculations was 0.0026 ft/ft.

6.7.2 Field Parameters

Following EZVI injections in the Pneumatic and Direct Injection test plots, the following groundwater field parameter trends were observed.

<u>Pneumatic Injection Test Plot</u>

- A moderate decrease in pH in some of the downgradient multilevel wells (ML-3-4, ML-4-7, ML-5-5, ML-6-4 to ML-6-6, and ML 7-3 to ML-7-5), with pH measurements dropping by as much as 1 pH unit in these wells by the post-demonstration sampling event.
- A general decrease in ORP in the fully screened monitoring wells and most of the multilevel wells (ML-1-5, ML-1-7, ML-2-3, ML-2-5, ML-2-7, ML-5-4, ML-5-5, ML-6-4 to ML-6-7, and ML-7-4 to ML-7-6), with ORP measurements dropping by as much as 250 millivolts (mV) in these wells by the post-demonstration sampling event. However, most wells exhibited a large degree of variability and fluctuation in groundwater ORP throughout the demonstration, thus making it difficult to assess areas where a true reduction in ORP was achieved.
- DO concentrations were low before injection and remained relatively constant over the demonstration period, with most wells exhibiting DO concentrations below 2 milligrams per liter (mg/L).
- Increases in ferrous iron concentration in the fully screened monitoring wells (including PMW-2 and PMW-4).

- Significant increases in sulfide concentrations in the fully screened monitoring wells (including PMW-2).

Direct Injection Test Plot

- pH levels in PMW-1 remained relatively constant between 5.8 and 6.3 over the demonstration period, and were near baseline levels by the post-demonstration sampling event.
- Virtually no change in groundwater ORP between the baseline and post-demonstration sampling events (although ORP measurements in PMW-1 did fluctuate between -88.5 mV and -169.9 mV over the demonstration period).
- DO concentrations decreased from approximately 1.5 mg/L to near zero (or non-detect) following EZVI injections, but had returned to near baseline concentrations by the January 2008 sampling event (after which time DO concentrations decreased once again).
- Increases in ferrous iron concentration, and significant increases in sulfide concentration.

6.7.3 Geochemical Parameters

Following EZVI injection into the Pneumatic Injection test plot, significant increases in groundwater VFA concentrations (primarily acetic, butyric and propionic acids) were observed in the downgradient multilevel wells and in fully screened wells PMW-5 and PMW-6. Significant increases in VFA concentrations were also observed in upgradient well ML-2-3 indicating that some EZVI may have moved outside the plot to the north although no EZVI was observed in the upgradient wells. Relatively little change in groundwater alkalinity was observed in any of the wells throughout the demonstration. Methane concentrations increased in upgradient well ML-1, in the downgradient multilevel wells, and in the fully screened wells (except PMW-4). Concentrations of ethene and ethane also increased in one of the upgradient wells (ML-2), in the downgradient multilevel wells (except ML-3), and in all fully screened wells except for PMW-2 and PMW-6 (ethene only). Following EZVI injection into the Direct Injection test plot, concentrations of ethene and methane increased in the downgradient fully screened well PMW-1.

6.7.4 Volatile Organic Compound Data

Groundwater and Soil VOC Concentrations

Changes in groundwater VOC and ethene concentrations during the demonstration are depicted in Figures 5-9 to 5-14 of the Final Report (Geosyntec Consultants, Inc., 2010). Using results from the baseline groundwater and soil sampling events, the total mass of target VOC in the Pneumatic Injection test plot was estimated to be approximately 38 kilograms (kg) (Table 3), of which roughly 29 kg (or ~76%) is attributed to PCE DNAPL. Following injection of EZVI,

Table 3. Pre-injection and post-demonstration VOC mass estimates in pneumatic injection plot.

Media	VOC	Pre-Injection Mass (g)			Post-Demonstration Mass (g)		
		Sorbed/Dissolved	DNAPL	Total	Sorbed/Dissolved	DNAPL	Total
Soil[1]	Tetrachloroethene	2760	29,028	31,788	730	2137	2867
	Trichloroethene	1317	0	1317	521	0	521
	Cis-1,2-dichloroethene	1254	0	1254	569	0	569
	Vinyl chloride	2214	0	2214	114	0	114
Groundwater[2]	Tetrachloroethene	577	0	577	333	0	333
	Trichloroethene	267	0	267	182	0	182
	Cis-1,2-dichloroethene	588	0	588	819	0	819
	Vinyl chloride	12	0	12	45	0	45
Total Mass (g)		8990	29,028	38,018	3312	2137	5449
% Reduction[3]					63%	93%	86%

Notes:
g – grams
[1] Soil data is based on SC-1 through SC-9 for Pre-Injection data and SC-10 and SC-13 for the post-demonstration sampling.
[2] Groundwater data is based on PMW-5 and PMW-6, the two fully screened wells within the plot.
[3] Reductions were calculated using pre-injection and post-demonstration total mass estimates.

downgradient multilevel wells and fully screened wells PMW-3, PMW-5, and PMW-6 showed significant decreases in PCE and TCE concentrations, with an increase in the concentration of degradation products, including ethene. Post-demonstration sampling results were used to calculate a target VOC total mass of approximately 5.5 kg (Table 3) in the Pneumatic Injection test plot, of which roughly 2.1 kg (or ~38%) is attributed to PCE DNAPL. Injection of EZVI into the Pneumatic Injection test plot resulted in approximately 93% reduction in the estimated mass of PCE DNAPL and approximately 86% reduction in the total mass of target VOC.

DNAPL was actually pumped out of well ML-2-5 prior to EZVI injections. After the injection of EZVI into the pneumatic injection plot, DNAPL was also pumped from wells PMW-4, PMW-5, and ML-2-7 where DNAPL was not seen prior to injection. This indicates that DNAPL moved in the subsurface during or soon after EZVI injection. However, analysis of groundwater VOC concentrations and pre-injection soil core VOC data suggests that DNAPL must have been in close proximity to these wells prior to injection activities. Thus it is possible that the EZVI injection pushed DNAPL into these wells or that the injection activities created fractures or preferential pathways that allowed DNAPL to migrate to these wells post-injection.

Based on the presence of DNAPL in the four wells (ML-2-5, ML-2-7, PMW-4 and PMW-5) post-EZVI injection, it appears that there was more DNAPL present in the plot than the pre-demonstration estimate suggested. Although there is evidence that some DNAPL may have been mobilized outside of the plot (DNAPL in PMW-4 and ML-2-7), there is evidence of a lot of degradation within and downgradient of the plot as evidenced by the increase in concentrations of daughter products (VC and ethene), indicating that mass was not just displaced but degraded.

In the Direct Injection test plot, PMW-1 exhibited slight decreases in PCE and TCE concentrations following injection of EZVI, with a moderate increase in the concentration of degradation products.

Pneumatic Injection Test Plot Mass Flux Estimates

Pre- and post-EZVI injection estimates of VOC and ethene mass fluxes for the Pneumatic Injection test plot were calculated using groundwater concentrations in the upgradient (ML-1 and ML-2) and downgradient (ML-3 through ML-7) multilevel well transects. Mass flux estimates were also calculated using results from the IPTs and were then compared to mass flux estimates from the downgradient (ML-4, ML-5 and ML-6) multilevel wells. A detailed discussion of the methods used to calculate the mass fluxes estimates is provided in Section 5.8.4 of the Final Report (Geosyntec Consultants, Inc., 2010).

