ESTCP
Cost and Performance Report

(ER-201330)

Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock

August 2017

This document has been cleared for public release; Distribution Statement A

ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Page Intentionally Left Blank

This report was prepared under contract to the Department of Defense Environmental Security Technology Certification Program (ESTCP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
08/16/2017	Cost & Performance Report	6/17/2013 - 6/17/2017

4. TITLE AND SUBTITLE
Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock

5a. CONTRACT NUMBER
Contract: 13-C-0016

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Charles Schaefer, Ph.D., CDM Smith
David Lippincott, P.G., CB&I Federal Services
Kirk Hatfield, Ph.D. and Harald Klammler, Ph.D., University of Florida

5d. PROJECT NUMBER
ER-201330

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
CDM Smith
110 Fieldcrest Avenue, #8, 6th Floor
Edison, NJ 08837

8. PERFORMING ORGANIZATION REPORT NUMBER
ER-201330

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Environmental Security Technology Certification Program
4800 Mark Center Drive, Suite 17D03
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
ESTCP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
ER-201330

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution A: unlimited public release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Fractured rock sites, impacted with chlorinated solvents such as tetrachloroethene (PCE) or trichloroethene (TCE), remain a significant environmental challenge for DoD. Efforts to apply in situ remedial technologies, such as chemical oxidation or bioaugmentation, have often proved challenging and/or unsuccessful with respect to attaining remedial objectives in fractured rock aquifers. Contaminant rebound typically is observed due to processes such as dense non-aqueous phase liquid (DNAPL) dissolution, matrix back-diffusion, and/or release of contaminants from low permeability/bypassed fracture zones.

15. SUBJECT TERMS
Rapid Assessment, Remedial Effectiveness, Rebound, Fractured Bedrock, QED Environmental Systems, polymerase chain reaction, rock quality designation, volatile organic analysis, volatile organic compound

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Charles Schaefer
UNCLASS	UNCLASS	UNCLASS	UNCLASS	66	19b. TELEPHONE NUMBER *(Include area code)* 609-895-5372

Page Intentionally Left Blank

COST & PERFORMANCE REPORT

Project: ER-201330

TABLE OF CONTENTS

Page

EXECUTIVE SUMMARY ES-1
1.0 INTRODUCTION 1
1.1 BACKGROUND 1
1.2 OBJECTIVES OF THE DEMONSTRATION 1
1.3 REGULATORY DRIVERS 2
2.0 TECHNOLOGY 3
2.1 TECHNOLOGY DESCRIPTION 3
2.1.1 Background – Contaminant Rebound 3
2.1.2 Overall Approach for Rapidly Assessing Treatment 4
2.2 TECHNOLOGY DEVELOPMENT 5
2.2.1 Monitoring and Assessment Tools 5
2.2.2 Rapid Assessment Testing 5
2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY 5
2.3.1 Advantages 5
2.3.2 Limitations 6
3.0 PERFORMANCE OBJECTIVES 7
4.0 SITE DESCRIPTION 9
4.1 SITE LOCATION AND HISTORY 9
4.1.1 Initial Screening Site – NAWC 9
4.1.2 Primary Demonstration Site – CPP 10
4.2 SITE GEOLOGY AND HYDROGEOLOGY 11
4.2.1 NAWC 11
4.2.2 CPP 11
4.3 CONTAMINANT SOURCE AND DISTRIBUTION 12
4.3.1 NAWC 12
4.3.2 CPP 12
5.0 TEST DESIGN 13
5.1 CONCEPTUAL EXPERIMENTAL DESIGN 13
5.2 BASELINE CHARACTERIZATION ACTIVITIES 13
5.2.1 Drilling and Rock Coring 13
5.2.2 Borehole Geophysical Logging 15
5.2.3 Borehole Discrete Interval Hydraulic Testing and Sampling 16
5.2.4 Permanent Packer Installation 16
5.2.5 Tracer Testing 17
5.2.6 Borehole Dilution Testing 18

TABLE OF CONTENTS (Continued)

Page

5.3 LABORATORY TREATABILITY STUDY 20
5.3.1 Objectives 20
5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS 21
5.5 FIELD TESTING 21
5.5.1 Baseline Sampling 23
5.5.2 Rapid Flushing and Sampling 23
5.5.3 Rebound Sampling 23
5.5.4 Demobilization 24
5.6 DATA ANALYSIS 24
5.6.1 Rebound Model – Rock Matrix 24
5.6.2 CSIA and Abiotic Dechlorination 24
5.7 SAMPLING METHODS 25
5.8 RESULTS 26
5.8.1 Results of Baseline Sampling 26
5.8.2 Results of Flushing 27
5.8.3 Results of Rebound 27
6.0 PERFORMANCE ASSESSMENT 31
6.1 SUBSTANTIAL DECREASES IN CHLORINATED SOLVENT CONCENTRATIONS FOLLOWING RAPID FLUSHING 31
6.2 REMOVAL OF PERMANGANATE PRIOR TO REBOUND PHASE 31
6.3 EFFECTIVE REBOUND MONITORING TO ASSESS POTENTIAL REMEDIAL PERFORMANCE 31
6.4 EASE OF IMPLEMENTATION 31
6.5 RECOMMENDED TESTING PROTOCOL 31
7.0 COST ASSESSMENT 33
7.1 COST MODEL 33
7.1.1 Capital Costs 33
7.1.2 O&M Costs 33
7.1.3 Demonstration-Specific Costs 33
7.2 COST DRIVERS 34
7.3 COST ANALYSIS 35
7.3.1 Base Cost Template 35
7.3.2 Rapid Assessment Approach 36
7.3.3 Bioremediation Recirculation Pilot Study 38
8.0 IMPLEMENTATION ISSUES 41
9.0 REFERENCES 43
APPENDIX A POINTS OF CONTACT A-1

LIST OF FIGURES

Page

Figure 2.1. Illustration Showing Possible TCE Rebound Mechanisms in Fractured Bedrock. 3

Figure 2.2. Conceptual Methodology for RA Testing..... 4

Figure 4.1. Demonstration Location at the NAWC Site. 9

Figure 4.2. Demonstration Location at CPP..... 10

Figure 4.3. Close-up View of the Demonstration Location at CPP. 10

Figure 4.4. Cross-sectional View of TCE Contamination at CPP Site 07. 12

Figure 5.1. CPP Demonstration Area..... 14

Figure 5.2. Newly Installed Well MW07-46R Shown in Proximity to Existing Well MW07-05R. 14

Figure 5.3. Generalized Geologic Cross-Section of the CPP Demonstration Area. 15

Figure 5.4. Increases in Bromide Concentration in the Deep Interval of MW07-46R as a Function of Volume Injected into MW07-05R..... 17

Figure 5.5. Results from the Borehole Dilution Testing Performed in the Injection Well (MW07-05R)..... 19

Figure 5.6. Linear Regression of the Bromide Data from the Borehole Dilution Test Performed at MW07-05R. 20

Figure 5.7. Abiotic Dechlorination of TCE in the Bench Scale Batch Testing. 21

Figure 5.8. Increases of TCE and DCE Relative to their Baseline (prior to rapid flushing) Levels during Rebound at MW07-46R-D..... 28

Figure 7.1. Base Plume Characteristics..... 35

Figure 7.2. Rapid Assessment Technology Approach 37

Figure 7.3. Bioremediation Recirculation Pilot Study 39

LIST OF TABLES

Page

Table 1.1. Federal Maximum Contaminant Levels (MCL) and New Jersey/Rhode Island Groundwater Quality Standards (GWQS) 2

Table 3.1. Performance Objectives 7

Table 5.1. cVOC Concentrations Measured in Groundwater during the March 2015 Pump Testing at MW07-46R and MW07-05R. 16

Table 5.2. Timeline of CPP Field Operations 22

Table 5.3. Analytical Methods, Preservation, and Containers – Groundwater 25

Table 5.4. Total Number and Types of Samples Collected During RA Testing 26

Table 5.5. Chlorinated Solvent and Anion Levels Present in Groundwater during the April 4, 2016, Baseline Sampling at MW07-46R and MW07-05R. 27

Table 5.6. CSIA Baseline Data ($\delta^{13}C$). 27

Table 5.7. CSIA Results for TCE and DCE. 29

Table 7.1. Demonstration Cost Components 34

Table 7.2. Summary of Base Case Site Characteristics and Design Parameters 36

Table 7.3. Cost Estimates for Treatment Approaches 38

Table 7.4. Summary of Costs for Treatment Alternatives 39

ACRONYMS AND ABBREVIATIONS

µg/L	micrograms per liter
µM	micromolar
AFB	Air Force Base
AFP	Air Force Plant
As	arsenic
ASTM	American Society for Testing and Materials
bgs	below ground surface
°C	degrees Celsius
^{13}C	a stable isotope of carbon with a nucleus containing six protons and seven neutrons
CB&I	Chicago Bridge and Iron Federal Services
cm	centimeter(s)
cm^2	square centimeter(s)
cm^3	cubic centimeters
cm^3/min	cubic centimeters per minute
cm^2/s	square centimeters per second
CO_2	carbon dioxide
COC	chain of custody
CPP	Calf Pasture Point
CSIA	compound specific isotope analysis
cVOC	chlorinated volatile organic compound
d	day(s)
DCE	*cis*-1,2-dichloroethene
DNAPL	dense non-aqueous phase liquid
DoD	U.S. Department of Defense
DOT	U.S. Department of Transportation
ESTCP	Environmental Security Technology Certification Program
Fe	iron
ft	foot or feet
g	gram(s)
GC-FID	gas chromatography-flame ionization detector
GWQS	ground water quality standards
h	hour(s)
HCl	hydrochloric acid
$HgCl_2$	mercuric chloride
HNO_3	nitric acid

ID	site identification
IPR	in-progress review
kg	kilogram
L	liter(s)
LNAPL	light non-aqueous phase liquid
MCL	maximum contaminant level
MDL	minimum detection limit
mg/L	milligrams per liter
min	minute(s)
mL	milliliters
mL/min	milliliters per minute
MLS	multi-level sampling
Mn	manganese
MNA	monitored natural attenuation
NaBr	sodium bromide
NAWC	Naval Air Warfare Center
NCBC	Naval Construction Battalion Center
NJDEP	New Jersey Department of Environmental Protection
NPV	net present value
O&M	operation and maintenance
OU	operable unit
PCE	tetrachloroethene
PFM	passive flux meter
PPE	personal protective equipment
PQL	practical quantification limit
QA	quality assurance
QC	quality control
QED	QED Environmental Systems
qPCR	polymerase chain reaction
RA	rapid assessment
RDG	reductive dehalogenase genes
RQD	rock quality designation
SERDP	Strategic Environmental Research and Development Program
SO_4^-	sulfate
SOP	standard operating procedure

TCA	1,1,1-trichloroethane
TCE	trichloroethene
TCL	target compound list
tDCE	*trans*-1,2,-dichloroethene
TeCA	1,1,2,2-tetrachloraethane
USEPA/EPA	U.S. Environmental Protection Agency
USGS	United States Geological Survey
VC	vinyl chloride
VFA	volatile fatty acid
VOA	volatile organic analysis
VOC	volatile organic compound

Page Intentionally Left Blank

ACKNOWLEDGEMENTS

We wish to thank the environmental staff at both the Naval Air Warfare Center (Trenton, New Jersey) and Calf Pasture Point (Rhode Island) for their support during this demonstration. In particular, special thanks to Jeffrey Dale, Naval Facilities Engineering Command, for his support of the project, and Pierre LaCombe at the USGS for assistance at the Naval Air Warfare Center. We wish to thank ESTCP for their financial support, and Dr. Andrea Leeson, the Environmental Restoration Program Manager at ESTCP, for her guidance. We would also like to thank Mr. Robert Shoemaker at AECOM for his onsite logistical support during the demonstration at Calf Pasture Point. Finally, we wish to acknowledge the capable staff at CB&I that conducted site assessment, performed laboratory studies, and provided analytical support and data management.

Page Intentionally Left Blank

EXECUTIVE SUMMARY

Fractured rock sites, impacted with chlorinated solvents such as tetrachloroethene (PCE) or trichloroethene (TCE), remain a significant environmental challenge for the Department of Defense. Efforts to apply *in situ* remedial technologies, such as chemical oxidation or bioaugmentation, have often proved challenging and/or unsuccessful with respect to attaining remedial objectives in fractured rock aquifers. Contaminant rebound typically is observed due to processes such as dense non-aqueous phase liquid (DNAPL) dissolution, matrix back-diffusion, and/or release of contaminants from low permeability/bypassed fracture zones. Unfortunately, the ineffectiveness of these remedial technologies is typically not recognized until after substantial time and resources have been expended via *in situ* pilot testing, and the mechanism(s) controlling the observed contaminant rebound often remain unidentified. This lack of understanding in the conceptual site model hinders effective site management, particularly with respect to designing an appropriate remedial approach and identifying the practical limits of remediation.

In this project, a rapid assessment (RA) protocol is developed to assess the potential effectiveness of *in situ* treatment such as chemical oxidation of bioaugmentation. The RA protocol assesses chlorinated ethene rebound, the potential of naturally occurring dechlorination reactions in low permeability zones, and the remedial effectiveness of using a pair of closely spaced bedrock wells. The RA technique involves identifying hydraulically conductive fracture zones, flushing contaminant from the fracture zones using water, then evaluating contaminant rebound within this zone while hydraulically isolating the zone from the surrounding contaminated aquifer (thereby preventing re-introduction of dissolved contaminant from the surrounding aquifer). The rate, composition, and isotopic signature of contaminant rebound is then used to evaluate the limits of remedial effectiveness, identify the local source/cause of any observed rebound, and provide improvement to the site conceptual model.

The demonstration of the RA protocol was performed in shallow bedrock at Calf Pasture Point (CPP) in Rhode Island, where TCE was the primary groundwater contaminant. While nearly 99% of the TCE was removed from the conductive fracture zone during the initial flushing, substantial contaminant rebound (up to approximately 5% of the baseline TCE concentration) was observed over the ensuing five-month rebound period. The rate and extent of observed contaminant rebound was reasonably described using a matrix back-diffusion model, thus serving as a line of evidence that the observed rebound was due to matrix back-diffusion. The back-diffusion model further predicts that over a decade of treatment likely would be needed to reduce TCE concentrations by 99% in the conductive fractures.

In addition to the back-diffusion model, compound specific isotope analysis (CSIA) on carbon for TCE and *cis*-1,2-dichlorethene (DCE) further confirmed the source of the observed rebound. The molar-average sum of TCE+DCE was isotopically (^{13}C) heavier at the end of rebound than at baseline conditions, thereby indicating that the “source” of the observed rebound could not be explained by any migration of contaminants from upgradient. The isotopic shift was consistent with TCE and DCE that had undergone abiotic dechlorination in the rock matrix; abiotic dechlorination of TCE in the rock matrix was confirmed in a separate bench-scale batch test using collected rock core. Thus, the CSIA testing not only served as a line of evidence demonstrating that the rock matrix was the source of the observed rebound, but also served as a useful tool for confirming that abiotic dechlorination of TCE and DCE were occurring within the rock matrix.