Table 4 provides a summary of the mass flux estimates as well as the total change in mass flux (as percent reduction) for the upgradient and downgradient multilevel wells. Figure 5 shows the change in mass flux graphically. Comparison of the pre- and post-EZVI injection mass flux estimates in multilevel wells on the upgradient side of the Pneumatic Injection test plot revealed an increase in mass flux for all VOC except for TCE and cDCE (Table 4 and Figure 5). The mass flux of ethene in the upgradient multilevel well transect also increased significantly. The increase in ethene and decrease in TCE and cDCE in the upgradient wells indicates increased degradation in this area. This increased degradation may mean that some EZVI was distributed

Table 4. VOC mass flux estimates in pneumatic injection plot based on multilevel well monitoring data.

	Units	Tetrachloroethene	Trichloroethene	cis-1,2-Dichloroethene	Vinyl Chloride	Total CEs	Ethene
Pre-Injection (August & October 2006 Mass Flux							
Upgradient MLs[1]	mmol/yr/ft^2	1040.0	245.4	2041.8	161.8	3526.9	54.5
Downgradient MLs[2]	mmol/yr/ft^2	101.9	49.7	1846.4	246.2	2289.1	52.2
% Reduction Across Plot		90.2%	79.7%	9.6%	-52.1%	35.1%	4.1%
Post-Injection (November 2006 & January 2007) Mass Flux							
Upgradient MLs[1]	mmol/yr/ft^2	3647.1	127.6	2135.7	321.3	6293.3	133.5
Downgradient MLs[2]	mmol/yr/ft^2	58.5	40.5	914.4	1104.0	2151.6	292.9
% Reduction Across Plot		98.4%	68.3%	57.2%	-243.6%	65.8%	-119.4%
Post-Injection (March & July 2007) Mass Flux							
Upgradient MLs[1]	mmol/yr/ft^2	1343.1	100.0	2147.7	703.1	4366.0	240.5
Downgradient MLs[2]	mmol/yr/ft^2	5.7	5.4	617.1	931.4	1576.8	513.5
% Reduction Across Plot		99.6%	94.6%	71.3%	-32.5%	63.9%	-113.5%
Post-Injection (January & July 2008) Mass Flux							
Upgradient MLs[1]	mmol/yr/ft^2	1431.3	117.0	2257.7	1781.8	5663.3	466.0
Downgradient MLs[2]	mmol/yr/ft^2	63	12.1	647.8	583.9	1261.5	1238.6
% Reduction Across Plot		99.6%	89.7%	71.3%	67.2%	77.7%	-165.8%
Post-Demonstration (March 2009) Mass Flux							
Upgradient MLs[1]	mmol/yr/ft^2	1271.6	217.2	1690.9	796.2	4044.2	612.7
Downgradient MLs[2]	mmol/yr/ft^2	15.4	7.0	531.2	422.0	986.6	883.2
% Reduction Across Plot		98.8%	96.8%	68.6%	47.0%	75.6%	-44.2%
Pre-Injection vs Post-Demonstration % Reduction in Mass Flux[3]							
% Reduction in Downgradient MLs[2]		84.8%	86.0%	71.2%	-71.4%	56.9%	-1590.7%

Notes:
mmol/yr/ft^2 – millimols per year per square foot
CEs – chlorinated ethenes
[1]Wells ML-1 and ML-2
[2]Wells ML-3 through ML-7
[3]Reduction in mass flux calculated using pre-injection (August & October 2006) and post-demonstration (March 2009) mass flux values. Positive value indicates a decrease in mass flux; negative value indicates an increase in mass flux.

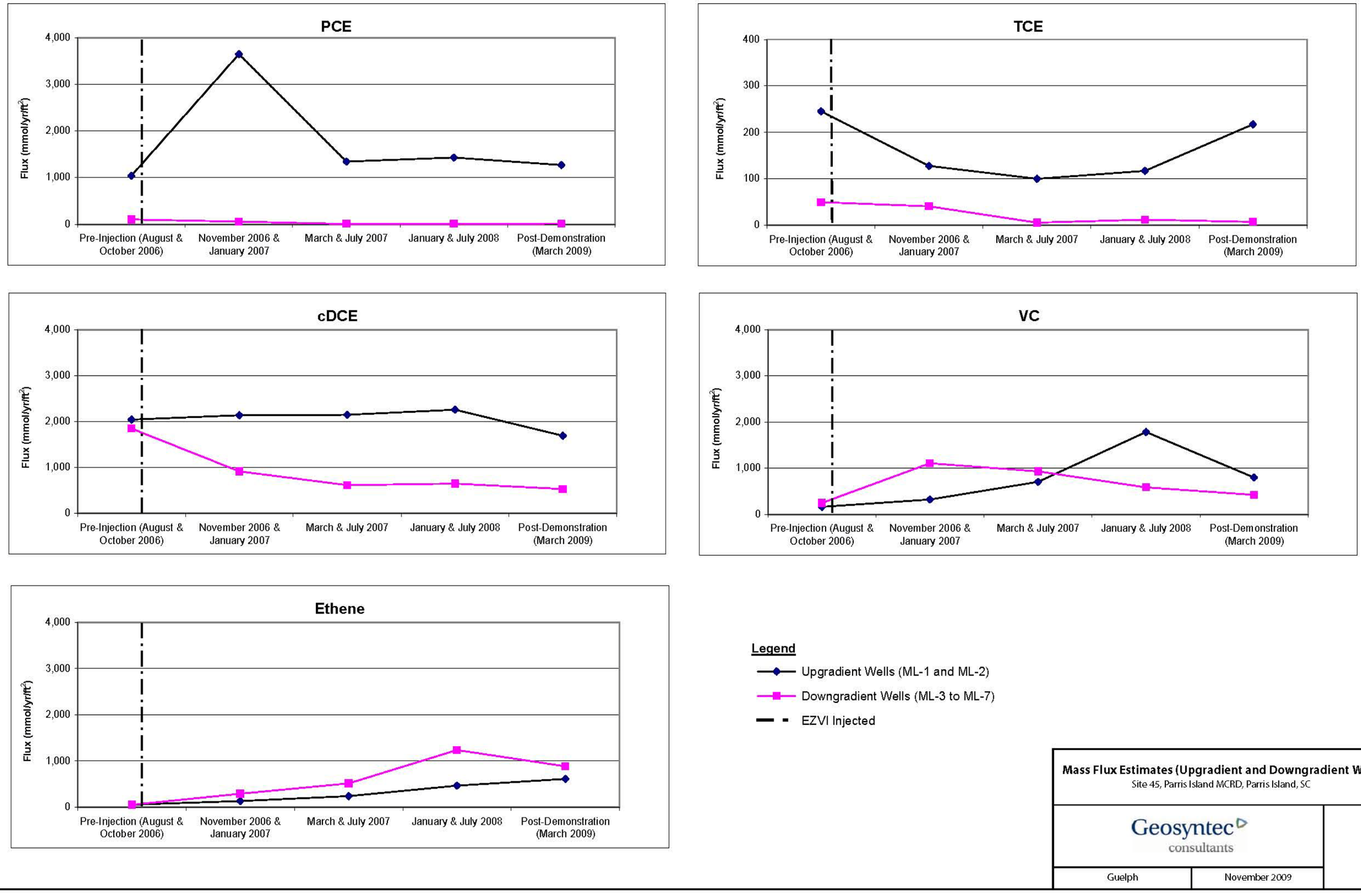

Figure 5. Mass flux estimates (upgradient and downgradient wells).

to this area during injection or simply that there is increased biodegradation in the area around the EZVI due to oil separation and oil breakdown products from the EZVI. Comparison of pre-injection and post-demonstration mass flux estimates calculated using VOC concentrations from the downgradient multilevel wells revealed significant reductions in mass flux of the parent compounds PCE (~85% reduction) and TCE (~86% reduction), and of the degradation product cDCE (~71% reduction) (Table 4 and Figure 5). In contrast, the mass flux of the degradation products VC and ethene increased significantly over the test period. The increase in ethene mass flux indicates that the reduction in PCE, TCE and cDCE concentrations were due to degradation and not just displacement of water or DNAPL out of the plot. The VC mass flux is expected to continue to decrease and ethene mass flux is expected to continue to increase or remain steady as degradation continues.

Estimates of VOC and ethene mass fluxes were also calculated using results of the IPTs, and then compared to mass flux estimates obtained using VOC and ethene concentrations for the three central downgradient multilevel wells (ML-4, ML-5, and ML-6), as these three wells are within the capture area that was inferred for the IPTs. A summary of the estimated mass fluxes and percent reductions in mass fluxes using both methods is provided in Table 5-11 of the Final Report (Geosyntec Consultants, Inc., 2010). Percent reductions in mass flux for the parent compounds PCE and TCE compare well for the two methods (IPT and 3-well downgradient transect): PCE mass flux reductions of 99% (IPTs) and 91% (3-well downgradient transect), and TCE mass flux reductions of 96% (IPTs) and 85% (3-well downgradient transect). The percent increases in VC mass flux also compare well for the two methods. However, for all compounds the mass flux estimated from the transect wells were much higher than those measured from the IPTs. This was to be expected due to the proximity of these wells to the source and the much smaller area of influence captured during sampling of these multilevel wells in comparison with PMW-3, which under pumping conditions would capture water from a larger area with lower concentrations. With the IPT and the 3-well transect mass flux calculations, evidence of increased VC and ethene mass flux from pre-injection to the post-demonstration period confirm degradation of the parent compounds.

6.7.5 USEPA Research Interests and Contributions

In addition to the work performed by Geosyntec Consultants, Inc., USEPA provided considerable support for the Dem/Val by providing the drill rig and materials for installing the monitoring wells and collecting the baseline soil cores, participating in each of the groundwater sampling events, collecting additional groundwater geochemical data beyond what was originally planned for in the Dem/Val, and providing field analytical instruments and conducting most of the laboratory sample analyses. The USEPA collected numerous groundwater samples for analysis of total organic and inorganic carbon, anions, dissolved and total metals, alkalinity, and stable isotopes. The USEPA also collected numerous soil and groundwater samples for X-ray diffraction analyses of colloids to observe the mineralogical changes that may be occurring within the subsurface as a result of the EZVI injections (i.e., corrosion products such as elemental iron and minor components of magnetite). The USEPA data is presented in Appendix E of the Final Report (Geosyntec Consultants, Inc., 2010).

Compound-specific carbon-13 ($\delta^{13}C$) isotope results suggest that degradation of PCE and its daughter products were occurring because most of the $\delta^{13}C$ isotope values increased (less negative) over time after EZVI injection. The chlorine-37 isotope ($\delta^{37}Cl$) values for all the extracted chlorinated solvents from groundwater measured in March 2007 also were greater than those measured before injection, further supporting the notion that chlorinated hydrocarbons were degrading. Thus both abiotic and biotic mechanisms may be operative at the Site.

X-ray diffraction results of suspended solids collected from monitoring wells during well purging showed transformation of elemental iron to magnetite (Fe_3O_4) and lepidocrocite (γ-FeOOH) in ML-3-1 and ML-3-2.

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7.0 PERFORMANCE ASSESSMENT

This section provides a summary of all data analysis in support of the assessment of performance objectives. Substantive analyses of data obtained during the demonstration that supports the conclusions summarized in Section 4 is provided. Where appropriate, references to discussions or data analysis presented in Section 6 are made rather than repeating information.

7.1 REDUCTION IN MASS FLUX OF VOC IN DOWNGRADIENT WELLS

A key performance objective was the reduction in mass flux of dissolved VOC in downgradient monitoring wells for areas in contact with EZVI. To evaluate this objective, groundwater samples were collected before and after EZVI injection and analyzed for VOC. Data from the post-demonstration sampling event (March 2009) are compared to data from the pre-injection (baseline) sampling event. Data included analyses of samples from five multilevel wells and from the IPT. Successful performance was set as >75% decrease in mass flux of dissolved VOC based on groundwater samples from multilevel wells over the baseline condition for areas in contact with EZVI.

This objective was met based on the significant reductions in mass flux of the parent compounds PCE (85% to 99%, based on multilevel transects and IPT respectively) and TCE (86% to 95%, based on multilevel transects and IPT respectively) using the various methods of estimating mass flux. Reductions in cDCE of 71% to 75% were also observed using the multilevel transect wells. Vinyl chloride showed increases in mass flux of 71% up to 240% (multilevel and IPT, respectively) but this increase is a transient effect and the cDCE and VC are degrading over time to form ethene. A significant increase in the ethene mass flux (1600% to 4600%) was also observed indicating that the degradation of PCE and TCE is not stalling at VC but continuing to complete dechlorination. The isotope fractionation data from USEPA (Section 6.7.5) supports the degradation of PCE and TCE to form the ethene observed.

Of note, it is expected that even higher reductions in mass flux would have been observed had there not been issues with short-circuiting of EZVI to surface and the targeted 850 gal of EZVI had been successfully distributed through the plot.

7.2 REDUCTION IN TOTAL VOC AND DNAPL MASS

The amount of VOC and DNAPL reduction in the Pneumatic Injection test plot was assessed by comparing results of pre-injection (baseline) and post-injection groundwater and soil core samples. A successful performance was set as a >75% decrease in VOC and DNAPL mass over baseline conditions in the Pneumatic Injection test plot.

This objective was met with a total VOC mass reduction of 86% in the pneumatic injection plot (Section 6.7.4 and Table 3). The pre-demonstration mass estimate was ~38 kg of VOC and the post-demonstration estimate was ~5.5 kg of VOC mass remaining in the plot. This breakdowns to an estimated reduction of 63% in the sorbed and dissolved phases and a 93% reduction in the DNAPL mass (Table 3).