Page Intentionally Left Blank

1.0 INTRODUCTION

1.1 BACKGROUND

Management and remediation of fractured bedrock aquifers impacted with chlorinated solvents such as tetrachloroethene (PCE) and trichloroethene (TCE) are among the most pressing environmental challenges facing the Department of Defense (DoD). The challenges associated with management and remediation of fractured rock sites are due to a combination of the complex fracture flow field; uncertainties associated with contaminant distribution among fractures, microfractures, and the rock matrix; and, ultimately, the difficulties with understanding these complexities as they relate to remedial impacts on both short- and long-term groundwater quality.

The difficulties associated with addressing chlorinated solvents in fractured bedrock are most often realized when assessing remedial performance and when determining if a selected remedial approach will be sufficient for attaining target groundwater concentrations. It is imperative to rapidly assess potential remedial performance of a selected technology at fractured rock sites so that determination can be made at early stages as to whether the technology will be effective for attainment of remedial goals.

Currently, a demonstrated and verified methodology for rapid assessment (RA) of a remedial technology in fractured bedrock does not exist. Due to the complexities associated with bedrock systems, the relationships between mass removal, groundwater quality, treatment quantity and timeframe, and the potential for post treatment rebound are not well understood—resulting in prolonged pilot tests that often are unsuccessful and costly. Thus, demonstrating a methodology and developing a protocol to rapidly assess the extent to which an *in situ* remedial technology (e.g., bioremediation, chemical oxidation) can impact groundwater quality will serve as a useful tool to the DoD and its stakeholders.

1.2 OBJECTIVES OF THE DEMONSTRATION

The overall goal of this project was to develop and evaluate the use of a novel RA remedial evaluation technique, coupled with compound specific isotope analysis (CSIA), for use as a rapid and cost-effective means to assess the limits of *in situ* fractured bedrock remediation on long-term groundwater quality. Specifically, the objective was to develop a relatively small-scale field testing approach and protocol for assessing the practical extent of remedial effectiveness that might be obtained by implementing *in situ* remedial technologies in fractured bedrock such as biostimulation/bioaugmentation and chemical oxidation. This demonstration was performed at two different sites: the former Naval Air Warfare Center (NAWC) in Trenton, New Jersey, and the former Naval Construction Battalion Center (NCBC) Davisville (Site 07 – Calf Pasture Point (CPP)) in North Kingston, Rhode Island. *The NAWC site was used as a preliminary test site to develop the methodology, while the CPP site was used for more quantitative purposes and to fully evaluate the RA testing protocol.*

1.3 REGULATORY DRIVERS

TCE, along with its reductive dechlorination daughter products *cis*-1,2-dichloroethene (DCE), and vinyl chloride (VC), are regulated in drinking water and groundwater by each of the U.S. Environmental Protection Agency (USEPA) and the states of New Jersey and Rhode Island. The applicable groundwater standards are provided in Table 1.1. TCE concentrations in the treatment areas were up to three orders of magnitude above both state and federal regulatory levels.

Table 1.1. Federal Maximum Contaminant Levels (MCL) and New Jersey/Rhode Island Groundwater Quality Standards (GWQS)

Constituents	USEPA MCL (µg/L)	New Jersey GWQS (µg/L)	Rhode Island GWQS (µg/L)
Trichloroethene (TCE)	5	1	5
cis-1,2-dichlorethene (DCE)	70	70	70
Vinyl Chloride (VC)	2	1	2

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

2.1.1 Background – Contaminant Rebound

Although many technologies have been shown to be effective for reducing dissolved chlorinated solvent concentrations in bedrock during active treatment, contaminant rebound following active treatment has resulted (in many instances) in non-attainment of remedial objectives. For example, Schaefer et al. (2012) showed in bench-scale studies using chemical oxidants that residual dense non-aqueous phase liquid (DNAPL) resulted in substantial rebound of PCE to near pre-treatment levels in fractured sandstone blocks. Kauffman et al. (2006) showed that substantial rebound in chlorinated solvents occurred following a field demonstration of chemical oxidation; the rebound was attributed to back-diffusion from low permeability fractures and fracture zones.

There are many mechanisms that can contribute to contaminant rebound and sustained groundwater impacts in fractured bedrock aquifers. As illustrated in Figure 2.1, these mechanisms include matrix back-diffusion (Lipson et al., 2005; Sterling et al., 2005; West and Kueper, 2010), slow migration of contaminants from small or microfractures (USEPA, 2006), and/or the presence of DNAPL (Schaefer et al., 2012). For many sites, it is difficult to determine which of these mechanisms is responsible for the observed rebound (if rebound occurs), as the complexities associated with the flow field, aperture distribution, and contaminant distribution within the bedrock aquifer are difficult to quantify. Furthermore, many pilot tests are impacted by upgradient sources that migrate into the treatment area prior to evaluating rebound mechanisms, thereby preventing proper assessment of rebound during the post-injection period of the pilot test. The ability to isolate the treatment area to eliminate upgradient impacts would improve the ability to assess remedial effectiveness during pilot tests. However, approaches for comprehensively and cost effectively characterizing fractured bedrock aquifers to quantify these impacts have hitherto not been demonstrated.

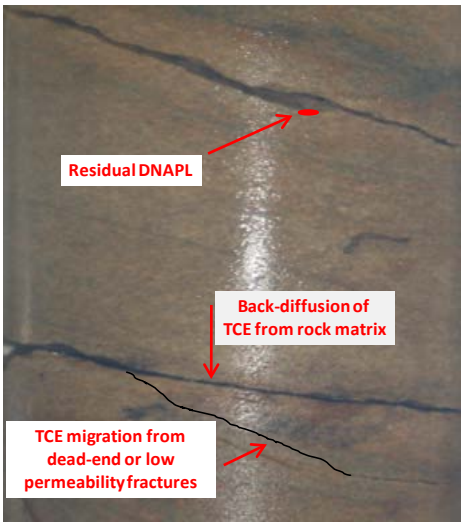


Figure 2.1. Illustration Showing Possible TCE Rebound Mechanisms in Fractured Bedrock.

2.1.2 Overall Approach for Rapidly Assessing Treatment

A demonstration of a novel RA technique, coupled with the use of a multilevel sampling well and CSIA, was employed for use as a rapid and cost-effective means to assess the limits of *in situ* remediation in fractured rock systems. The overall approach is to rapidly remove TCE in conductive fractures in or near the source area, then measure the rate and extent of contaminant rebound after oxidant removal. A conceptual diagram of the process is provided in Figure 2.2. The RA technique involves the use of two wells: a standard injection well and a multi-level sampling (MLS) well located approximately 5 to 10 feet downgradient of the injection well. In the first step of the test, either a chemical oxidant (e.g., permanganate) or uncontaminated water is injected into the injection well to rapidly remove PCE/TCE from the hydraulically conductive fractures. For the NAWC site, permanganate was injected and allowed to incubate for several weeks prior to subsequent water injection to remove the permanganate. However, due to the difficulties associated with the oxidant, only water flushing was used in the subsequent test performed at CPP, as illustrated in Figure 2.2. This initial step of removing the chlorinated solvents from the hydraulically conductive fractures is the first injection phase of the test.

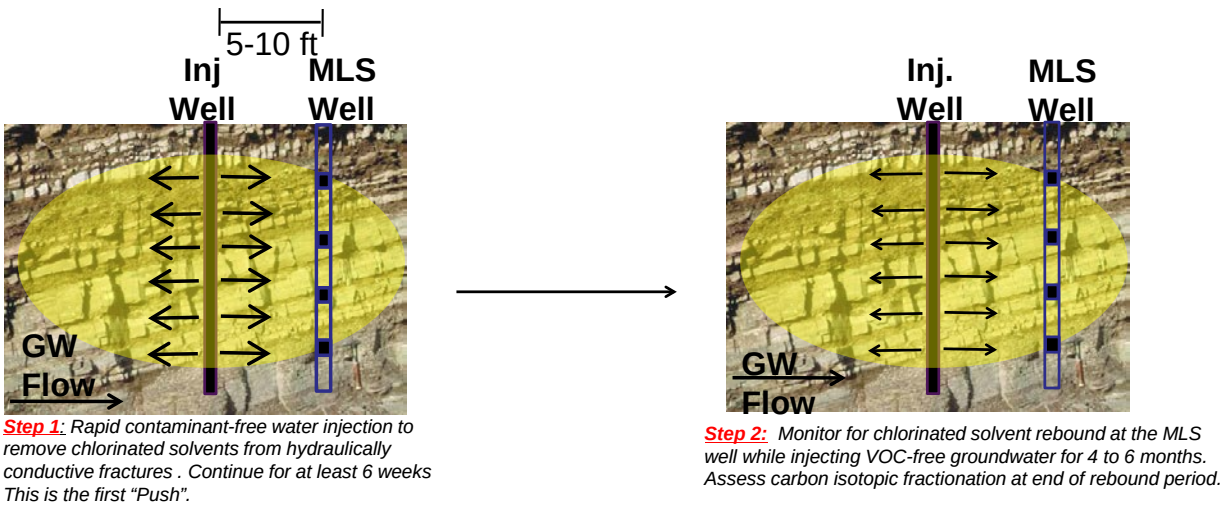


Figure 2.2. Conceptual Methodology for RA Testing.

To illustrate the concept, a simplified homogeneous flow regime is shown. The distance between the injection and MLS well may be increased depending upon the groundwater velocity, fracture connectivity, and fracture porosity.

After removal of the chlorinated solvents, non-contaminated water was slowly injected into the injection well at a rate sufficient to prevent upgradient chlorinated solvent-contaminated groundwater from impacting the MLS well. During this slow injection, chlorinated solvent concentrations were monitored in the MLS well to assess the extent of rebound during the slow injection of clean water into the injection well. Testing continued for up to five months. At the end of the rebound, CSIA analysis was performed on the carbon isotopes for the chlorinated ethenes that were present. The changes in isotopic ratio, coupled with the observed contaminant rebound, provided information regarding rebound mechanisms and the potential benefits of additional remedial amendment injection or contact time on groundwater quality.

2.2 TECHNOLOGY DEVELOPMENT

2.2.1 Monitoring and Assessment Tools

Detailed understanding of the permeability field, coupled with both the contaminant and amendment distribution, often can provide useful insight into the potential for contaminant rebound and ultimately the time needed to attain remedial goals. To assess the effectiveness of *in situ* remedial technologies with respect to their distribution and contaminant mass removal, several tools have been developed and implemented. High-resolution vertical multi-level sampling wells have proven very useful for understanding amendment and mass distribution in heterogeneous systems (Smith et al., 1991; Thomson et al., 2007). Such data often can be used to demonstrate the potential for rebound, particularly in cases when contaminants are not well contacted by remedial amendments.

CSIA has become a useful tool for evaluating treatment effectiveness and for identifying where amendment reactions (chemical or biological) with contaminants are occurring (Morrill et al., 2009; Hunkeler et al., 2011). Identification of reactive zones via CSIA relative to the permeability field and contaminant distribution can be a powerful tool for assessing the extent to which contaminant rebound might occur following treatment.

2.2.2 Rapid Assessment Testing

Several researchers have employed the use of "push-pull" tests to assess mass transfer in subsurface systems (Haggerty et al., 2001; Istok et al., 2002; Singha et al., 2007; Doughty, 2010). Push-pull tests typically involve injection of tracers and/or other amendments to assess hydraulic, physical, and/or biochemical properties of the aquifer in the vicinity of the injection well. This injection is the "push" portion of the test.

While the majority of push-pull testing has been performed in unconsolidated media, this approach has been successfully applied in fractured bedrock. Doughty (2010) used a series of push-pull tests to assess the impacts of solute diffusion and sorption in rock matrices. Haggerty et al. (2001) used push-pull tests to assess mass transfer in fractured dolomite, noting that diffusion length scales may substantially impact solute tailing. By extension, each of these studies suggest that such testing could be useful in assessing the potential for contaminant rebound due to back-diffusion following remedial treatment.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

2.3.1 Advantages

The primary advantages of developing the proposed assessment approach are as follows:

1. Limits to remedial success via *in situ* technologies such as biostimulation/ bioaugmentation, chemical oxidation, and *in situ* chemical reduction will be identified early in the remedial evaluation process, and the potential for contaminant rebound will be assessed without the need for long-term and costly testing.
2. Improved insight into the causes and mechanisms of rebound will be attained.

3. A field pilot demonstration using minimal resources (e.g., minimal well installations), while still answering the critical question as to the implementability and overall effectiveness of the *in situ* RA technique, will be performed.

2.3.2 Limitations

As with all technologies, there are also limitations with the proposed assessment approach:

1. Understanding the natural flow field in fractured rock can be challenging; however, the use of closely spaced wells coupled with intensive geophysical characterization can help to mitigate this limitation.
2. Fractures with a very high linear velocity would require large injection volume (oxidant or water), thereby likely making application of the technology impractical.
3. Fractured rock sites with multiple impacted geologic units will likely require multiple RA tests to provide the necessary information.

3.0 PERFORMANCE OBJECTIVES

Performance objectives are summarized in Table 3.1 and presented in detail in the project Final Report (Schaefer et. al., 2017).

Table 3.1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Substantial decreases in chlorinated solvent concentrations during the initial rapid flushing	Measured TCE/DCE concentrations in discrete intervals before and during rapid flushing or oxidant delivery	>99% reduction in TCE and DCE concentrations in the monitoring well prior to initiation of the rebound period	At least 98.6% reduction was achieved at each site
Removal of permanganate from conductive fractures during the start of the rebound phase	Measured permanganate concentrations during the rebound phase (during the second slow injection phase)	Permanganate concentrations less than 5 mg/L	Achieved at NAWC (permanganate not used at CPP)
Effective monitoring of rebound during the second slow injection phase to assess remedial performance	Measured TCE/DCE concentrations in the discrete intervals CSIA values	Quantitative interpretation of the rebound data, as discussed in detail in Section 5.8	Attained for CPP (challenges are discussed for NAWC)
Qualitative Performance Objectives			
Ease of Implementation	Time needed to maintain system during testing Feedback from field technician	Fouling due to oxidant byproducts Effectiveness of packer system Minimal costs	Use of permanganate was discontinued Determining the fracture flow field was the greatest challenge

Page Intentionally Left Blank

4.0 SITE DESCRIPTION

Two bedrock sites were selected for the RA demonstration. Based on the overall ranking performed during the site selection process, the NAWC and CPP were determined to be the most suitable locations for the demonstration. Due to the close proximity of the NAWC site to CB&I's research laboratory, as well as our intimate knowledge of the bedrock attained through ongoing SERDP Project ER-1685 and close collaborations with the USGS, initial project efforts focused on the NAWC site. ***It is noted that the initial testing performed at the NAWC site was for screening purposes only, as the knowledge gained during implementation of the testing at NAWC was used to refine the RA testing protocol outlined in Figure 2.2. For example, our experience at NAWC taught us to discontinue the use of oxidant injection. Results for the second demonstration performed at CPP are the focus of this Cost and Performance Report.***

4.1 SITE LOCATION AND HISTORY

4.1.1 Initial Screening Site – NAWC

The NAWC, shown in Figure 4.1, is located in West Trenton, New Jersey. The approximately 67-acre site, used as a jet-engine test facility beginning in the 1950s, was decommissioned in 1998 (http://nj.usgs.gov/nawc/site_description.html). Past activities at the site lead to the release of TCE, jet fuel, and other chemicals into the subsurface. Portions of the site have been sold to commercial developers, but the majority of the site remains undeveloped.