Based on the presence of DNAPL in the four wells (ML-2-5, ML-2-7, PMW-4, and PMW-5) post-EZVI injection, it appears that there was more DNAPL present in the plot than the pre-demonstration estimate suggested. Although there is evidence that some DNAPL may have been mobilized outside of the plot (DNAPL was observed in PMW-4 and ML-2-7), there is evidence of significant degradation within and downgradient of the plot as evidenced by the increase in concentrations of daughter products (VC and ethene), indicating that mass was not just displaced but degraded.

The injection strategy was also designed to minimize mobilizing DNAPLs outside the injection plot. Injections were conducted initially at each of the four corners of the plot such that it was expected that DNAPL within the plot would be pushed further towards the center of the plot and only DNAPL outside the plot would be pushed away from the plot during these injections. Subsequent injections were made along the perimeter of the plot, again pushing DNAPL towards the center of the plot. The final injections were made into the center of the plot, but the volume of the injected fluid would not be sufficient to push mobile DNAPL outside the plot to a significant degree.

Again, it is expected that even higher reductions in mass would have been observed had the targeted 850 gal of EZVI been successfully distributed through the plot.

7.3 RADIUS OF INFLUENCE

The ROI of each injection technology was assessed through visual inspection of soil cores collected post-injection. For the Pneumatic Injection and Direct Injection test plots, the objective was the presence of EZVI at distances greater than 5 ft and 1 ft, respectively.

This objective was met with measured ROIs of 5 to 7 ft with pneumatic injection and 1 to 2.5 ft with direct injection. Soil cores were collected after all EZVI injections were complete to reduce the likelihood of providing short-circuit pathways through boreholes. As a result, it was not possible to determine which direction the EZVI observed in each soil boring came from. We have used the most conservative estimate by using the closest injection points as the assumed point of origin for any EZVI observed in a core. Thus, it is possible that the injection technologies moved the EZVI further than 7 ft or 2.5 ft for the pneumatic and direct injections, respectively.

In order to evaluate the ROI, multiple lines of evidence should be used. The immediate vicinity of the injection point was visually monitored for heave (tilt meters) and day lighting (i.e., EZVI being observed at the ground surface). Wells in the vicinity of the injection points were monitored using real-time performance monitoring during each injection to see if the pressure in the wells increased. Monitoring wells within 20 ft from the active injection point were fitted with pressure gauges to monitor any immediate influence during injection. In addition, downhole pressure transducers were deployed in all the fully screened monitoring wells in the plot. The data collected from the pressure gauges and transducers, surface heave, and daylighting supported the evaluation of ROIs of 5 to 7 ft.

In addition, ORP measurements were conducted in select fully screened monitoring wells following injection activities to see if changes in ORP could be used to indicate the distribution

of the EZVI. Wells PMW-1, PMW-5, and PMW-6 all displayed visual evidence of EZVI inside the well and were clearly within the influence of injection. ORP values were not measured in these wells as a result of the potential to damage the ORP probe if used in these wells. ORP was measured in wells PMW-2, PMW-3, and PMW-4, but none of these wells displayed ORP readings that were significantly different from baseline values, suggesting they were not within the influence of injection.

7.4 ABILITY TO INJECT EZVI WITHOUT DAMAGING EMULSION STRUCTURE

The ability to inject EZVI without damage to the emulsion structure was evaluated by examining the EZVI under microscope in the cores collected to evaluate the distribution. For this performance criterion, success was achieved if the injection technologies were able to deliver the EZVI within the source zone without damage to the emulsion structure.

This objective was met with both technologies being able to inject the EZVI without damage to the emulsion structure. Samples of the EZVI from two cores (one from each plot) were collected and evaluated using a light microscope. Droplets of EZVI on the sand grains suspended in water were located in the samples and the emulsion structure was visually determined to be intact.

7.5 ABILITY TO EVENLY DISTRIBUTE EZVI

The ability of each injection technology to evenly distribute EZVI in a controlled manner over an optimum ROI was assessed by collecting groundwater and soil core samples from the test plots. Success was marked by the ability of the injection technology to deliver the EZVI within the source zone in a way that will allow some control of the direction of EZVI injection so as to evenly distribute the EZVI over the injection interval.

This objective was partially met. There were complications with the shallow nature of the injections and preferential flow paths created by previous borings in the area providing short circuit pathways for the EZVI to surface. There was a significant amount of fingering and a very uneven distribution of EZVI over the target treatment depth interval. The injections in both plots were complicated by the shallow nature of the Site and short-circuiting or daylighting to surface. It is believed that the pneumatic injection would have been capable of greater ROI and less fingering or preferential flow path development had the target injection interval been deeper. This would have allowed the injections to occur at higher pressures and velocities while minimizing the risk of short-circuiting to ground surface. In addition, we were only able to inject approximately 576 gal of EZVI into the pneumatic injection plot and were not able to follow the planned injection strategy. This also limited the ability to evenly distribute the EZVI over the target depth interval since we did not have as much EZVI to distribute.

7.6 EASE OF IMPLEMENTATION

The ease of use of this technology was evaluated based on the experience of field staff and the costs of the manufacturing of the EZVI and the injection of EZVI. The success criterion for this objective is that the EZVI manufacturing and injection can be readily accomplished using standard industry procedures and contractors.

This objective was achieved based on experience with the actual manufacturing and injection of EZVI at the Site. The equipment required for the manufacturing of EZVI on Site was readily available through the food manufacturing industry (industrial mayonnaise mixer) and the option to purchase EZVI manufactured by vendors and shipped to the Site ready for injection also exists. The injection equipment used to injection the EZVI was all readily available through local drillers, pneumatic injection companies, and plumbing suppliers. The procedures used to manufacture the EZVI were well established procedures and were simple enough to be conducted by field technicians with training in the manufacturing techniques. The procedures used to inject the EZVI were standard and well established procedures for local drillers (direct injection) and pneumatic injection contractors, and the procedures were simple enough to be conducted by field technicians with training in basic injection techniques and handling techniques of the EZVI.

Although there were difficulties with short-circuiting of the EZVI to surface during injection, this was believed to be site-specific with the shallow nature of the target treatment interval and the presence of pre-existing short-circuit pathways (old boreholes).

7.7 VERSATILITY

For this performance criterion, the technology was deemed successful if it could be applied in a variety of geological and hydrogeological settings were DNAPL source areas are present.

This objective was met although there are some restrictions on the depth in which the injection technologies tested can be applied. As long as the direct push injection and pneumatic injection equipment can be deployed in a geologic media, there should be no restriction to injection of EZVI using this equipment in these formations. Both injection technologies have been applied in many geological and hydrogeological settings including sandy and clay formations and fractured rock formation (injections through drilled boreholes or wells). If using pneumatic injection there are some restrictions on how shallow the application can be. If the injections were to occur underneath a building, that would provide an overburden pressure that would limit the risk of daylighting of the injection fluid; then the injections could occur within a few feet in depth from the base of the foundation. However, in an open area it is recommended that pneumatic injection be limited to applications greater than 10 ft bgs to minimize the risk of daylighting and increase the control of the injections.

If coring, drilling, or other disruptions to the subsurface due to activities such as site characterization has been conducted at a particular site, care must be taken in the plugging or abandoning of these holes and in the locating of the injection points to minimize the formation of preferential flow pathways and daylighting of EZVI to surface.

8.0 COST ASSESSMENT

This section presents the results of a cost assessment to implement remediation of a DNAPL source area using EZVI. Section 8.1 describes a cost model that was developed for the application of EZVI with a comparison to treatment using ISCO and a conventional P&T system; Section 8.2 presents an assessment of the cost drivers for the application of the technology; and Section 8.3 presents the results of an analysis of the cost model.

8.1 COST MODEL

A cost model was developed to assist remediation professionals in understanding costs associated with the EZVI technology. The cost model identified the major cost elements required to implement the EZVI technology at a typical site with a PCE or TCE DNAPL source area. A summary of the actual costs for pilot-scale implementation of the EZVI technology at Site 45, Parris Island MCRD is presented in Table 5.

Table 5. Actual costs for EZVI technology Dem/Val at Site 45, Parris Island MCRD.

Cost Element	Data Tracked During the Demonstration	Cost[1]	
Capital Costs			
Design & planning	- Personnel required and associated labor	Labor	$38,300
		Expense	$900
Well installation	- Personnel required and associated labor - Mobilization costs - Drilling contractor cost	Labor	$25,400
		Expense	$16,300
EZVI injections (Pneumatic Injection)	- Personnel required and associated labor for EZVI injection activities - Mobilization costs - Costs for EZVI and injection equipment	Labor	$14,400
		Expense	$91,200
EZVI injections (Direct Injection)	- Personnel required and associated labor for EZVI injection activities - Mobilization costs - Costs for EZVI and injection equipment	Labor	$9600
		Expense	$22,800
Performance Monitoring Costs			
Baseline characterization	- Personnel required and associated labor - Mobilization costs - Supplies and equipment for groundwater and soil sampling - Sample shipment and laboratory analytical costs - Labor associated with data reporting	Labor	$40,300
		Expense	$21,500
Performance monitoring	- Personnel required and associated labor - Mobilization costs - Supplies and equipment for groundwater and soil sampling - Sample shipment and laboratory analytical costs - Labor associated with data reporting	Labor	$179,200
		Expense	$99,800

Notes:
[1]Cost does not include labor and expenses for well installation and additional monitoring incurred by USEPA.

The cost model was developed for a template site with a PCE DNAPL source area. The specific site characteristics are similar to those observed at the test site used in the technology Dem/Val at Site 45, Parris Island MCRD. Cost estimates for the EZVI technology were prepared for both pneumatic and direct injection technologies using EZVI made with either nZVI or mZVI in order to provide a comparison between two types of ZVI. Cost estimates were also prepared for treatment using ISCO and for a conventional P&T system to provide a comparison with the EZVI technology. Using the template site conditions, estimates of costs for the capital, O&M, and long-term monitoring were developed for each alternative. Capital costs included design and permitting activities, mobilization, site preparation, well installation, EZVI, chemical reagents, and injection equipment. O&M costs included mobilization, equipment replacement and supplies. Long-term monitoring costs included field supplies, sampling equipment, laboratory analysis, and regulatory reporting. Labor associated with the planning, procurement, and implementation of all aspects of the remedies are also included. Specifically excluded from consideration are the costs of pre-remediation investigations (e.g., source area and plume delineation, risk determination, and related needs), treatability studies, and post-remediation decommissioning. Also excluded are costs for waste (e.g., soil cuttings and well development water) characterization and disposal.

While most of the identified cost elements are applicable to other remediation technologies, the EZVI material used in the technology Dem/Val at Site 45, Parris Island MCRD is unique to the technology. The volume of EZVI required is a function of the size of the treatment area and the mass of DNAPL present, so a larger treatment area and more mass will require a larger volume of EZVI. The type of ZVI used will also impact capital costs of the technology; alternate ZVI material, such as mZVI, can reduce capital costs significantly.

To obtain a clearer picture of life-cycle costs for the various treatment alternatives, cost estimates include the net present value (NPV) of future costs. The NPV calculations provide cash flow analysis for 30 years, showing the costs by category for each year. The future costs are only carried forward for 30 years on the basis that the NPV of future costs beyond the 30-year time frame are small and the future costs beyond the 30-year period of time are difficult to predict.

O&M and long-term monitoring costs are discounted at a rate of 2.7% based on the real discount rate provided by the U.S. Office of Management and Budget for 30-year notes and bonds (Office of Management and Budget, 2008).

The template site assumes a homogenous silty sand aquifer to a depth of 20 ft bgs with a hydraulic conductivity of 71 ft/year, a horizontal gradient of 0.0026 ft/ft and an effective porosity of 0.3. These aquifer characteristics result in a groundwater seepage velocity of approximately 0.62 ft/year. Depth to water is 4 ft bgs. The source area measures 40 ft in width by 150 ft in length. The total estimated mass of VOC in the source area is approximately 1521 kg. Maximum concentrations of PCE, TCE, cDCE, and VC at the downgradient edge of the source area are 22 mg/L, 6 mg/L, 44 mg/L, and 3 mg/L, respectively.

For the EZVI injection alternatives, the EZVI used is the same formulation as that used in the technology Dem/Val at Site 45, Parris Island MCRD and will be manufactured on site. However, during full-scale implementation where large volumes of EZVI are required it may be

more practical to source a bulk supplier of EZVI such as Toxicological & Environmental Associates, Inc. (Baton Rouge, LA), who are a bulk supplier of EZVI consisting of a blend of nZVI and mZVI particles (0.2 to 3 micrometer [µm] size range). The costs to manufacture the EZVI using nZVI on site from purchased components is essentially the same as purchasing the bulk-supplied material, so the costs presented later in the section are applicable to either option.

The EZVI application using pneumatic injection assumes EZVI will be injected into twenty injection points (each injection point having an ROI of 10 ft) in the source area. The impact of the EZVI injections will be monitored using four downgradient 2-inch monitoring wells screened within the saturated zone. The injection strategy is to inject EZVI using 2 ft vertical lifts between 4 and 20 ft bgs. EZVI will first be injected around the perimeter of the source area (each a 180° injection inwards), pushing the EZVI and potentially mobile DNAPL toward the center of the source area, followed by injections of EZVI along the centerline of the source area (each injection point consisting of a total of 360° injection, consisting of four 90° injections at each depth) to help promote mixing of the DNAPL and EZVI as the EZVI is pushed back toward the edges of the source area. The volume of EZVI to be injected is based on 15% of the source area pore volume. The downgradient monitoring wells will be sampled on a quarterly basis for a period of 10 years following EZVI injection activities to assess the effect of source area treatment and natural attenuation of the VOC plume.

The EZVI application using direct injection assumes EZVI will be injected into 240 injection points (each injection point having an ROI of 2.5 ft) in the source area. The impact of the EZVI injections will be monitored using four downgradient 2-inch monitoring wells screened within the saturated zone. The injection strategy is to inject EZVI using 1-ft vertical lifts between 4 and 20 ft bgs. The injection points will be spaced to cover the entire source area. The volume of EZVI to be injected is based on 15% of the source area pore volume. The downgradient monitoring wells will be sampled on a quarterly basis for a period of 10 years following EZVI injection activities to assess the effect of source area treatment and natural attenuation of the VOC plume.