Figure 4.1. Demonstration Location at the NAWC Site.

The shaded area represents the bedrock TCE plume, where TCE is present at detectable concentrations (left). Demonstration wells (92BR and 93BR) and other local bedrock wells also are shown (right).

4.1.2 Primary Demonstration Site – CPP

CPP, part of the former U.S. NCBC Davisville located in North Kingston, Rhode Island, is bordered by Narragansett Bay and Allen Harbor (Figure 4.2). The facility originated as a Rhode Island militia encampment in 1893, and was eventually transferred to the Navy in 1939. While CPP was briefly inactive between World War II and the Korean War, the facility remained active until its decommissioning in 1994 (EA Engineering Science & Technology, 1999). The demonstration location is shown in Figures 4.2 and 4.3.

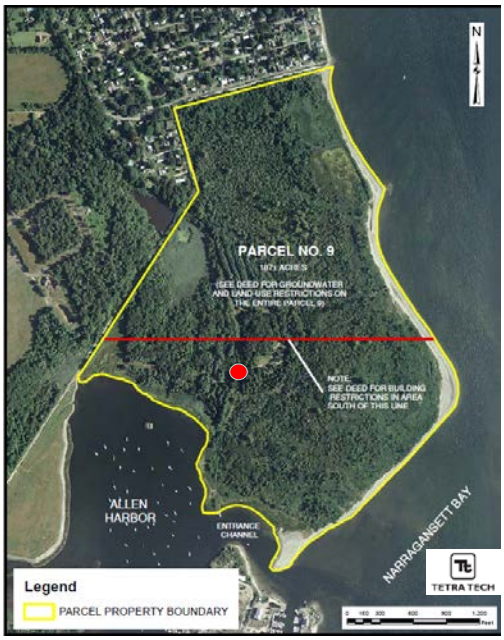


Figure 4.2. Demonstration Location at CPP.

The red dot shows the approximate location of the demonstration area.

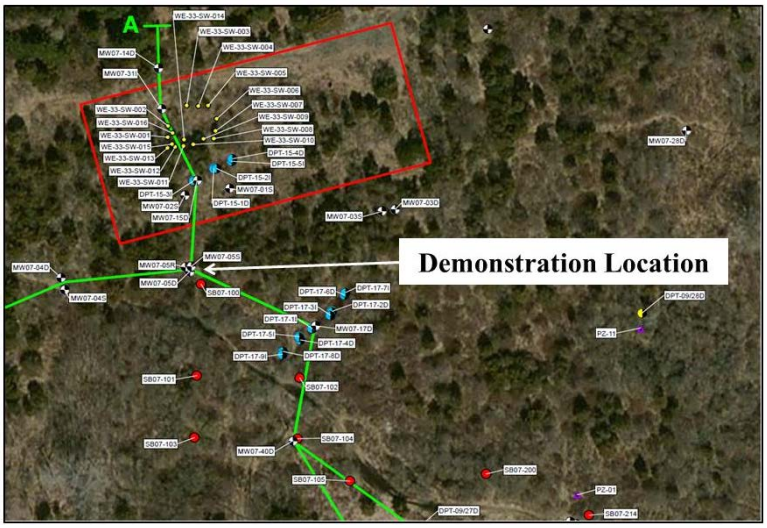


Figure 4.3. Close-up View of the Demonstration Location at CPP.

Centered at existing bedrock well MW07-05R.

4.2 SITE GEOLOGY AND HYDROGEOLOGY

4.2.1 NAWC

The geology and hydrogeology of the NAWC has been extremely well characterized by the U.S. Geological Survey (USGS) and others. The NAWC site lies within the Newark Basin and is underlain by Triassic-age clastic sedimentary rocks, consisting primarily of mudstone in the Lockatong Formation and sandstone in the Stockton Formation (http://nj.usgs.gov/nawc/site_description.html). The general strike and dip of these rock units is approximately N50^{o}E and 30°NW. A fault that strikes approximately N50^{o}E and dips approximately 60°SE separates rocks of the Lockatong and Stockton Formations at the site. The study site lies to the west of the fault, within the mudstone rocks of the Lockatong Formation.

The NAWC site is underlain by approximately 0 to 10 ft of unconsolidated sediments, consisting primarily of fill or heavily weathered rock, and behaves like an unconsolidated aquifer (http://nj.usgs.gov/nawc/site_description.html). Bedrock from approximately 10 to 50 feet below grade ranges from very weathered to unweathered, with groundwater being primarily transmitted in heavily weathered zones and within fractures and along bedding planes. At depths greater than 50 ft below land surface, the bedrock is generally unweathered, and groundwater is primarily transmitted via fractures or bedding planes. The unstressed regional hydraulic gradient in the bedrock aquifer is to the south, while the groundwater preferential flow direction in bedrock is generally towards the west, along bedding, strike, and dip.

4.2.2 CPP

CPP is located within the Narragansett Basin, a large structural syncline approximately 12 miles wide and up to 12,000 ft deep. The bedrock unit underlying the site is the Pennsylvanian-age Rhode Island Formation, which consists of quartzite, phyllite, gneiss, and schist, with quartzite and phyllite being observed in the rock cores collected during this demonstration (Section 5.2.1). The depth of the bedrock varies across the site, with weathered bedrock being observed at approximately 50 ft below ground surface (bgs) and competent bedrock being observed at approximately 58 ft bgs in the demonstration area (Site 07). Overlying the weathered bedrock is approximately 50 ft of anthropogenic fill (dredged material) and Quaternary glacial deposits (EA Engineering, 1998). A geologic cross-section of Site 07 that includes groundwater TCE concentrations measured in 2012 is provided in Figure 4.4.

Our demonstration was performed within the competent bedrock of the Bedrock Groundwater Zone. Groundwater in this unit is interpreted to flow generally southeast in this unit, with minor groundwater elevation impacts resulting from tidal influence (EA Engineering, 1998). Generally downward vertical gradients have been measured between the Shallow and Deep Groundwater Zones (well pairs MW07-05S/D), and the Deep and Bedrock Groundwater Zones (well pairs MW07-05D/05R) in the demonstration area (EA Engineering, 1998).

Most groundwater is transmitted through secondary openings, including joints, fractures, and openings along bedding planes, with fracture density generally decreasing with depth. Due to low groundwater yield, the bedrock is not the principal aquifer in the CPP area (TRS, 1993).

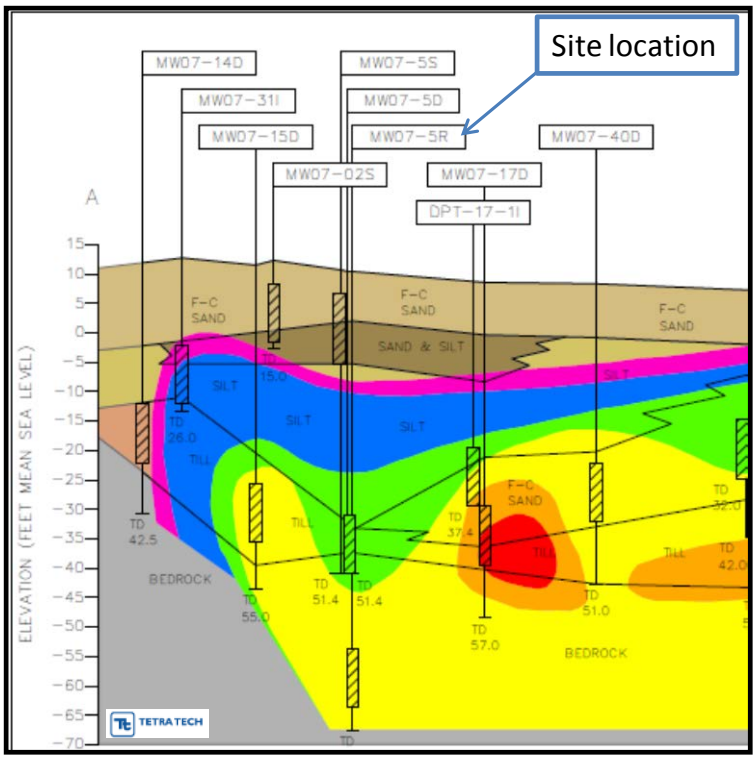


Figure 4.4. Cross-sectional View of TCE Contamination at CPP Site 07.

4.3 CONTAMINANT SOURCE AND DISTRIBUTION

4.3.1 NAWC

Investigations of the groundwater contamination at the site began in the late 1980s. The primary contaminants in bedrock at NAWC were determined to be TCE, along with its dechlorination daughter products DCE and VC. The TCE plume is shown in Figure 4.1. By the mid-1990s, a pump-and-treat facility was in operation to remove contaminant mass and to limit the offsite migration of contaminants. As part of our SERDP Project ER-1685, discrete interval TCE concentrations at nearby borehole location 90BR (location shown in Figure 4.1) were determined; concentrations ranged from 200 to 25,000 µg/L at depth intervals similar to those targeted for the rapid assessment testing.

4.3.2 CPP

The bedrock contamination near the demonstration location consists primarily of TCE, 1,1,2,2-tetrachloethane (TeCA), and 1,1,1-trichloroethane (TCA). The 2012 groundwater data at bedrock monitoring well MW07-05R showed TCE, PCA, and TCA concentrations of 4800, 410, and 80 µg/L, respectively. The cross-section shown in Figure 4.4 shows the distribution of TCE measured at that time. Concentrations of chlorinated volatile organic compound (cVOCs) measured within isolated zones of the open borehole well (MW07-46R) installed during this demonstration are discussed in Section 5.2.3.

5.0 TEST DESIGN

The testing, design, and results attained for the preliminary test site (NAWC) are provided in Appendix A of the Final Report (Schaefer et. al., 2017). It is noted that results from the preliminary testing at NAWC were used to refine the approach used for CPP. Most notable, the use of permanganate was discontinued, and the contaminant removal step at CPP was performed via water flushing only.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

As discussed in Section 2.1, the demonstration of a novel RA technique, coupled with the use of a multilevel sampling well and CSIA analyses, was evaluated for use as a rapid and cost-effective means to assess the limits of *in situ* remediation in fractured rock systems. The RA technique involves the use of two wells: a standard injection well and an MLS well located approximately 5 to 10 ft downgradient of the injection well; the distance between the injection and extraction well will depend, in part, upon the groundwater velocity and fracture connectivity. The proposed RA approach relies on high-resolution sampling within a limited portion of the contaminated aquifer.

Existing bedrock well MW07-05R at CPP was used as the injection well for this ESTCP demonstration. Boring and well installation logs indicate that the monitoring (and injection) zone for this well is isolated from 63.5 ft to 74.5 ft bgs, and from the water bearing fractures that intercept this 11-ft interval. The MLS well consisted of a packer system within the borehole to discretely sample multiple water-bearing zones within the targeted treatment interval. Sampling intervals were determined by various geophysical and hydraulic testing, as described in Section 5.2. The depth interval used for the MLS wells was based on the anticipated fracture flow path emanating from the injection well. Monitoring of rebound at the MLS well intervals facilitated assessment of the contaminant distribution within the treatment zone.

5.2 BASELINE CHARACTERIZATION ACTIVITIES

Site characterization activities at CPP were focused within the immediate vicinity of existing bedrock well MW07-05R and are summarized in the following subsections. Details of each of these activities are presented in the Final Report (Schaefer et. Al., 2017).

5.2.1 Drilling and Rock Coring

Characterization activities included drilling and coring one borehole located approximately eight feet downgradient from existing bedrock well MW07-05R. The newly installed open-borehole well was designated MW07-46R, and its location is shown in Figures 5.1 and 5.2.

During installation of monitoring well MW07-46R, rock cores were collected in approximately five-foot lengths from 58.3 to 80.6 ft bgs using a triple tube wire line PQ Core Barrel system for the collection of minimally disturbed 3.25-in diameter rock cores. The PQ coring system created a nominal 4.8-in diameter core hole. The rock core collected consisted of interbedded quartzite and phyllite. A generalized geologic cross-section of the demonstration area is provided in Figure 5.3. Visual logging of the rock core indicated that several water-bearing fractures were located between 58.3 and 63 ft bgs, and very few fractures were noted between 63 and 80.6 ft bgs.

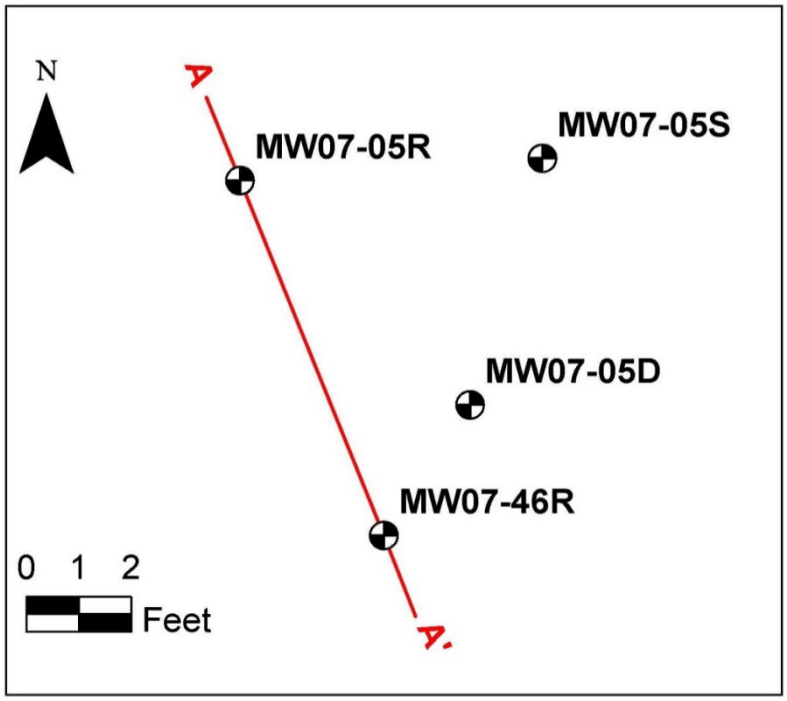


Figure 5.1. CPP Demonstration Area¶with location of newly installed borehole (MW07-46R) identified (approximately eight feet from existing well MW07-05R.

Figure 5.2. Newly Installed Well MW07-46R Shown in Proximity to Existing Well MW07-05R.