To facilitate the cost analysis, it was assumed that a single injection event for both the Pneumatic and Direct Injection alternatives is required. Furthermore, it was assumed that pre-existing investigation borings are not present or have been decommissioned using grout and that daylighting of EZVI is not a concern.

The ISCO approach assumes construction of a recirculation system to facilitate distribution of oxidant within the source area. The ISCO recirculation system will consist of one groundwater extraction well positioned downgradient of the source area and two upgradient injection wells. The impact of the ISCO system will be monitored using four downgradient 2-inch monitoring wells. All wells will be screened within the saturated zone. The extraction well will be equipped with an electrically operated submersible pump. The maximum total groundwater extraction rate is assumed to be 2 gal per minute (gpm). Extracted groundwater will be amended with sodium permanganate and re-injected via the injection wells. The total mass of permanganate, which is based upon providing sufficient permanganate to meet the demand exerted by both uncontaminated soil (assumed to be 1.5 grams [g] of sodium permanganate [$NaMnO_4$] per kg of soil) and VOC (1.1 milligram [mg] $NaMnO_4$/mg PCE, 2.2 mg $NaMnO_4$/mg TCE, 3.9 mg

$NaMnO_4$/mg cDCE, and 7.6 mg $NaMnO_4$/mg VC; ITRC, 2005), is 10,045 kg. It is assumed that three years of system operation are required; each year consists of 3 weeks of recirculation with permanganate injection followed by 4 weeks of recirculation without permanganate injection. The downgradient monitoring wells will be sampled on a quarterly basis during ISCO operational activities, and then for an additional 10 years following the final year of system operation to assess the effect of source area treatment and natural attenuation of the VOC plume.

The P&T system assumed for this cost analysis will consist of two groundwater extraction wells screened within the saturated zone and equipped with electrically operated submersible pumps. The maximum total groundwater extraction rate is assumed to be 2 gpm. Extracted groundwater will be treated using an air stripping tower. The vapor stream from the air stripping tower will be treated using granular activated carbon, and treated groundwater will be recharged into the shallow aquifer via an infiltration gallery. The treated groundwater effluent and the vapor stream from the activated carbon will be sampled on a weekly basis for a period of 30 years to assess system performance.

8.2 COST DRIVERS

The costs to implement the EZVI technology for source area remediation will vary significantly from site to site. The key costs drivers are listed below, along with a brief discussion of their impact on cost.

Nature and Extent of Contamination

- **DNAPL mass and distribution** – A greater area of DNAPL distribution will require more injection points and more EZVI, thus increasing the capital costs of the technology.
- **Depth to source area** – Costs for the injection of EZVI and for the installation of monitoring wells will increase as the depth to the target treatment zone increases, but other costs, such as EZVI costs, will remain similar.

Aquifer Geochemistry

- **Concentration of other organic and inorganic constituents** – For the biological component of degradation, dehalorespiration of PCE/TCE can be inhibited in the presence of chloroform and 1,1,1-trichloroethane (1,1,1-TCA) (Duhamel et al., 2002). However, one advantage of the EZVI technology over conventional enhanced in-situ bioremediation is the ability of the ZVI to degrade other organic contaminants that are resistant to or inhibit biodegradation. Large amounts of inorganic constituents may react with the ZVI, thus consuming some of the capacity of the EZVI.
- **Groundwater pH** – For the biological component of degradation, biological activity is sensitive to pH, and the optimal pH range for dehalorespiration of PCE/TCE is ~7 to 8 (Middeldorp et al., 1999). Thus rates of biodegradation are likely to be inhibited at a pH outside of this range.

Aquifer Geology and Hydrogeology

- **Hydraulic conductivity** – EZVI may be more readily distributed in more permeable media. Application of the EZVI technology at sites with a low hydraulic conductivity (K) will generally be more expensive because a greater number of injection points are required to treat a given area.
- **Geological heterogeneity** – High heterogeneity limits the uniform distribution of EZVI within the target treatment area. Thus, treatment of sites with high heterogeneity will generally be more expensive as they may require a greater number of injection points or longer time frames for remediation.

Available Infrastructure and Site Access

- **Available infrastructure** – The availability of existing infrastructure (e.g., existing groundwater injection or monitoring wells, storage buildings, and utilities) can reduce the cost of technology implementation.
- **Site Access** – Sites having limited access for equipment and personnel (e.g., difficult terrain, overhead obstructions, or treatment beneath a building) may incur higher costs when implementing the technology.

8.3 COST ANALYSIS

A summary of the costs for each alternative is provided in Table 6. The capital costs for the EZVI alternatives using pneumatic injection, which include installation of monitoring wells, the EZVI, and injection equipment, are approximately $1,013,000 (nZVI) and $672,000 (mZVI). The capital costs for the EZVI alternatives using direct injection are approximately $1,014,000 (nZVI) and $672,000 (mZVI). The annual long-term monitoring cost is estimated to be $30,000 per year for all EZVI injection alternatives and represents a NPV of $263,000 over a 10-year monitoring period. The capital cost for the ISCO alternative is $418,000, which is significantly lower than the capital costs for the EZVI using nZVI alternatives and moderately lower than the capital costs for the EZVI using mZVI alternatives. However, the average annual cost for O&M and performance monitoring during ISCO operational activities is $169,000, and the annual long-term monitoring cost for the remaining years is $30,000. The NPVs of O&M and long-term monitoring for the ISCO alternative are $402,000 and $329,000, respectively. The capital cost for the P&T alternative is $380,000, which is significantly lower than the capital costs for the EZVI and ISCO alternatives. However, the annual long-term monitoring cost of $49,000 per year is higher than those of the EZVI and ISCO alternatives. The P&T alternative also has an annual O&M cost of $57,000 over a 30-year period. The NPVs of O&M and long-term monitoring for the P&T alternative are $1,202,000 and $1,030,000, respectively. Figure 6 provides a comparison of the NPV capital, O&M, and long-term monitoring costs for each alternative.

The bulk volume of the source area for this scenario is 96,000 ft^3 (2718 m^3). Therefore, the NPV of total remedy costs for the EZVI alternatives using nZVI and mZVI are approximately \$13.29/ft^3 (\$470/m^3) and \$9.73/ft^3 (\$344/m^3), respectively. The NPV of total remedy costs for the ISCO and P&T alternatives are \$11.96/ft^3 (\$423/m^3) and \$27.21/ft^3 (\$961/m^3), respectively.

Table 6. Summary of costs for treatment of PCE DNAPL source area.