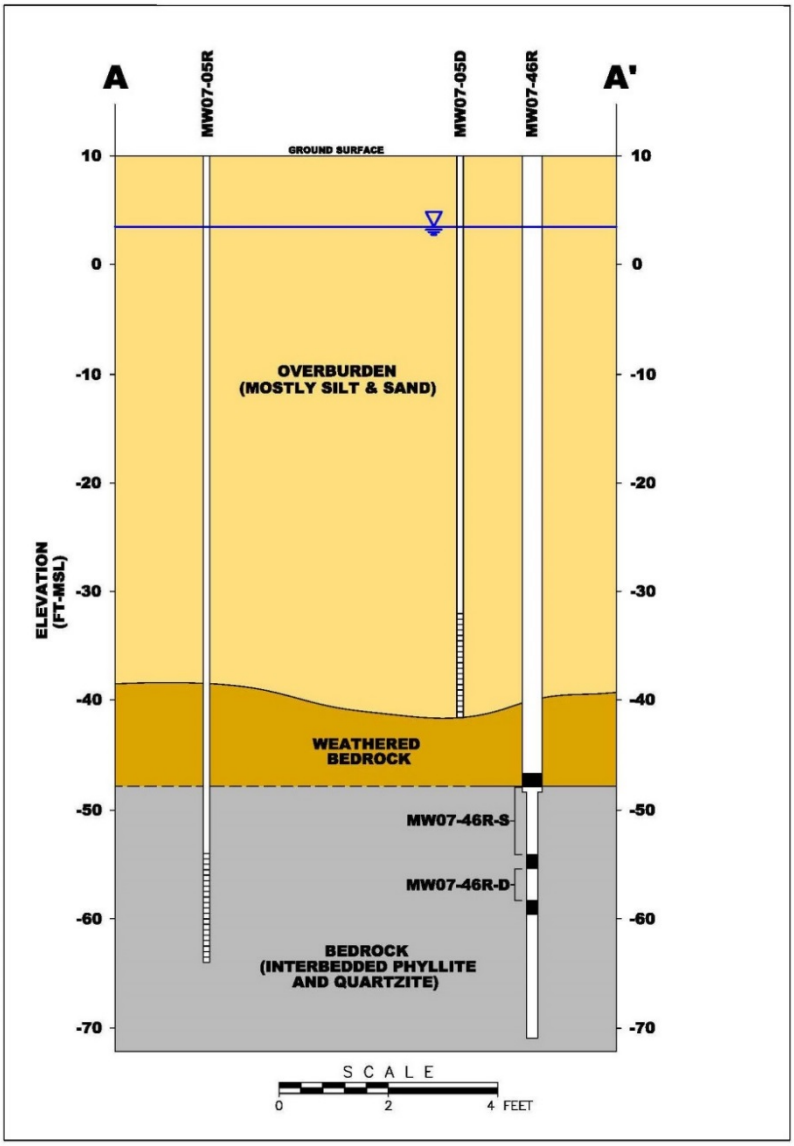


Figure 5.3. Generalized Geologic Cross-Section of the CPP Demonstration Area.

5.2.2 Borehole Geophysical Logging

Borehole geophysical logging was performed to facilitate the identification of transmissive fractures and fracture zones, and included optic and acoustic borehole imaging, caliper logging, and heat-pulse flow meter testing. Results of the borehole geophysical testing for MW07-46R are provided in Appendix D of the Final Report (Schaefer et. al., 2017). Consistent with the field observations on the collected rock core, several fractures were identified between approximately 58 and 63 ft bgs. Results of the heat-pulse flow meter testing suggested that these fractures were transmissive. In addition, the borehole geophysical testing identified two closely spaced fractures at approximately 67 ft bgs that also (based on the heat-pulse flow meter data) also appeared to be transmissive. Thus, both shallow (58 to 63 ft bgs) and deep (approximately 67 ft bgs) transmissive zones were identified.

5.2.3 Borehole Discrete Interval Hydraulic Testing and Sampling

Bedrock characterization activities included borehole discrete zone pump testing and groundwater sampling performed at well MW07-46R to assess the flow field and contaminant distribution throughout the open borehole interval (approximately 58 to 80 ft bgs). A custom designed straddle packer system was used to sequentially isolate discrete intervals (four feet or greater) within the open borehole for four individual short term (< two hours each) pump tests.

During two of the pump tests, groundwater samples were collected from the target intervals and analyzed for volatile organic compounds (VOCs) via USEPA Method 8260B. Two of the target zones did not produce sufficient water to collect representative samples. Sampling results, including groundwater samples collected from well MW07-05R during testing activities, are provided in Table 5.1. The data show that TCE was the primary chlorinated solvent present.

While pumping two of the discrete intervals at MW07-46R (58.3 to 64.7 and 65.0 to 69.0 ft bgs), drawdown was observed in well MW07-05R, indicating a direct hydraulic connection between select water-bearing fractures in each of these wells. Estimated hydraulic conductivities were 1.7 and 0.93 ft/day in these shallow and deep intervals, respectively.

Table 5.1. cVOC Concentrations Measured in Groundwater during the March 2015 Pump Testing at MW07-46R and MW07-05R.

Constituents	MW07-46R (58.3 to 64.7 ft bgs)	MW07-46R (65.0 to 69.0 ft bgs)	MW07-05R
Vinyl Chloride	<525	<525	320 J
trans-1,2-Dichlorethene	77 J	490 J	200 J
cis-1,2-Dichlorethene	210 J	1,000	3,500
Trichloroethene	9,800	26,000	7,700
1,1,2-Trichloroethane	<525	170 J	76 J
Tetrachloroethene	100 J	62 J	<525
1,1,2,2-Tetrachloroethane	620	2,000	350 J

Notes:

J=Estimated value greater than the minimum detection limit (MDL) but less than practical quantification limit (PQL).

Concentrations are shown in µg/L.

5.2.4 Permanent Packer Installation

The discrete zone pump test and contaminant concentration data, along with the previously collected borehole geophysical data and rock core data were analyzed to determine discrete zones within borehole MW07-46R to be targeted for monitoring. Based on these data, the following intervals were selected to be isolated for monitoring during the rapid assessment testing:

- MW07-46R-S: 57.8 to 64.0 ft bgs (6.2 ft)
- MW07-46R-D: 65.3 to 68.2 ft bgs (2.9 ft)

Straddle packer assemblies were designed, constructed, and installed in open borehole well MW07-46R to isolate these two target intervals. Dedicated sampling pumps were installed within each of the isolated intervals. A single packer and dedicated sampling pump were installed in injection well MW07-05R to isolate the 10-ft screen interval in this well (64 to 74 ft bgs) after tracer testing was performed (Section 5.2.5) and prior to borehole dilution testing at this well (Section 5.2.6).

5.2.5 Tracer Testing

A tracer test was performed to further assess hydraulic connectivity and travel time between the injection well (MW07-05R) and the monitoring well (shallow and deep intervals of MW07-46R). A 500 mg/L bromide solution was injected at rates between approximately 75 milliliters per minute (mL/min) and 200 mL/min over the course of three days. Groundwater samples were collected from shallow and deep packer intervals in MW07-46R during this injection.

Bromide data for the shallow and deep intervals for MW07-46R are provided in Figure 5.4. No measurable bromide was observed in the shallow, indicating that no significant flow path (despite observing a hydraulic connection during the short-term pumping tests) exists between the injection well (MW07-05R) and the shallow interval of MW07-46R.

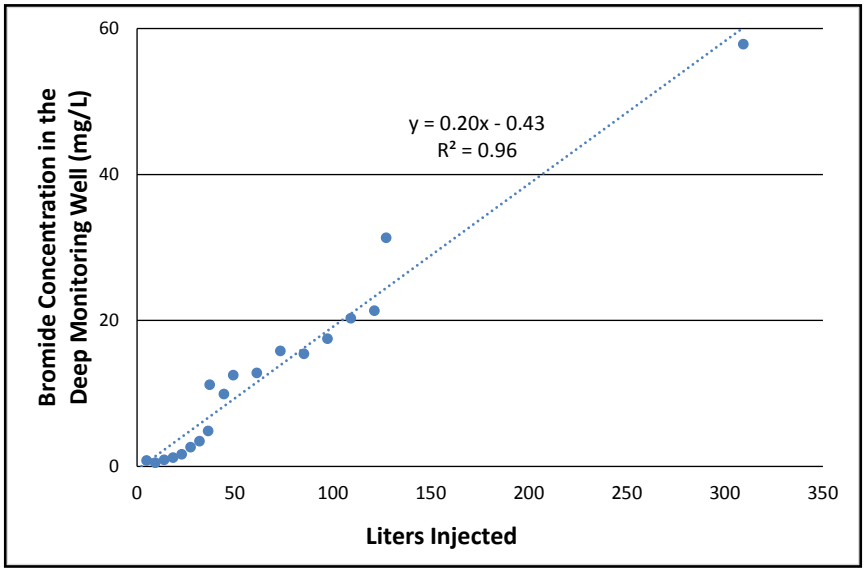


Figure 5.4. Increases in Bromide Concentration in the Deep Interval of MW07-46R as a Function of Volume Injected into MW07-05R.

The dashed line shows the linear regression to the data.

Bromide tracer results indicated that bromide appeared rapidly (approximately 3.5 hours) in the deep interval of MW07-05R. The bromide concentration in the deep interval increased linearly with the injected volume. The fraction (f) of injected flow that entered the deep monitoring interval during bromide injection is estimated assuming plug flow by calculating the slope in Figure 5.4 as follows:

$$C_{Br} = \left[\frac{C_{Br,inj}}{V}\right] V_e + C_{Br,0} \qquad \text{Eq. 1}$$

$$V_e = fV_T \qquad \text{Eq. 2}$$

where C_{Br} is the measured bromide concentration in the well, $C_{Br,inj}$ is the injected bromide concentration (500 mg/L), V is the estimated borehole volume isolated in the deep interval of MW07-46R (10 L), V_e is the volume of injected water that has entered the deep interval of monitoring well MW07-46R, $C_{Br,0}$ is the initial bromide concentration in the groundwater (<0.5 mg/L), and V_T is the total volume injected into the injection well at a given time. Linear regression (Figure 5.4) and application of Eqs. 1 and 2 results in the fraction f of injected flow entering the borehole of 0.004.

To estimate the fracture aperture along the fracture flow path from the injection well to the deep interval of MW07-46R, radial fracture flow emanating from the injection well is assumed. The fracture aperture (a) is calculated as follows:

$$a = \frac{V_b}{n\pi r^2} \qquad \text{Eq. 3}$$

where V_b is the volume of tracer injected until breakthrough of the tracer in the monitoring well (16,000 cm^3), n is the number of fractures in the deep interval (three, based on visual and geophysical boring logs), and r is the radial distance between the injection and monitoring well (240 cm). Eq. 3 results in an estimated fracture aperture of 0.029 cm. Assuming three hydraulically conductive fractures with an aperture of 0.029 cm each intersect the injection well along its 330 cm interval, the effective porosity in the deep interval is 0.00026.

At the completion of the bromide tracer tests, approximately 48 gallons of groundwater were extracted from the injection well to reduce the concentration of bromide in the groundwater to 61 mg/L in preparation of the borehole dilution testing (Section 5.2.6).

5.2.6 Borehole Dilution Testing

A borehole dilution tracer test (Pitrak et al., 2007) was performed at injection well MW07-05R to verify the ambient groundwater flow rate through the injection well. A 250 mL solution containing 8.9 grams of sodium bromide (NaBr) was added to the 11-ft interval below the packer in this well to achieve a target bromide tracer concentration in the water column of 500 mg/L. Immediately following the addition of the bromide tracer, water was recirculated within the well to sufficiently mix the bromide tracer within the interval. Bromide samples were collected from MW07-05R after recirculation (time=0), and on days 4, 11, 19, and 25. These data are presented in Figure 5.5.

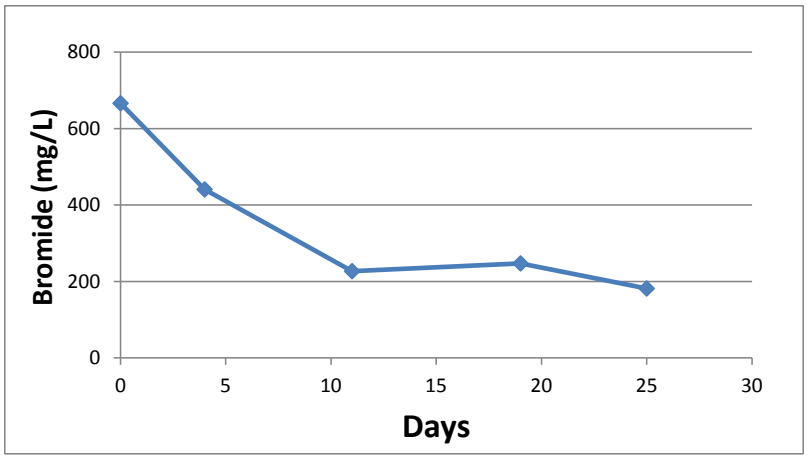


Figure 5.5. Results from the Borehole Dilution Testing Performed in the Injection Well (MW07-05R).

The rate of decay of bromide from the injection well provides an estimate of the Darcy velocity. The Darcy velocity is calculated as follows (Pitrak et al., 2007; Nordqvist et al., 2008):

$$\ln(C/C_0) = -\frac{Q}{V_{IW}} t \qquad \text{Eq. 4}$$

where C is the bromide concentration at time t, C_0 is the initial bromide concentration in the borehole, Q is ambient flow rate into the well, and t is the time. V_{IW} is the water volume of the injection well, including the porosity within the sandpack, which is approximately 12,000 cm^3. Linear regression of the data to Eq. 4 is shown in Figure 5.6, with a resulting ambient flow rate (Q) into the well of 564 cm^3/day (0.39 cm^3/minute). The Darcy flow of the aquifer is subsequently calculated as:

$$q_D = -\frac{Q}{2 r_{IW} L \alpha} \qquad \text{Eq. 5}$$

where q_D is the Darcy velocity, r_{IW} is the borehole radius of injection well MW07-05R, L is the length interval of the sandpack (11 ft), and α is flow convergence correction factor (estimated at two). The calculated value of q_D is 0.091 cm/day (average over the 11-ft interval of MW07-05R). Using the calculated effective porosity of 0.00026 (Section 5.2.5), the linear velocity is 350 cm/day, resulting in a travel time of 16 hours between the injection and extraction wells under ambient (no injecting) conditions; this residence time assumes all the flow moves towards the deep interval of MW07-46R, and thus may underestimate the actual ambient residence time.

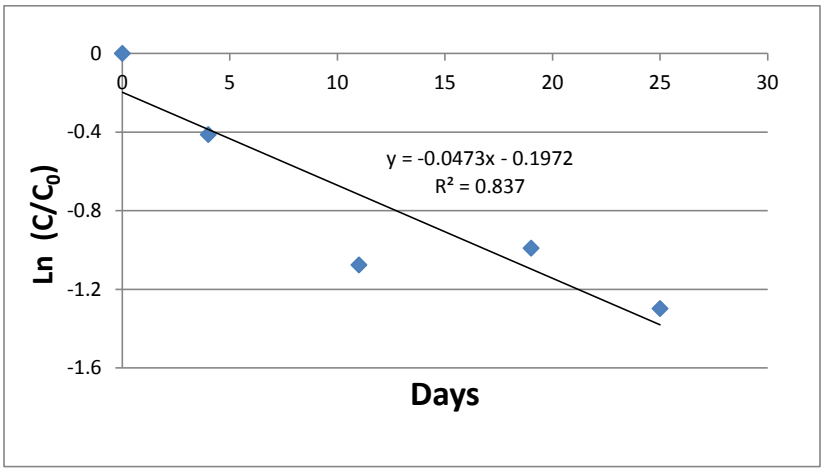


Figure 5.6. Linear Regression of the Bromide Data from the Borehole Dilution Test Performed at MW07-05R.

The bromide data are plotted in the form of Eq. 4 to facilitate determination of the ambient water flow rate into the borehole via linear regression. The linear regression to the data is represented by the solid line.

5.3 LABORATORY TREATABILITY STUDY

5.3.1 Objectives

Laboratory treatability studies were conducted with rock samples collected during coring of borehole MW07-46R in August 2014 (described in Section 5.2.1). The overall goal of the laboratory treatability testing was to assess the rock matrix at the CPP site to attain the parameters necessary to model the coupled diffusion and reaction of TCE through the rock matrix. Specifically, laboratory testing entailed: 1) measurement of the rock porosity and 2) determination of the abiotic TCE dechlorination rate constant within the rock matrix. Details of the laboratory testing are provided in the Final Report (Schaefer et al., 2017).

Results from the water-uptake method (Schaefer et. al., 2012b) showed that the rock matrix porosity was approximately 3.9%. This value was used to model TCE migration within the rock matrix (Section 5.6.1).

Results of the abiotic batch dechlorination testing showed that abiotic dechlorination transformation products ethane and propane were generated in the TCE-spiked vials, consistent with previous abiotic testing in bedrock (Schaefer et al., 2013, 2015). Results plotted at total millimoles of TCE per gram of rock transformed are provided in Figure 5.7. Using a trial-and-error approach to estimate (within a factor of two) the first-order TCE transformation rate constant via application of a coupled diffusion and first-order TCE transformation model (Schaefer et al., 2013) yields a rate constant of 2.7×10^{-8} s^{-1}. These results indicate that abiotic dechlorination of TCE occurs within the rock matrix. This information was used to develop the model and to provide insight regarding observations made during the field demonstration.

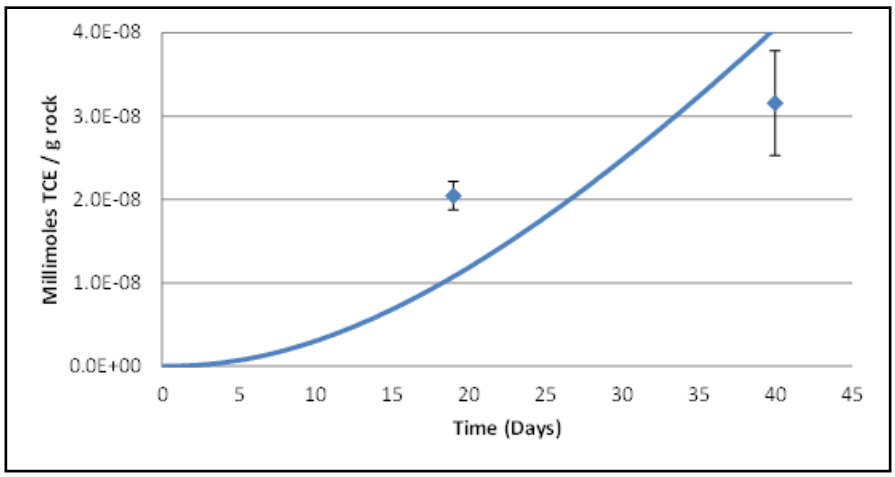


Figure 5.7. Abiotic Dechlorination of TCE in the Bench Scale Batch Testing.

Total TCE transformation was based on the generation of ethane and propane. Error bars represent 95% confidence intervals. Only data from two of the three replicates was used, as one of the replicates exhibited clear indications of leakage. The solid line represents the model regression (Schaefer et al., 2013, 2015) to the data.

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The RA technique at CPP involved the use of two wells: existing bedrock monitoring well MW07-05R that was used as the injection well, and bedrock MLS well MW07-46R located approximately 7.5 ft downgradient of the injection well (Figures 5.1 through 5.3). The MLS well consisted of a packer system within the borehole to discretely sample two water bearing zones within the targeted treatment interval. The depth interval used for the MLS well was selected based on the anticipated fracture flow path emanating from the injection well. Monitoring of rebound at the MLS well facilitated assessment of the contaminant distribution within the treatment zone.

Two vertical poly tanks (3,200 and 2,500 gallons) were installed in the demonstration area to hold the potable water used during testing. The tanks were connected to a flow meter assembly with ¼-inch site identification (ID) tubing. The flow meter assembly included rotameters that could measure the flow of injected potable water in the desired range and allowed for the adjustment of flow rates via needle valves.

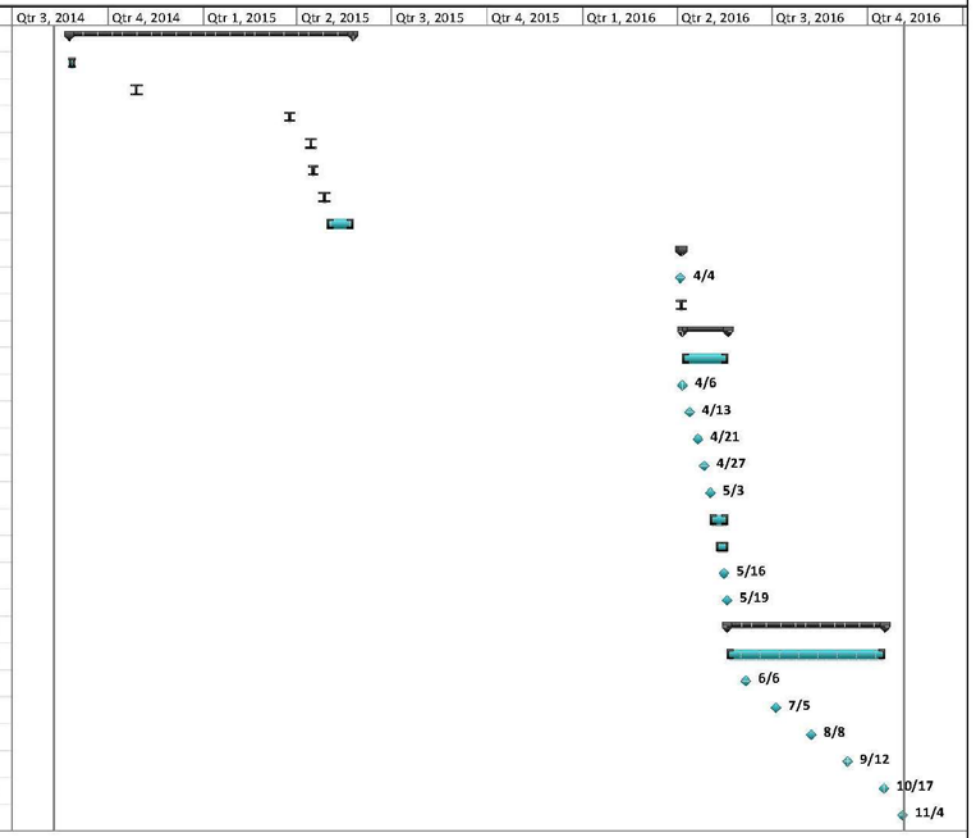
5.5 FIELD TESTING

The field testing at CPP was performed in three phases: 1) baseline sampling and analysis, 2) rapid flushing and sampling, and 3) rebound sampling. This sequence of testing allowed for assessment of the mass transfer mechanisms that could contribute to observed contaminant rebound following implementation of *in situ* remedial technologies, thereby proving information regarding the practical limits of remediation. In addition, as discussed in Section 5.8, the field testing provided insight into abiotic dechlorination processes occurring in the rock matrix. The timeline of field activities at CPP is provided in Table 5.2.

Table 5.2. Timeline of CPP Field Operations

Table 5.2 - Timeline of Field Operations
ESTCP Project ER-201330

ID	Task Name	Duration	Start	Finish
1	**MW07-46R Installation and Testing**	**195 days**	**Mon 8/25/14**	**Sun 5/24/15**
2	Rock Coring and MW07-46R Installation	5 days	Mon 8/25/14	Fri 8/29/14
3	Borehole Geophysics	1 day	Tue 10/28/14	Tue 10/28/14
4	Borehole Discrete Interval Hydraulic Testing & Sampling	2 days	Tue 3/24/15	Wed 3/25/15
5	Packer Assembly and Installation: MW07-46R	1 day	Tue 4/14/15	Tue 4/14/15
6	Tracer Test	3 days	Wed 4/15/15	Fri 4/17/15
7	Packer Assembly and Installation: MW07-05R	1 day	Mon 4/27/15	Mon 4/27/15
8	Borehole Dilution Test	18 days	Thu 4/30/15	Sun 5/24/15
9	**Baseline Sampling and System Installation**	**2 days**	**Mon 4/4/16**	**Tue 4/5/16**
10	Baseline Sampling	0 days	Mon 4/4/16	Mon 4/4/16
11	System Installation	2 days	Mon 4/4/16	Tue 4/5/16
12	**Rapid Flushing and Sampling**	**32 days**	**Wed 4/6/16**	**Thu 5/19/16**
13	Rapid Flushing at MW07-05R	32 days	Wed 4/6/16	Thu 5/19/16
14	Start Rapid Flushing at MW07-05R	0 days	Wed 4/6/16	Wed 4/6/16
15	Rapid Flushing Sampling Event #1	0 days	Wed 4/13/16	Wed 4/13/16
16	Rapid Flushing Sampling Event #2	0 days	Thu 4/21/16	Thu 4/21/16
17	Rapid Flushing Sampling Event #3	0 days	Wed 4/27/16	Wed 4/27/16
18	Rapid Flushing Sampling Event #4	0 days	Tue 5/3/16	Tue 5/3/16
19	Rapid Flushing at MW07-46R-S	13 days	Tue 5/3/16	Thu 5/19/16
20	Rapid Flushing at MW07-46R-D	9 days	Mon 5/9/16	Thu 5/19/16
21	Rapid Flushing Sampling Event #5	0 days	Mon 5/16/16	Mon 5/16/16
22	Rapid Flushing Sampling Event #6	0 days	Thu 5/19/16	Thu 5/19/16
23	**Slow Flushing and Rebound Sampling**	**108 days**	**Thu 5/19/16**	**Mon 10/17/16**
24	Slow Flushing at MW07-05R	108 days	Thu 5/19/16	Mon 10/17/16
25	Rebound Sampling Event #1	0 days	Mon 6/6/16	Mon 6/6/16
26	Rebound Sampling Event #2	0 days	Tue 7/5/16	Tue 7/5/16
27	Rebound Sampling Event #3	0 days	Mon 8/8/16	Mon 8/8/16
28	Rebound Sampling Event #4	0 days	Mon 9/12/16	Mon 9/12/16
29	Rebound Sampling Event #5	0 days	Mon 10/17/16	Mon 10/17/16
30	**System Decommissioning**	**0 days**	**Fri 11/4/16**	**Fri 11/4/16**



Date:
Tue 7/18/17

Task | Split | Milestone | Summary | Project Summary | External Tasks | External Milestone | Inactive Task | Inactive Milestone | Inactive Summary | Manual Task | Duration-only | Manual Summary Rollup | Manual Summary | Start-only | Finish-only | Deadline | Progress

Page 1

5.5.1 Baseline Sampling

Baseline sampling was performed to determine VOC concentrations and to perform CSIA on TCE, DCE, and TeCA. Baseline groundwater sampling was performed at both the injection well (MW07-05R) and the shallow and deep intervals of the monitoring well (MW07-46R). VOC and anion samples were analyzed by CB&I's New Jersey Department of Environmental Protection-certified analytical laboratory, located in Lawrenceville, New Jersey. CSIA analysis was performed by Pace Analytical, located in Pittsburgh, Pennsylvania.

5.5.2 Rapid Flushing and Sampling

Once baseline sampling was complete, the field testing was started. The initial rapid flushing step (Figure 2.2) was intended to remove dissolved chlorinated solvent mass from the hydraulically conductive fractures, with a target of 99% decrease in concentration. Rapid flushing was performed by injecting potable water into injection well MW07-05R at a constant rate of approximately 300 mL/min for a total of 43 days. The two MLS well intervals (MW07-46R-S and MW07-46R-D) were monitored to assess contaminant flushing from the water bearing fractures between the wells.

Groundwater samples were collected from the two MLS well intervals for VOCs and anions on days 7, 15, 21, 27, 40, and 43 of rapid water injection. After 27 days of potable water injection at well MW07-05R, cVOC concentrations did not decrease sufficiently in either of the MLS well intervals, and potable water injections were started at the two MLS well intervals. The injection rate at each of these well intervals was maintained at a constant rate of between 100 and 200 mL/min for the remainder of the rapid flushing phase. Potable water injection at MW07-05R was continued at a rate of approximately 150 mL/min during this period. Groundwater samples were collected again from the two MLS well intervals for VOCs and anions twice (day 40 and 43) during simultaneous potable water injections with both well intervals.

The VOC data indicated a 98.6 percent decrease in TCE at MW07-46R-D, which was the focus of the demonstration, as the tracer test data showed that only the deep interval was well-connected to the injection well. A volume of 17,300 L of potable water was injected during this rapid flushing phase.

5.5.3 Rebound Sampling

Following the rapid flushing of cVOCs at the injection well and the MLS well intervals, potable water injection was halted at the two MLS well intervals, and a significantly reduced flow rate of approximately 20 mL/min (28.8 L/day) was initiated at injection well MW07-05R. The slow water injection continued for 151 days (until day 194 of field testing) to allow for assessment of contaminant rebound. Bromide tracer (in the form of NaBr) was added to the potable water tanks at a concentration of approximately 200 mg/L. Bromide concentrations were measured at the MLS well intervals during this phase to verify that hydraulic influence was maintained during testing.

Five sets of groundwater samples were collected from the MLS well intervals approximately once per month and analyzed for VOCs and anions (including bromide) during this phase. Additionally, CSIA analysis to determine the carbon isotopic enrichment of TCE and DCE was performed during the final sampling event.

5.5.4 Demobilization

Decommissioning at CPP included removal of the materials and equipment used during the demonstration. The U.S. Navy took possession of well MW07-46R, which had been installed during the demonstration. Therefore, abandonment of this well was not required.

5.6 DATA ANALYSIS

5.6.1 Rebound Model – Rock Matrix

To determine if the observed TCE rebound during the demonstration (as part of the rebound testing phase as described in Section 5.5.3) could be attributed to matrix back-diffusion, a numerical model was developed to describe the back-diffusion of TCE from the rock matrix into the three fracture planes connecting the injection well MW07-05R to the deep interval of the MLS well (MW07-46R). The model is presented in detail in the Final Report (Schaefer et al., 2017).

5.6.2 CSIA and Abiotic Dechlorination

CSIA for carbon was performed on both TCE and DCE in the deep interval of the MLS well (MW07-46R). This testing was performed immediately prior to initiation of the rapid flushing and again at the last rebound sampling point at the completion of the demonstration. Samples were collected for TCE and DCE concentrations at the same time samples were collected for CSIA analysis. DCE was included with TCE because DCE likely was present as a result of biotic reductive dechlorination of TCE; VC concentrations were negligible compared to TCE and DCE.

CSIA testing was used to interrogate the source of the rebound to determine if it was enriched in ^{13}C relative to the water migrating through the hydraulically conductive fractures prior to the rapid flushing. An enriched (heavier) TCE+DCE at the end of rebound, without significant accumulation of VC, would serve as a line of evidence that these contaminants had migrated from a low permeability zone (i.e., the rock matrix) where abiotic dechlorination was enhanced relative to the fracture zones. Previous studies have shown that ferrous mineral-induced abiotic dechlorination can result in ^{13}C enrichment (Zwank, 2005 among others). Furthermore, a recent field study by Damgaard et al. (2013) in a clay till demonstrated that naturally occurring abiotic dechlorination reactions could be identified via carbon isotopic enrichment. In contrast, Morrill et al. (2009) suggest that rebound caused by DNAPL sources is unlikely to exhibit significant isotopic enrichment.