Alternative	Duration of O&M (years)	Duration of Monitoring (years)	Capital Costs	Total O&M Costs	Average Annual O&M Costs	NPV of O&M Costs	Total Monitoring Costs	Average Annual Monitoring Costs	NPV of Monitoring Costs	Total Remedy Costs	NPV of Total Remedy Costs
EZVI – Pneumatic Injection (nZVI)	0	10	$1,013,297	$0	$0	$0	$295,200	$29,520	$262,597	$1,308,497	$1,275,894
EZVI – Pneumatic Injection (mZVI)	0	10	$671,785	$0	$0	$0	$295,200	$29,520	$262,597	$966,985	$934,382
EZVI – Direct Injection (nZVI)	0	10	$1,013,975	$0	$0	$0	$295,200	$29,520	$262,597	$1,309,175	$1,276,572
EZVI – Direct Injection (mZVI)	0	10	$672,463	$0	$0	$0	$295,200	$29,520	$262,597	$967,663	$935,060
ISCO	3	13	$417,731	$418,578	$139,526	$402,216	$383,760	$29,520	$328,664	$1,220,069	$1,148,610
Pump-and-treat	30	30	$380,376	$1,723,680	$57,456	$1,202,475	$1,476,000	$49,200	$1,029,688	$3,580,056	$2,612,539
Source area bulk volume (ft^3)	96,000	96,000	96,000	96,000	96,000	96,000	96,000	96,000	96,000	96,000	96,000
Source area bulk volume (m^3)	2718	2718	2718	2718	2718	2718	2718	2718	2718	2718	2718

Unit Cost Basis ($ per ft^3 source area)

Alternative	Duration of O&M (years)	Duration of Monitoring (years)	Capital Costs	Total O&M Costs	Average Annual O&M Costs	NPV of O&M Costs	Total Monitoring Costs	Average Annual Monitoring Costs	NPV of Monitoring Costs	Total Remedy Costs	NPV of Total Remedy Costs
EZVI – Pneumatic Injection (nZVI)	0	10	$10.56	$0.00	$0.00	$0.00	$3.08	$0.31	$2.74	$13.63	$13.29
EZVI – Pneumatic Injection (mZVI)	0	10	$7.00	$0.00	$0.00	$0.00	$3.08	$0.31	$2.74	$10.07	$9.73
EZVI – Direct Injection (nZVI)	0	10	$10.56	$0.00	$0.00	$0.00	$3.08	$0.31	$2.74	$13.64	$13.30
EZVI – Direct Injection (mZVI)	0	10	$7.00	$0.00	$0.00	$0.00	$3.08	$0.31	$2.74	$10.08	$9.74
ISCO	3	13	$4.35	$4.36	$1.45	$4.19	$4.00	$0.31	$3.42	$12.71	$11.96
Pump-and-treat	30	30	$3.96	$17.96	$0.60	$12.53	$15.38	$0.51	$10.73	$37.29	$27.21

Unit Cost Basis ($per m^3 source area)

Alternative	Duration of O&M (years)	Duration of Monitoring (years)	Capital Costs	Total O&M Costs	Average Annual O&M Costs	NPV of O&M Costs	Total Monitoring Costs	Average Annual Monitoring Costs	NPV of Monitoring Costs	Total Remedy Costs	NPV of Total Remedy Costs
EZVI – Pneumatic Injection (nZVI)	0	10	$372.75	$0.00	$0.00	$0.00	$108.59	$10.86	$96.60	$481.35	$469.35
EZVI – Pneumatic Injection (mZVI)	0	10	$247.12	$0.00	$0.00	$0.00	$108.59	$10.86	$96.60	$355.72	$343.72
EZVI – Direct Injection (nZVI)	0	10	$373.00	$0.00	$0.00	$0.00	$108.59	$10.86	$96.60	$481.59	$469.60
EZVI – Direct Injection (mZVI)	0	10	$247.37	$0.00	$0.00	$0.00	$108.59	$10.86	$96.60	$355.97	$343.97
ISCO	3	13	$153.67	$153.98	$51.33	$147.96	$141.17	$10.86	$120.90	$448.82	$422.53
Pump-and-treat	30	30	$139.93	$634.07	$21.14	$442.34	$542.96	$18.10	$378.78	$1,316.96	$961.05

Notes:
ft^3 – cubic feet
m^3 – cubic meters
O&M – Operation and Maintenance
NPV – net present value

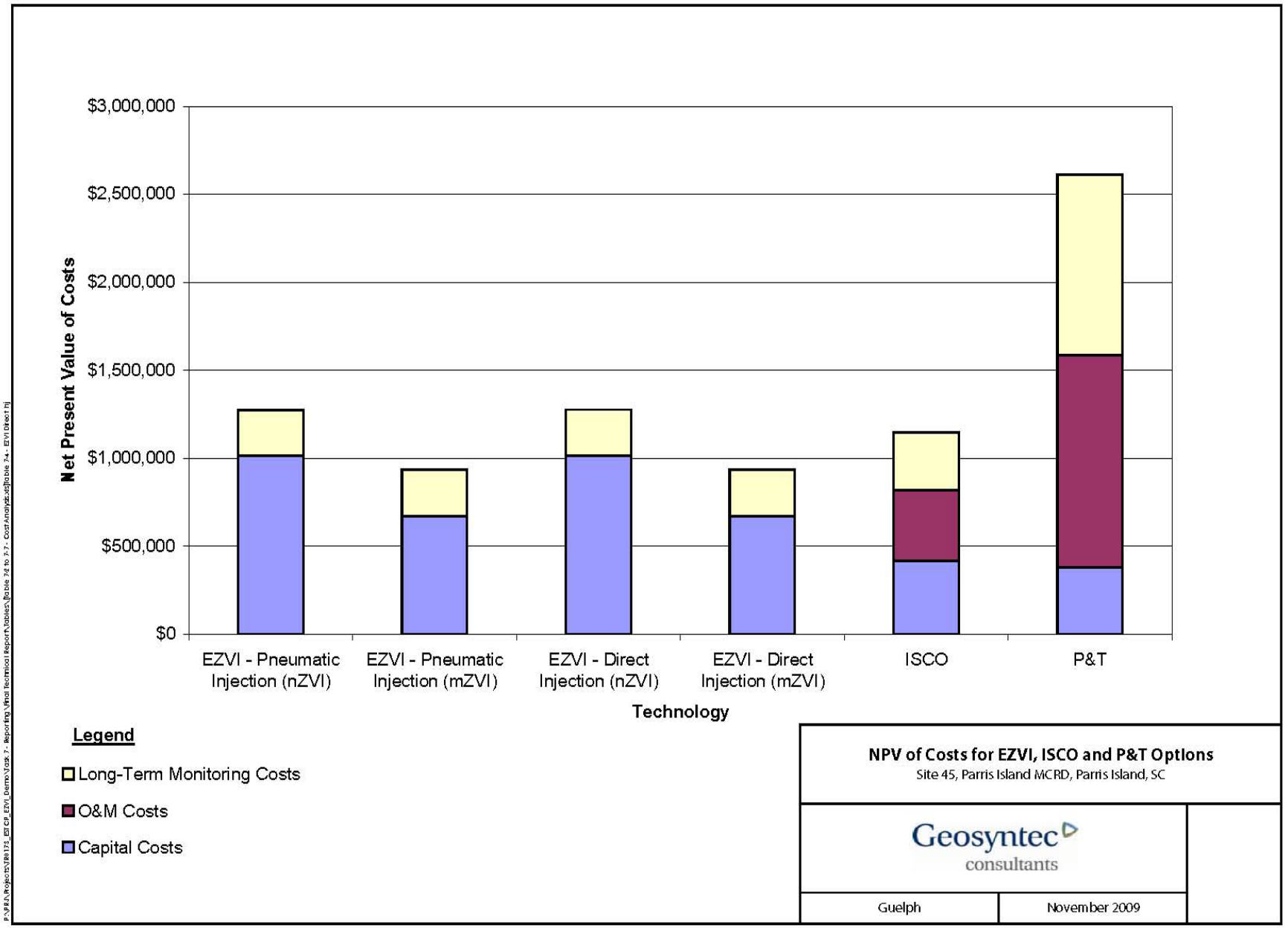

Figure 6. NPV of costs for EZVI, ISCO, and P&T options.