Enrichment of the combined TCE and DCE was determined based on the following molar isotopic balance:

$$\delta^{13}C_{TCE+DCE} = x_{TCE}\,\delta^{13}C_{TCE} + x_{DCE}\,\delta^{13}C_{DCE} \qquad \text{Eq. 6}$$

where $\delta^{13}C$ represents the ^{13}C enrichment (per mL) and x represents the molar fraction of either TCE or DCE. An increase in $\delta^{13}C_{TCE+DCE}$ after rebound in the absence of VC generation suggests that further dechlorination of TCE and/or DCE likely has occurred via an abiotic pathway, with transformation products (e.g., acetylene, propane, ethene) that are amenable to biotic or abiotic oxidation to CO_2 (Schaefer et al., 2015). ***Since such processes have been shown to occur in the rock matrix of CPP (Section 5.3), observation of such enrichment provides a strong line of evidence that the observed rebound is due to matrix back-diffusion, and that abiotic dechlorination is occurring within the rock matrix.***

5.7 SAMPLING METHODS

The procedures used in collecting groundwater samples during the demonstration, including quality assurance sampling and analysis, are described in detail in the Final Report (Schaefer et. al., 2017). The analytical methods and sample preservation used for the analyses that were part of this demonstration are summarized in Table 5.3. Groundwater samples were submitted to CB&I's Analytical and Testing Laboratory in Lawrenceville, New Jersey, for analysis of VOCs and anions (including bromide). CSIA (^{13}C) sample analyses were performed by Pace Analytical, located in Pittsburgh, Pennsylvania. The numbers and types of groundwater samples collected during the demonstration are provided in Table 5.4.

Table 5.3. Analytical Methods, Preservation, and Containers – Groundwater

Analyte	Method/ Laboratory	Preservative	Bottle
VOCs	EPA 8260/CB&I	4°C with HCl	8.8 mL VOA vial (x3)
Anions	EPA 300.0/CB&I	4°C	15 mL conical tube (x1)
CSIA (^{13}C)	AM24/Pace Analytical	4°C with HCl	40 mL VOA vial (x9)

Table 5.4. Total Number and Types of Samples Collected During RA Testing

Phase	Event	Date	Occurrence	Number of Samples	Analysis	Location
Baseline Sampling	Baseline Sampling	4/4/2016	Day -2	3	VOCs Anions CSIA	MW07-05R, MW07-46R-S, MW07-46R-D
Rapid Flushing and Sampling	Rapid Flush Sampling Event #1	4/13/2016	Day 7	3	VOCs Anions	MW07-05R, MW07-46R-S, MW07-46R-D
	Rapid Flush Sampling Event #2	4/21/2016	Day 15	3	VOCs Anions	MW07-05R, MW07-46R-S, MW07-46R-D
	Rapid Flush Sampling Event #3	4/27/2016	Day 21	2	VOCs	MW07-46R-S, MW07-46R-D
	Rapid Flush Sampling Event #4	5/3/2016	Day 27	2	VOCs	MW07-46R-S, MW07-46R-D
	Rapid Flush Sampling Event #5	5/16/2016	Day 40	3	VOCs Anions	MW07-05R, MW07-46R-S, MW07-46R-D
	Rapid Flush Sampling Event #6	5/19/2016	Day 43	3	VOCs	MW07-05R, MW07-46R-S, MW07-46R-D
Rebound Sampling	Rebound Sampling Event #1	6/6/2016	Day 61	3	VOCs Anions	MW07-05R, MW07-46R-S, MW07-46R-D
	Rebound Sampling Event #2	7/5/2016	Day 90	2	VOCs Anions	MW07-46R-S, MW07-46R-D
	Rebound Sampling Event #3	8/8/2016	Day 124	1	VOCs Anions	MW07-46R-D
	Rebound Sampling Event #4	9/12/2016	Day 159	1	VOCs Anions	MW07-46R-D
	Rebound Sampling Event #5 (final)	10/17/2016	Day 194	2	VOCs Anions CSIA	MW07-46R-S, MW07-46R-D

5.8 RESULTS

5.8.1 Results of Baseline Sampling

Results of the baseline sampling for cVOCs and anions are provided in Table 5.5. Baseline CSIA data are provided in Table 5.6. Data show that cVOC contaminant levels are slightly greater in the deep interval of MW07-46R than in the other monitoring locations. TCE is the primary contaminant present. The DCE is more enriched in ^{13}C than TCE, likely owing to the fact that DCE is a biotic transformation product of TCE. The trace levels of VC present suggest that the continued biotic dechlorination of DCE to VC is negligible.

Table 5.5. Chlorinated Solvent and Anion Levels Present in Groundwater during the April 4, 2016, Baseline Sampling at MW07-46R and MW07-05R.

Constituents	Unit	MW07-46R-S (57.8 to 64 ft bgs)	MW07-46R-D (65.3 to 68.2 ft bgs)	MW07-05R
Vinyl Chloride	µg/L	15 J	23 J	627
1,1-Dichloroethene	µg/L	32 J	26 J	39 J
trans-1,2-Dichlorethene	µg/L	101 J	342	234
cis-1,2-Dichlorethene	µg/L	769	2690	5360
Trichloroethene	µg/L	7110	14,620	8850
1,1,2-Trichloroethane	µg/L	57 J	123	88 J
Tetrachloroethene	µg/L	40 J	36 J	33 J
1,1,2,2-Tetrachloroethane	µg/L	351	1230	434
Chloride	mg/L	76	126	125
Sulfate as SO_4	mg/L	36	51	41
Bromide	mg/L	0.4	2.0	3.8

Notes:

J – Estimated value greater than the MDL but less than the PQL.

Table 5.6. CSIA Baseline Data ($\delta^{13}C$).

Constituents	MW07-46R (65.3 to 68.2 ft bgs)	MW07-46R (57.8 to 64 ft bgs)	MW07-05R
Trichloroethene	-26.26	-20.82	-24.20
cis-1,2-Dichlorethene	-19.38	-16.79	-19.95
1,1,2,2-Tetrachloroethane	49.84	38.74	46.09

5.8.2 Results of Flushing

Rapid flushing was initiated on April 5, 2016, and terminated on May 19, 2016. The rapid flushing was effective in removing >90% of the cVOCs in both the shallow and deep monitoring locations (approximately 98.6% of the TCE was removed in the deep monitoring interval). However, the shallow monitoring location only showed substantial cVOC removal after water was injected directly into the monitoring interval. This result was not unexpected, as the tracer testing showed that the injection well and shallow monitoring interval were poorly connected. As described in Section 5.8.3, evaluation of rebound was therefore limited to the deep interval.

5.8.3 Results of Rebound

The slow injection (rebound) phase of the demonstration was initiated on May 19, 2016, and continued until October 31, 2016. Based on the results of the bromide tracer testing (Section 5.2.5) that showed the shallow monitoring interval had a poor hydraulic connection to the injection well, assessment of rebound during the slow injection phase was focused on the deep interval of monitoring well MW07-46R.

Increases in TCE and DCE relative to baseline (Table 5.5) plotted as a function of time are shown in Figure 5.8. Results show that TCE and DCE and concentrations increased with time, indicating that there was a persistent contaminant mass present between the demonstration wells that was not removed during the rapid flushing.

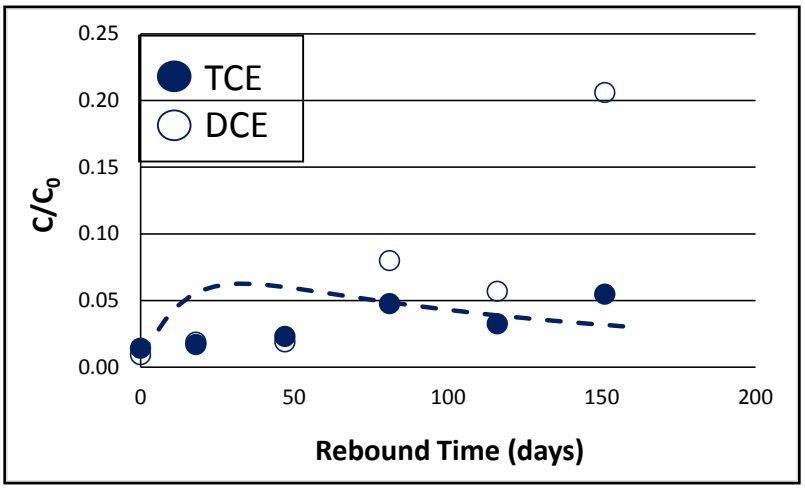


Figure 5.8. Increases of TCE and DCE Relative to their Baseline (prior to rapid flushing) Levels during Rebound at MW07-46R-D.

The dashed line represents the TCE model prediction.

Results of the CSIA analysis, along with the TCE and DCE concentrations just prior to rapid flushing and at the end of the rebound phase, are provided in Table 5.7.

Comparison of the molar averaged ^{13}C enrichment shows that the sum of TCE+DCE was enriched at the end of rebound compared to baseline conditions. This result provides a line of evidence for the following:

- The observed rebound was not simply from improper hydraulic control and migration of upgradient contaminated water. If this was the case, no enrichment would be expected due to this dilution.
- That the origin of the TCE and DCE that was observed during rebound had undergone further dechlorination that what was originally present in the hydraulically conductive fractures. Thus, the TCE and DCE were emanating from a location where there was enhanced dechlorination of these compounds.
- Since the absence of appreciable levels of VC indicates that biotic reactions likely were not responsible for the continued TCE and DCE dechlorination, abiotic dechlorination serves as a plausible explanation for the enhanced transformation.
- Bench scale testing showed that abiotic dechlorination occurs in the rock matrix, thus the CSIA results provide a line of evidence that the observed contaminant rebound is due to matrix back-diffusion.

Table 5.7. CSIA Results for TCE and DCE.

Contaminant	Baseline (Prior to Rapid Flushing)		End of Rebound	
	Concentration (µM)	$\delta^{13}C$ (per mil)	Concentration (µM)	$\delta^{13}C$ (per mil)
TCE	111	-26.3	6.1	-16.6
DCE	27	-15.6	5.6	-21.6
$\delta^{13}C_{TCE+DCE}$ (Eq. 20)	-24.2		-19.0	

In addition to the CSIA data, the diffusion model (Section 5.6.1) serves as another line of evidence that the observed rebound is due to matrix back-diffusion. As shown in Figure 5.8, the model provides a generally reasonable prediction of the observed TCE rebound.

The ratio of DCE to TCE increased following rebound. This ratio increase was likely due to biotransformation of TCE to DCE that occurred within the rock matrix, suggesting that biotic transformation of TCE to DCE also was enhanced within the rock matrix. While DCE can be generated from the biotic degradation of TeCA, such biodegradation has been shown to be accompanied by significant generation of *trans*-1,2,-dichloroethene (tDCE) (Chen et al., 1996); no significant increasing trend in the ratio of tDCE to TCE was observed during rebound, suggesting that biodegradation of the relatively low concentrations of TeCA (Table 5.5) were not responsible for the observed increasing ratio of DCE to TCE during rebound.

Based on the increase in DCE to TCE ratio observed during rebound, approximately 20% (on average) of the TCE that back-diffused was transformed to DCE. Thus the TCE plotted in Figure 5.8 would be approximately 20% greater in absence of biotic transformation to DCE. This increase in the DCE to TCE ratio may have also been due, in part, to the fact that DCE abiotic dechlorination likely is less than that of TCE (Lee and Batchelor, 2002).

Page Intentionally Left Blank

6.0 PERFORMANCE ASSESSMENT

6.1 SUBSTANTIAL DECREASES IN CHLORINATED SOLVENT CONCENTRATIONS FOLLOWING RAPID FLUSHING

As discussed in Section 5.5.2, rapid flushing resulted in a substantial (nearly 99%) decrease in TCE at the completion of the rapid flushing stage in both the injection well and the deep interval of the MLS well. A 96% decrease was attained in the shallow interval of the MLS well.

6.2 REMOVAL OF PERMANGANATE PRIOR TO REBOUND PHASE

Trace levels of permanganate persisted at the NAWC site and may have impacted the observed rebound rate. No oxidant was used for the subsequent demonstration performed at CPP.

6.3 EFFECTIVE REBOUND MONITORING TO ASSESS POTENTIAL REMEDIAL PERFORMANCE

As discussed in Section 5.8.3, the rate of rebound, the TCE:DCE ratio, and CSIA analyses all provided useful information regarding the likely source of the observed TCE rebound, and were useful in developing a conceptual model for the site. It is important to note that the extent of rebound observed during the RA testing is not necessarily proportional to the extent of rebound that would be observed following remedial treatment. The RA testing provides a rate of contaminant increase (or, equilibrium contaminant concentration) for a given residence time, and for a given "treatment" time that is equal to the duration of the rapid flushing. Results from the RA testing would need to be scaled to the residence time and length scales of the targeted treatment zone.

6.4 EASE OF IMPLEMENTATION

As discussed in Appendix A of the Final Report (Schaefer et. al., 2017), the initial efforts for the demonstration using permanganate were problematic due to permeability loss in fractures and the persistence of trace levels of permanganate despite aggressive water flushing. Implementation of the demonstration at CPP using only water flushing (no permanganate injection) was more effective and did not suffer from implementation issues. Relying on gravity drainage from the tank required regular operation and maintenance (O&M) efforts; if power was available, use of a small pump would have alleviated much of the labor efforts needed to maintain a relatively constant injection flow rate.

6.5 RECOMMENDED TESTING PROTOCOL

Based on the findings attained from this demonstration, a generalized RA protocol has been developed for potential future applications of this technique in fractured rock. This protocol is meant to serve as an incremental approach for planning and implementation of this testing method, but is not meant to serve as an exhaustive or constrictive guidance under the wide range of site-specific conditions that may be encountered. The protocol is provided in Appendix F of the Final Report (Schaefer et. al., 2017).

Page Intentionally Left Blank

7.0 COST ASSESSMENT

7.1 COST MODEL

To evaluate the cost of the RA remedial evaluation technique, and compare it against other remedial approaches, costs associated with various aspects of the demonstration were tracked throughout the course of the project. Table 7.1 summarizes the various cost elements and total cost of the demonstration project. The costs have been grouped by categories as recommended in the Federal Remediation Technologies Roundtable Guide to Documenting Cost and Performance for Remediation Projects (FRTR, 1998). Many of the costs shown on this table are a product of the innovative and technology validation aspects of this project and would not be applicable to a typical site application. Therefore, a separate "discounted costs" column that excludes or appropriately discounts these costs has been included in Table 7.1 to provide a cost estimate for implementing this technology at the same scale as the demonstration (i.e., pilot scale).

Costs associated with the demonstration were tracked from June 2013 to June 2017. The total cost of the demonstration was $696,880, which included $181,785 in capital costs, $173,190 in O&M costs, and $341,905 in demonstration-specific costs (cost related to ESTCP requirements, site selection, and characterization).

7.1.1 Capital Costs

Capital costs (primarily system design and installation) accounted for $181,785 (26%) of the total demonstration costs. As indicated in Table 7.1, these costs exceed what would be expected during a typical remediation project mainly due to the demonstration being performed at two separate sites.

7.1.2 O&M Costs

O&M costs accounted for $173,190 (25%) of the total demonstration cost. These costs consisted primarily of groundwater monitoring (including analytical), system O&M, and reporting costs. System O&M costs were $112,491 (16%) of total demonstration costs. Extensive performance monitoring activities were conducted to effectively validate this technology; including one baseline and 11 demonstration monitoring groundwater sampling events.

7.1.3 Demonstration-Specific Costs

Other demonstration-specific costs (those costs not expected to be incurred during non-research-oriented remediation projects) accounted for $341,905 (49%) of the total demonstration cost. These costs included site selection, laboratory treatability studies, laboratory buffer testing, laboratory electrode testing, hydrogeologic testing, tracer tests, ESTCP demonstration reporting and meeting (IPR) requirements, and preparation of extensive technical, cost, and performance reports.

Table 7.1. Demonstration Cost Components

Cost Element	Details	Tracked Demonstration Costs	Discounted Costs[1]
	CAPITAL COSTS		
System Design	Labor	$17,752	$8,000
Well Installation & Development, site prep	Labor & Travel	$52,098	$20,000
	Materials	$11,210	$5,600
	Subcontracts (driller)	$44,012	$30,000
	Subcontracts (waste T&D)	$2,451	$2,451
System Installation (inc. system components and materials)	Labor & Travel	$29,977	$19,000
	Equipment & Materials	$24,284	$14,000
	Subtotal	**$181,785**	**$99,051**
	OPERATION AND MAINTENANCE COSTS		
System O&M (inc. groundwater sampling)	Labor	$74,941	$37,500
	Materials & Equipment	$34,378	$17,200
	Travel	$3,171	$1,600
Analytical	In-House Labor	$22,145	$0
	Outside Labs	$3,275	$15,000
Quarterly Reporting & Data Management	Labor	$29,977	$10,000
	Subcontractor (CDM Smith)	$5,302	$0
	Subtotal	**$173,190**	**$81,300**
	OTHER TECHNOLOGY-SPECIFIC COSTS		
Site Selection	Labor & Travel	$12,612	$0
Site Characterization (geophysical logging, packer testing, pump tests, borehole dilution and tracer testing)	Labor (including in-house analytical)	$59,424	$28,200
	Travel	$5,802	$3,000
	Materials & Equipment	$20,373	$10,200
	Outside Lab	$2,387	$2,387
	Subcontractor (geophysical)	$5,082	$5,082
Treatability Studies	Labor (including in-house analytical)	$6,765	$0
Demonstration Plan/Work Plan	Labor	$29,755	$15,000
IPR Meetings	Labor	$7,494	$0
	Subcontractor (CDM Smith)	$7,954	$0
Project Management (financial/administrative)	Labor	$26,128	$17,000
Data Evaluation and Model Development	Labor	$16,429	$10,000
	Subcontractor (CDM Smith)	$7,954	$0
	Subcontractor (Univ. of Florida)	$46,936	$0
Technology Transfer (presentations, papers)	Labor & Travel	$20,240	$0
	Subcontractor (CDM Smith)	$13,256	$0
Final Report and Cost & Performance Report	Labor	$34,756	$20,000
	Subcontractor (CDM Smith)	$18,559	$0
	Subtotal	**$341,905**	**$110,869**
	TOTAL COSTS	**$696,880**	**$291,220**

Notes:

[1]Discounted costs are defined as estimated costs to implement this technology at the same scale as the demonstration. These costs do not include the technology validation apects of this ESTCP demonstrations, such as site selection, treatability studies, extensive groundwater sampling, ESTCP demonstration reporting and meeting (IPR) requirements, and preparation of technical and cost and performance reports.

7.2 COST DRIVERS

The expected cost drivers for performing the RA remedial evaluation technique, and those that will contribute to determining the cost/selection of this technology over other options, include the following:

- Depth of the treatment area below ground surface

- Aquifer lithology and hydrogeology
- Duration of testing
- Number of RA test locations needed, determined by site geology, contaminant distribution, and targeted treatment area
- Site logistics (accessibility, availability of utilities, etc.)
- Length scale (i.e., distance between injection and monitoring well), which is controlled by fracture connectivity and system heterogeneity

7.3 COST ANALYSIS

A cost analysis of the RA remedial evaluation technique and one of the traditional cVOC groundwater treatment approaches (active bioremediation with recirculation) was performed. Cost estimates for the RA remedial evaluation technique and a pilot scale application of active bioremediation with recirculation were developed. The cost analyses comparing the above approaches are presented below based on a three-year operating scenario.

7.3.1 Base Cost Template

The base case presented in Krug et al. (2009) is modified as a template for the cost analysis of the above technologies/approaches. The base case presents a situation where a bedrock aquifer contains a dissolved TCE source area extending to 75 ft bgs and is 60 ft long and 30 ft wide, perpendicular to groundwater flow (Figure 7.1). The specific base case site characteristics, including aquifer characteristics and design parameters for each of the remedial assessment approaches analyzed, are summarized in Table 7.2.

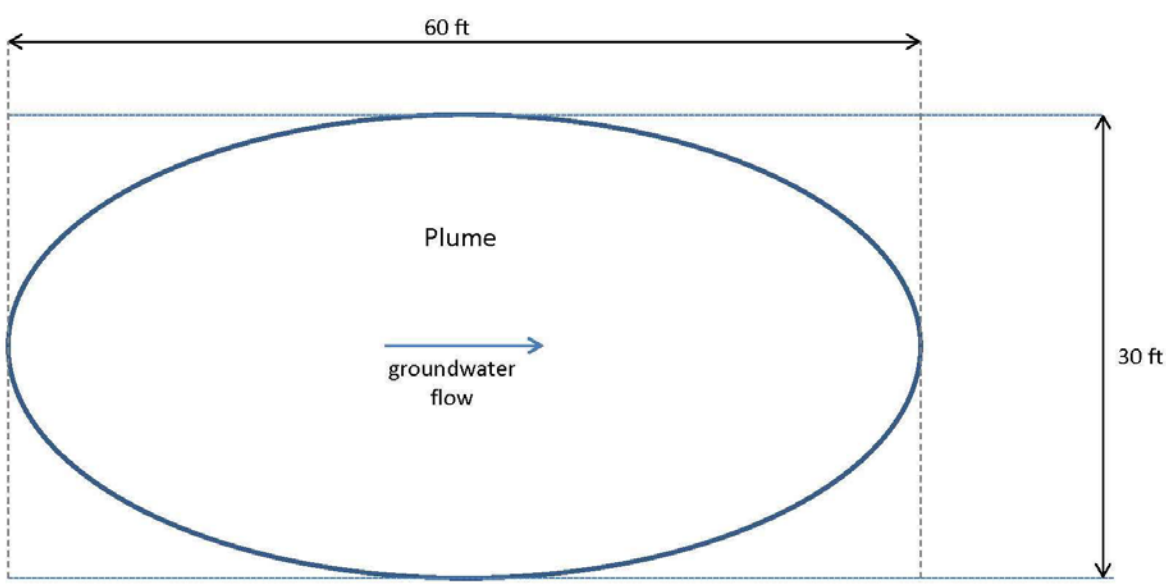


Figure 7.1. Base Plume Characteristics

The following subsections provide cost estimates for implementation of each of the two remedial assessment approaches for the base case. The cost estimates provide insight into the comparative capital, O&M, and long-term monitoring costs to better identify cost drivers for each technology/approach. Total costs for each of the assessment approaches were calculated. Net present value (NPV) of future costs were not calculated, as these assessment approaches are short-term tests, with no long-term monitoring costs. Specifically excluded from consideration are the costs of pre-assessment site characterization activities, assuming the costs for these activities would be similar for each alternative.

Table 7.2. Summary of Base Case Site Characteristics and Design Parameters

Design Parameter	Units	Alternative	
		Rapid Assessment Technology	Bioaugmentation Recirculation Pilot Test
Width of Source Area	feet	N/A	30
Length of Source Area	feet	10	60
Treatment Area	sq. ft.	N/A	1,800
Depth to Top of Treatment Zone	feet	25	25
Depth to Bottom of Treatment Zone	feet	75	75
Thickness of Overburden in Treatment Area	feet	10	10
Thickness of Bedrock in Treatment Area	feet	65	65
Depth to Water	feet	25	25
Vertical Saturated Thickness in Treatment Area	feet	50	50
Porosity	dimensionless	0.05	0.05
Treatment Zone Volume	cu. ft.	N/A	4,500
Number of Injection Wells	each	1	1
Diameter of Injection Well Borehole	inches	4	8
Number of Extraction Wells	each	0	1
Diameter of Extraction Well Borehole	inches	N/A	8
Number of Monitoring Wells	each	1	2
Diameter of Monitoring Well Borehole	inches	4	8
Recirculation System Required	Yes/No	No	Yes
Treatment Timeframe	months	6	12
Rebound Assessment Period	months	N/A	6

7.3.2 Rapid Assessment Approach

The RA alternative assumes that one injection and one monitoring well will be installed in the source area as shown in Figure 7.2. The alternative will be operated as it was at CPP, discussed earlier in this document, with an operational period of six months.

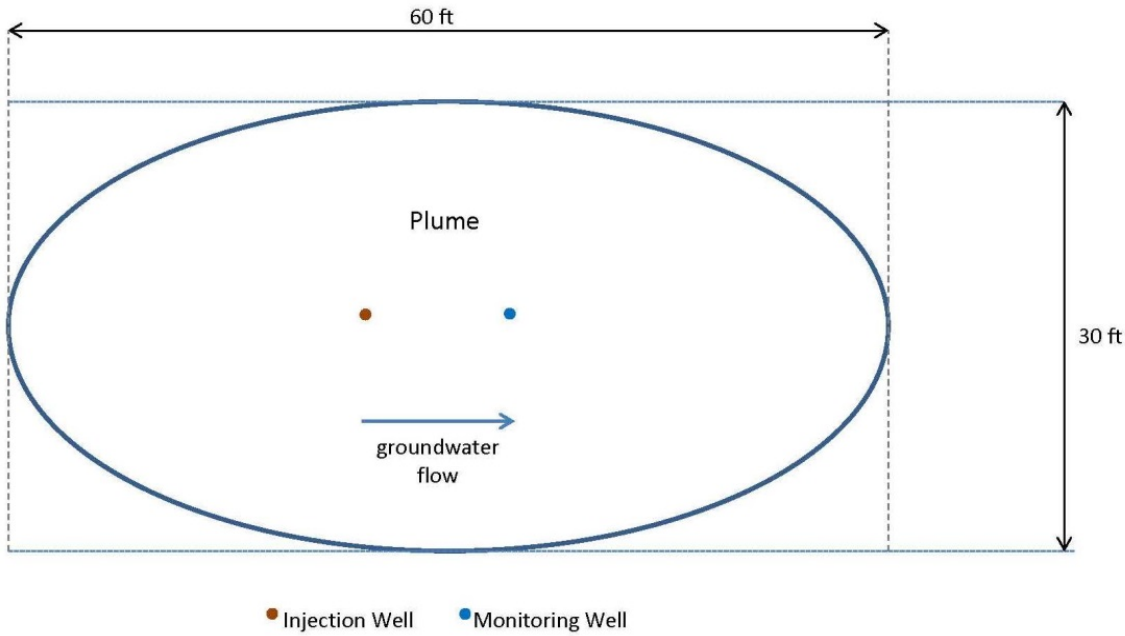


Figure 7.2. Rapid Assessment Technology Approach

As summarized in Table 7.3, the estimated total cost for this alternative over the one-year project duration is $284,400. The capital cost including design, work plan, installation of the two bedrock wells, site characterization (including packer testing, pump testing, borehole dilution testing, and tracer testing), construction of the water delivery system, system start up and testing, data evaluation, and final reporting is approximately $214,000. The cost of O&M is estimated at approximately $45,900 for the six months of active treatment. The O&M costs include the labor associated with system O&M, equipment repair and replacement, utilities/fuel, waste disposal, and well abandonment. Groundwater monitoring costs are estimated at approximately $24,500 over the six months of testing. The estimate assumes that five groundwater monitoring events occur during that time: one baseline round followed by three monthly rounds and one quarterly round.

This alternative ranks lower in estimated total remedy cost (see Table 7.4) when compared to the bioremediation recirculation pilot test (see Section 7.3.3), mainly due to the lower capital costs associated with the well drilling and system components, as well as the lower O&M and groundwater monitoring costs.

Table 7.3. Cost Estimates for Treatment Approaches

Rapid Assessment Approach			Bioremediation Recirculation Pilot Study		
Capital Costs		*$214,000*	*Capital Costs*		*$364,000*
System Design	$8,000		**System Design**	$15,000	
Workplan	$15,000		**Workplan**	$15,000	
Site Planning/Permitting	$2,000		**Site Planning/Permitting**	$2,000	
Project Management	$31,200		**Project Management**	$62,400	
Well Installation			**Well Installation**		
Mobilization	$3,000		Mobilization	$3,000	
Oversight Labor	$6,000		Oversight Labor	$12,000	
Travel/Per Diem	$1,000		Travel/Per Diem	$2,000	
Subcontract Driller	$36,000		Subcontract Driller	$72,000	
Subcontract Surveyor	$3,000		Subcontract Surveyor	$3,000	
Materials/Consumables	$1,000		Materials/Consumables	$1,000	
Utilities/Fuel	$1,000		Utilities/Fuel	$1,000	
Waste Disposal	$2,000		Waste Disposal	$5,000	
Site Characterization			**Site Characterization**		
Packer/Pump/Dilution/Tracer Testing Labor	$28,000		Packer/Pump Testing Labor	$15,000	
Travel/Per Diem	$3,000		Travel/Per Diem	$3,000	
Geophysics	$5,000		Geophysics	$5,000	
Materials/Equipment	$6,000		Materials/Equipment	$6,000	
System Installation			**System Installation**		
Oversight Labor	$12,000		Oversight Labor	$24,000	
Travel/Per Diem	$2,000		Travel/Per Diem	$4,000	
Shed System	$10,000		Conex Box System	$75,000	
Subcontract System Install	$0		Subcontract System Install	$5,000	
Materials/Consumables	$1,000		Materials/Consumables	$1,000	
Utilities/Fuel	$3,000		Utilities/Fuel	$3,000	
System Start-Up Testing	$4,800		**System Start-Up Testing**	$9,600	
Data Evaluation/Final Report	$30,000		**Data Evaluation/Final Report**	$20,000	
Operation and Maintenance Costs		*$45,900*	*Operation and Maintenance Costs*		*$93,800*
Labor (System Operation)	$24,960		Labor (System Operation)	$49,920	
Labor (Data Management)	$6,240		Labor (Data Management)	$12,480	
Travel/Per Diem	$5,200		Travel/Per Diem	$10,400	
Subcontractor (well abandon)	$4,000		Subcontractor (well abandon)	$8,000	
Equipment/Parts	$500		Equipment/Parts	$1,000	
Materials/Consumables	$2,000		Materials/Consumables	$5,000	
Utilities/Fuel	$2,500		Utilities/Fuel	$5,000	
Waste Disposal	$500		Waste Disposal	$2,000	
Groundwater Monitoring Costs		*$24,500*	*Groundwater Monitoring Costs*		*$74,700*
Labor (Sample Crew)	$12,000		Labor (Sample Crew)	$43,200	
Analytical	$10,000		Analytical	$27,000	
Sampling Equipment	$2,500		Sampling Equipment	$4,500	
	TOTAL	*$284,400*		TOTAL	*$532,500*

7.3.3 Bioremediation Recirculation Pilot Study

The Bioremediation Recirculation System alternative assumes that one injection and one extraction well will be installed in the source area as shown in Figure 7.3, with two monitoring wells in between along the groundwater flow path. Groundwater will be recirculated between the extraction and injection wells, and substrate added periodically over a period of one year, after which time the system will be shut down and a six month-long rebound assessment period will commence.