The total remedy costs for the two EZVI injection alternatives (pneumatic and direct injection) where nZVI is used are virtually the same at $1,309,000. The costs for the EZVI injection alternatives (pneumatic and direct injection) where mZVI is used are lower at about $967,000. The costs for the ISCO alternative falls between the EZVI injection alternatives where mZVI and nZVI are used at about $1,220,000. The costs for the P&T alternative are over $3,500,000.

9.0 IMPLEMENTATION ISSUES

This section provides information that will assist in future implementations of the technology. The following are key issues related to implementation of the EZVI technology.

9.1 POTENTIAL ENVIRONMENTAL ISSUES

9.1.1 Regulatory Issues

For this pilot test, a UIC permit was required by SDHEC. At full-scale, a UIC permit will be required in most jurisdictions for the injection of EZVI and the extraction and re-injection of contaminated groundwater if co-injection of groundwater with the EZVI is being conducted. EZVI is composed of vegetable oil, food grade surfactant, and ZVI particles, all of which are routinely injected or emplaced into the subsurface for groundwater remediation purposes. It is therefore expected that acquiring a UIC permit should not be difficult.

9.1.2 Air Discharge

The EZVI process described will not normally result in discharge of chemicals to the atmosphere.

9.1.3 Wastewater Discharge

The EZVI process described will not normally result in the generation of wastewater streams. Any extracted groundwater is normally re-injected into the injection points to aid in the distribution of the EZVI. Some small quantities of wastewater may be generated during well installation and groundwater sampling events and must be managed as they would be for other investigation derived waste.

9.1.4 Waste Storage, Treatment, and Disposal

The EZVI process described will not normally result in the generation of significant waste streams. Some waste may be generated during well installation and groundwater sampling and must be managed as they would be for other investigation derived waste.

9.2 END-USER ISSUES

Potential end users of this technology include responsible parties for contaminated sites where DNAPL is present in groundwater. End users will have an interest in the technology because it can potentially treat groundwater in situ at an overall cost much less than for conventional pump-and-treat remediation approaches and other source zone remediation technologies like ISCO. End users and other stakeholders may have concerns regarding (1) the effectiveness of the technology in reducing concentrations of target compounds below appropriate criteria, (2) potential negative impacts of using nano-scale iron in the environment, and (3) potential negative impacts of the EZVI addition on secondary water characteristics.

9.3 PROCUREMENT ISSUES

There are no specialized equipment components required to implement EZVI and no specialized services required. There are a number of nano-scale iron and micro-scale iron vendors as well as vendors of pre-made EZVI. There are no significant procurement issues with the application of this technology.

9.4 DESIGN ISSUES

Based on the results of the demonstration conducted at Site 45, Parris Island MCRD and a review of other applications of the technology, potential design issues to be considered in the development of the design of EZVI treatments were identified. These design issues are discussed briefly below and in greater detail in the Final Report (Geosyntec Consultants, Inc., 2010).

- *Daylighting of EZVI.* Vertical fractures may exist naturally or may be created during site investigation or EZVI injection activities, and could provide a preferential flow path for EZVI to daylight at the surface. Vertical pathways should be plugged with bentonite prior to EZVI injections (and during injections if new pathways are discovered) to help prevent daylighting of EZVI.
- *Distribution of EZVI in subsurface.* Based on the injection testing that was done at LC34, pneumatic injection should have been able to evenly distribute the EZVI over a 5 ft ROI in a uniform sandy aquifer. Thus, despite the distribution issues that were observed during this demonstration, it is expected that if there were less short-circuit pathways and we had been focused on a deeper treatment interval (below 15 ft bgs) we would have achieved a more even distribution. In addition, if a less viscous EZVI could be formulated it is possible that improved delivery could be achieved with an ease of injection similar to the injection of emulsified vegetable oil (EVO).
- *Micro-scale iron versus nano-scale iron in EZVI.* Although nZVI particles have a greater surface area available for reaction with contaminants and are potentially more mobile in the subsurface than mZVI particles, EZVI made with mZVI is almost as stable and as reactive as EZVI made up with nZVI. Furthermore, once the nZVI is emulsified to form EZVI, the emulsion droplets are on the micron scale, and due to size and viscosity issues, are not mobile in the subsurface. So the advantage of using nZVI versus mZVI in EZVI is solely one of increased rate of reactivity. Although, if the effective degradation rate for target compounds with EZVI is limited by the rate of diffusion across the oil liquid membrane, then there may not be significant differences in the performance of EZVI made with mZVI or nZVI. The price for nZVI is approximately $20 per pound versus $5 per pound for mZVI. Thus, the use of mZVI instead of nZVI will significantly improve the economics of the EZVI technology. An additional consideration for using mZVI rather than nZVI is the perceived public and regulatory concerns with the potential health and environmental risks associated with nano-scale particles in the environment.

- *Bioaugmentation.* Bioaugmentation cultures can be added to the subsurface at the time of injection to improve the rate of complete degradation of chlorinated ethenes to ethene. Although bioaugmentation was not conducted during the demonstration at Parris Island, is likely that bioaugmentation will significantly improve the rate of degradation of chlorinated ethenes associated with the biodegradation component of the EZVI technology.
- *EZVI versus Co-Injection.* Alternate injection approaches that still use nZVI or mZVI and EVO may be considered. Rather than creating EZVI aboveground, it is possible to inject each of the components (ZVI and EVO) as separate materials either at the same time (co-injection) or during different injection events. No experimental work has been conducted to evaluate how the different approaches to injection of ZVI and EVO will impact the effectiveness of the technology, but the advantages of the two approaches (i.e., emulsifying ZVI into the EVO prior to injection and injecting ZVI and EVO as separate components) are summarized below.

Advantages of EZVI over ZVI and EVO Injection

- EZVI has the ability to reduce flux more quickly than straight vegetable oil.
- It is believed that EZVI can enhance contact between ZVI and the DNAPL. Thus, degradation of the DNAPL is likely to occur faster with the EZVI than with ZVI and oil separately.
- The oil membrane of the EZVI protects the ZVI particles from being used up in unwanted secondary reactions (i.e., with inorganics or oxygen).
- The use of EZVI reduces the potential for the oil to coat the surface of the iron during or after injection, reducing the reactivity of the iron.

Advantages of ZVI and EVO over EZVI Injection

- EVO is much easier to inject and distribute in the subsurface than EZVI. However, if a less viscous EZVI could be formulated, it is possible that improved delivery of EZVI could be achieved with an ease of injection similar to the injection of EVO.
- The ZVI would require a similar injection density as the EZVI. However, the injection could be more aggressive since there would be no concern with damaging the emulsion structure, so there might be some slight advantages on the distribution compared with EZVI.

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