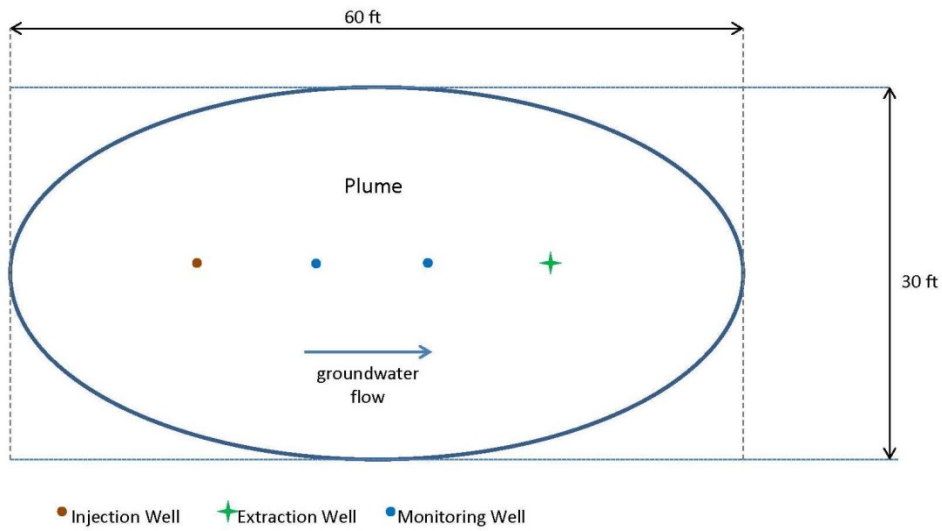


Figure 7.3. Bioremediation Recirculation Pilot Study

As summarized in Table 7.3, the estimated total cost for this alternative over two years is $532,500. The capital cost including design, work plan, installation of recirculation and monitoring wells, site characterization (including packer and pump testing), construction of the groundwater recirculation and amendment mixing systems, system start up and testing, data evaluation, and final reporting is approximately $364,000. The cost of O&M is estimated at approximately $93,800 for the one year of active treatment. The O&M costs include the labor associated with system O&M, equipment repair and replacement, substrate (electron donor/nutrient), utilities/ fuel, waste disposal, and well abandonment. Groundwater monitoring costs are estimated at approximately $74,700 over 18 months (12 months of active treatment and six months for rebound assessment). The estimate assumes that nine groundwater monitoring events occur during that time: one baseline round followed by three monthly rounds and five quarterly rounds.

This alternative has an estimated total remedy cost almost double that of the RA approach, mainly due to the higher capital costs associated with the well drilling and higher O&M and groundwater monitoring costs during the one-year active treatment period (see Table 7.4). ***It also is critical to note that the bioremediation recirculation study likely will not provide the mechanistic information that the RA approach provides.***

Table 7.4. Summary of Costs for Treatment Alternatives

Alternative	Capital Costs	O&M Costs	Groundwater Monitoring Costs	Total Alternative Costs
Rapid Assessment Approach	$214	$46	$25	$284
Bioremdiation Recirculation Pilot Test	$364	$94	$75	$533

Notes:
All costs are in thousands of dollars
O&M - Operation and Maintenance

Page Intentionally Left Blank

8.0 IMPLEMENTATION ISSUES

The primary issues related to implementation of the RA testing were as follows:

- ***Complexity of the fracture flow paths.*** Despite the close distance and identification of (apparently) connected fracture planes at the CPP site (as indicated by the hydraulic response during the short-term pump testing), injected tracer and amendments did not appreciably migrate to the shallow monitoring location. The likely cause was that the injected flow moved along preferential flow paths and did not intersect the shallow zone. Such flow complexities would complicate the rapid assessment testing and would likely require the use of a more complex forced-gradient approach (e.g., use of both an injection and extraction well, with the monitoring well located in between).

  – The complexity of the fracture flow path will impact the length scale of the RA test (i.e., the distance between the injection well and monitoring well). If this length scale is insufficient to capture a representative zone of the bedrock hydrogeology, then additional RA tests (using additional well pairs) may be needed to assess the site.

- ***Long-term injection into the injection well***. Delivery of water into the injection well was maintained using gravity feed coupled with a flow controller. While some variability in the flow was expected as the feed tank slowly drained, the flow controller required constant adjustment to maintain a relatively steady flow (much more adjustment than could be explained by the hydraulic head variability). For future implementation of this approach, use of a chemical feed pump to maintain a consistent low injection flow is recommended to overcome this issue. These pumps typically have low power requirements, which could be supplied via battery and/or solar sources. Additionally, they require limited maintenance and their operation, as well as water levels within the feed tank, could be remotely observed through solar-powered telemetry.

Page Intentionally Left Blank

9.0 REFERENCES

Annable, M.D., K. Hatfield, J. Cho, H. Klammler, B.L. Parker, J.A. Cherry, and P.S.C. Rao. 2005. Field-Scale Evaluation of the Passive Flux Meter for Simultaneous Measurement of Groundwater and Contaminant Fluxes. *Environ. Sci. Technol*. 39:7194-7201.

Boving, T.B. and P. Gratwohl. 2001. Tracer diffusion coefficients in sedimentary rocks: correlation to porosity and hydraulic conductivity. *J. Contam. Hydrol.* 53:85-100.

Chapman, S.W. and B.L. Parker. 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resour. Res*. 41: 1-16.

Chen, C., J. Puhakka, and J.F. Ferguson. 1996. Transformations of 1,1,2,2-tetrachloroethane under methanogenic conditions. *Environ. Sci. Technol.* 30:542-547.

Damgaard, I., P.L. Bjerg, J. Baelum, C. Scheutz, D. Hunkeler, C.S. Jacobsen, N. Tuxen, and M.M. Broholm. 2013. Identification of chlorinated solvents degradation zones in clay till by high resolution chemical, microbial and compound specific isotope analysis. *J. Contam. Hydrol.* 146:37-50.

Doughty, C. 2010. Analysis of three sets of SWIW tracer-test data using a two-population complex fracture model for matrix diffusion and sorption. Lawrence Berkeley National Laboratory, LBNL-3006E.

EA Engineering, Science & Technology, 1998. Final IR Program Site 07, Calf Pasture Point, Phase III Remedial Investigation, Volume I: Technical Report. Naval Construction Battalion Center Davisville, Rhode Island. September 1998.

EA Engineering Science & Technology, 1999. Final ROD. Site 07 – Calf Pasture Point.

Haggerty, R., S.W. Fleming, L.C. Meigs, and S.A. McKenna. 2001. Tracer tests in a fractured dolomite. 2. Analysis of mass transfer in single-well injection-withdrawal tests. *Water Resour. Res*. 37:1129-1142.

Hansen, M.W., T. MacHarg, J. Specht, and M. Pehlivan. 2004. Results from a Two-phase Extraction Pilot Study with Low-level Chlorinated Hydrocarbons and Aromatics. The Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, California). Paper 3C-14. May 24-27.

Huang, Q., H. Dong, R.M. Towne, T.B. Fischer, and C.E. Schaefer**.** 2014. Permanganate diffusion and reaction in sedimentary rocks. *J. Contam. Hydrol*. 159:36-46.

Hunkeler, D., Y. Abe, M.M. Broholm, S. Jeannottat, C. Westergaard, C.S. Jacobsen, R. Aravena, and P.L. Bjerg. 2011. Assessing chlorinated ethene degradation in a large scale contaminant plume by dual carbon-chlorine isotope analysis and quantitative PCR. *J. Contam. Hydrol*. 119:69-79.

Istok, J.D., J.A. Field, M.H. Schroth, B.M. Davis, and V. Dwarakanath. 2002. Single-well "Push-Pull" partitioning tracer test for NAPL detection in the subsurface. *Environ. Sci. Technol*. 36: 2708-2716.

Kauffman, M., A. Traviglia, J. Vernon, and J. LaChance. 2006. CVOC source identification through *in situ* chemical oxidation in fractured bedrock. *Contam. Soil Sediments Water* 7: 277-285.

Krug, T.A., C. Wolfe, R.D. Norris, and C.J. Winstead. 2009. Cost Analysis of In Situ Perchlorate Bioremediation Technologies. In Situ Remediation of Perchlorate in Groundwater. H.F. Stroo and C.H. Ward, Eds. SERDP/ESTCP Environmental Remediation Technology.

Lee, W. and B. Batchelor. 2002. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and magnetite. *Environ. Sci. Technol.* 36:5147-5154.

Lipson, D.S., B.H. Kueper, and M.J. Gefell. 2005. Matrix diffusion-derived plume attenuation in fractured bedrock. *Ground Water* 43:30-39.

Morrill, P.L., B.E. Sleep, D.J. Seepersad, M.L. McMaster, E.D. Hood, C. LeBron, D.W. Major, E.A. Edwards, and B.S. Lollar. 2009. Variations in expression of carbon isotope fractionation of chlorinated ethenes during biologically enhanced PCE dissolution close to a source zone. *J. Contam. Hydrol.* 110:60-71.

NJDEP. 2005. Field Sampling Procedures Manual. Online: http://www.nj.gov/dep/srp/guidance/fspm/.

Nordqvist, R., E. Gustafsson, P. Andersson, and P. Thur. 2008. Groundwater flow and hydraulic gradients in fractures and fracture zones at Forsmark and Oskarshamn. Swedish Nuclear Fuel and Waste Management Co. Report R-08-103. Online: http://www.skb.com/publication/1784919/R-08-103.pdf.

Pitrak, M., Mares, S., Kobr, M., 2007. A simple borehole dilution technique in measuring horizontal ground water flow. *Ground Water* 45, 89-92.

Schaefer, C.E., R.M. Towne, S. Vainberg, J.E. McCray, and R.J. Steffan. 2012. Assessment of chemical oxidation for treatment of DNAPL in fractured sandstone blocks. *J. Environ. Engin.*, 138:1-7.

Schaefer, C.E., R.M. Towne, V. Lazouskaya, M.E. Bishop, and H.Dong. 2012. Diffusive flux and pore anisotropy in sedimentary rocks. *J. Contam. Hydrol*. 131, 1-8.

Schaefer, C.E., R.M. Towne, D.R. Lippincott, V. Lazouskaya, T.B. Fischer, M.E. Bishop, and H. Dong. 2013. Coupled diffusion and abiotic reaction of trichloroethene in minimally disturbed rock matrices. *Environ. Sci. Technol.* 47:4291-4298.

Schaefer, C.E., R.M. Towne, D.R. Lippincott, P. Lacombe, M.E. Bishop, and H. Dong. 2015. Abiotic Dechlorination in Rock Matrices Impacted by Long-Term Exposure to TCE. *Chemosphere* 119, 744-749.

Schaefer, C.E., E.B. White, G.M. Lavorgna, and M.D. Annable. 2016. Dense nonaqueous-phase liquid architecture in fractured bedrock: implications for treatment and plume longevity. *Environ. Sci. Technol.* 50:207-213.

Schaefer, C.E., D. Lippincott, K. Hatfield, and H. Klammler. 2017. Rapid Assessment of Remedial Effectiveness and Rebound in Fractured Bedrock, ESTCP Project ER-2010330, Final Report. July 2017.

Singha, K., F.D. Day-Lewis, and J.W. Lane Jr. 2007. Geoelectrical evidence of bicontinuum transport in groundwater. *Geophys. Res Letters* 34:1-5.

Smith, R.L., R.W. Harvey, and D.R. LeBlanc. 1991. Importance of closely spaced vertical sampling in delineating chemical and microbiological gradients in groundwater studies. *J. Contam. Hydrol*. 7:285-300.

Sterling, S.N., B.L. Parker, J.A. Cherry, J.H. Williams, J.W. Lane Jr., and F.P. Haeni. 2005. Vertical cross contamination of trichloroethylene in a borehole in fractured sandstone. *Ground Water* 43:557-573.

Thomson, N.R., E.D. Hood, and G.J. Farquhar. 2007. Permanganate treatment of an emplaced DNAPL source. *Ground Water Monitor. Remed*. 27:74-85.

TRC, 1993. Draft Phase II Remedial Investigation Report – Volume I, Naval Construction Battalion Center, Davisville, Rhode Island. Contract No. N62472-85-C-1026. November 1993.

USEPA. 1991. Management of Investigation-Derived Wastes During Site Inspections. EPA/540/G-91/009. OERR Directive 9345.3-02. Online: https://nepis.epa.gov/Exe/ZyNET.exe/10001WN4.TXT?ZyActionD=ZyDocument&Client=EPA&Index=1991+Thru+1994&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n&Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFieldOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C91thru94%5CTxt%5C00000000%5C10001WN4.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Display=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL.

USEPA. 2006. Microfracture surface characterizations: implications for in situ remedial methods in fractured rock, EPA/600/R-05/121.

Wang, F., M.D. Annable, C.E. Schaefer, T.D. Ault, J. Cho, and J.W. Jawitz. 2014. Enhanced Aqueous Dissolution of a DNAPL Source to Characterize the Source Strength Function. *J. Contam. Hydrol*. 169, 75-89

West, M.R. and B.H. Kueper. 2010. Plume detachment and recession times in fractured rock. *Ground Water.* 48:416-426.

Zwank, L., M. Elsner, A. Aeberhard, and R.P. Schwartzenbach. 2005. Carbon isotope fractionation in the reductive dehalogenation of carbon tetrachloride at iron (hydr)oxide and iron sulfide minerals. *Environ. Sci. Technol.* 39:5634-5641.

APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Fax Email	Role in Project
Charles Schaefer	CDM Smith 110 Fieldcrest Avenue, #8 6th Floor Edison, NJ 08837	732-590-4633 direct 609-332-0346 cell schaeferce@cdmsmith.com	Principal Investigator
David Lippincott	CB&I Federal Services 17 Princess Road Lawrenceville, NJ 08648	609-895-5380 direct 609-605-0883 cell david.lippincott@aptim.com	Project Manager Project Geologist
Kirk Hatfield	Environmental School of Sustainable Infrastructure and Environment (ESSIE), University of Florida, 365 Weil Hall, Gainesville, FL 32611	352-392-9537 direct kirk.hatfield@essie.ufl.edu	Technical Support
Harald Klammler	Environmental School of Sustainable Infrastructure and Environment (ESSIE), University of Florida, 365 Weil Hall, Gainesville, FL 32611	haki@ufl.edu	Technical Support
Andrea Leeson	SERDP/ESTCP 901 N Stuart Street, Suite 303 Arlington VA 22203	703-696-2118 direct 703-696-2114 fax andrea.leeson@osd.mil	ESTCP Environmental Restoration Program Manager

ESTCP Office
4800 Mark Center Drive
Suite 17D08
Alexandria, VA 22350-3605
(571) 372-6565 (Phone)
E-mail: estcp@estcp.org
www.serdp-estcp.org