Final Technical Report

for

Reductive Anaerobic Biological In Situ Treatment Technology (RABITT) Treatability Testing

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Contents

Page

Figures v
Tables ix
Abbreviations and Acronyms xi

1.0 Introduction 1
1.1 Background 1
1.2 Official DoD Requirement Statements 2
1.3 Objectives of the Demonstration 3
1.4 Regulatory Issues 3
1.5 Previous Testing of the Technology 4

2.0 The Draft Protocol – Technology Description 5
2.1 Overview 5
2.2 Strengths and Weaknesses 6

3.0 Application of the Draft Protocol 7
3.1 Technical Approach 7
3.1.1 Site Selection 7
3.1.1.1 Technical Considerations 7
3.1.1.2 Regulatory Considerations 8
3.1.1.3 Political Considerations 8
3.1.2 The Process: Implementing the Draft Protocol 9
3.1.3 Assessment and Revision of the Protocol 11
3.2 Cape Canaveral Air Station – Facility 1381 12
3.2.1 Site Description – Facility 1381 12
3.2.2 Site Assessment/Selection – Facility 1381 12
3.2.3 Microcosm Testing – Facility 1381 13
3.2.3.1 Setup 13
3.2.3.2 Results 14
3.2.4 Field Testing – Facility 1381 15
3.2.4.1 System Design/Installation 15
3.2.4.2 Tracer Testing 19
3.2.4.3 Treatability Testing 20
3.2.4.4 Results 23
3.2.4.5 Conclusions 33
3.3 Alameda Point – Site 4 34
3.3.1 Site Description – Site 4 34
3.3.2 Site Assessment/Selection – Site 4 34
3.3.3 Microcosm Testing – Site 4 36
3.3.3.1 Microcosm Setup 36
3.3.3.2 Microcosm Results 36
3.3.4 Field Testing – Site 4 39

3.3.4.1 System Design/Installation 39
3.3.4.2 Tracer Testing 39
3.3.4.3 Treatability Testing 43
3.3.4.4 Results 45
3.3.4.5 Conclusions 59
3.4 Fort Lewis – East Gate Disposal Yard 60
3.4.1 Site Description – East Gate Disposal Yard 60
3.4.2 Site Assessment/Selection – East Gate Disposal Yard 61
3.4.3 Microcosm Testing – East Gate Disposal Yard 63
3.4.3.1 Microcosm Setup 63
3.4.3.2 Microcosm Results 64
3.4.4 Field Testing – East Gate Disposal Yard 67
3.4.4.1 System Design/Installation 67
3.4.4.2 Tracer Testing 68
3.4.4.3 Treatability Testing 70
3.4.4.5 Results 72
3.4.4.5 Conclusions 87
3.5 Camp Lejeune – Site 88 88
3.5.1 Site Description – Site 88 88
3.5.2 Site Assessment/Selection – Site 88 88
3.5.3 Microcosm Testing – Site 88 89
3.5.3.1 Microcosm Setup 89
3.5.3.2 Microcosm Results 92
3.5.4 Field Testing – Site 88 95
3.5.4.1 System Design/Installation 95
3.5.4.2 Tracer Testing 95
3.5.4.3 Treatability Testing 99
3.5.4.5 Results 99
3.5.4.5 Conclusions 116

4.0 Performance Assessment 119
4.1 Overview of Field Results 119
4.2 Overview of Microcosm Results 120
4.3 Microcosm Testing versus Field Testing 124

5.0 Revising the Draft Protocol 127
5.1 Technical Approach 127
5.2 Individual Protocol Components 127
5.2.1 Preliminary Site Assessment 127
5.2.1.1 Project Goals 128
5.2.1.2 Site History and Existing Data Review 128
5.2.1.3 Development of Conceptual Model 128
5.2.1.4 Site Potential 128

5.2.2 Component 2: Selecting a Testing Method – Microcosm versus Field Testing 129
5.2.3 Component 3a: Microcosm Testing 129
5.2.4 Component 3b: Field Testing 130
5.2.4.1 Selecting a Testing Location 130
5.2.4.2 Administrative Preparations 132
5.2.4.3 System Design 132
5.2.4.4 Electron Donor Selection.... 135
5.2.4.5 Field System Installation 135
5.2.4.6 Tracer Testing.... 136
5.2.4.7 Treatability Testing.... 136
5.2.4.8 Data Analysis.... 136

6.0 Cost Assessment 138
6.1 Microcosm Testing Option.... 138
6.2 Field Testing Option.... 139
6.3 Cost Drivers and Potential Cost Impacts.... 140
6.3.1. Cost Variables for Microcosm Testing....140
6.3.2 Cost variables for Field Testing 140
6.4 Cost Comparison 141

7.0 Regulatory Issues 142

8.0 Technology Implementation 143
8.1 DoD Need.... 143
8.2 Transition 143

9.0 References.... 145

Appendix A: Points of Contact A-1
Appendix B: Data Archive and Demonstration Plans ....CD-ROM
Appendix C: DoD Requirement Statements ....CD-ROM
Appendix D: Draft RABITT Protocol ....CD-ROM

Figures

Figure 3-1. RABITT Decision Flowchart....10
Figure 3-2. Generic RABITT System Design 11
Figure 3-3. Results from CCAS Microcosm Set 2, for A Bottle (5D-I) Fed 3mM Lactate + 20 mg/L YE + 0.05 mg/L B_{12} 16
Figure 3-4. Plan View of RABITT Demonstration Site at Facility 1381, Cape Canaveral Air Station, Florida 17

Figure 3-5. Cross-Sectional View of the Subsurface RABITT Test System Components at Facility 1381, Cape Canaveral Air Station, Florida 18
Figure 3-6. Facility 1381 System Well Design Schematic; Cape Canaveral Air Station, Florida 19
Figure 3-7. Bromide Tracer Testing Results from Facility 1381, Cape Canaveral Air Station, Florida 21
Figure 3-8. Average Chloroethene and Ethene Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 25
Figure 3-9. Average Dissolved Gas Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 27
Figure 3-10. Average Organic Acid Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 28
Figure 3-11. Average pH and Alkalinity Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 29
Figure 3-12. Average Dissolved Oxygen and Ferrous Iron Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 29
Figure 3-13. Average Nitrate, Nitrite, and Ammonia Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 30
Figure 3-14. Average Sulfate Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 30
Figure 3-15. Average Chloride Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 31
Figure 3-16. Average Dissolved Organic Carbon Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 32
Figure 3-17. Average Redox Potential and Groundwater Temperature at Facility 1381, Cape Canaveral Air Station, Florida 33
Figure 3-18. Results from Alameda Microcosm (5D-II) Fed 3mM Lactate + 20 mg/L YE + 0.05 mg/L B_{12} 38
Figure 3-19. Results from Alameda Microcosm (6-III) Fed 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} 38
Figure 3-20. Plan View of RABITT Demonstration at Site 4, Alameda Point, California 40
Figure 3-21. Bromide Tracer Testing Results from Site 4, Alameda Point, California 42
Figure 3-22. TCE Concentration Contours at Site 4, Alameda Point, California 46
Figure 3-23. *cis*-DCE Concentration Contours at Site 4, Alameda Point, California 48
Figure 3-24. VC Concentration Contours at Site 4, Alameda Point, California 50
Figure 3-25. Ethene Concentration Contours at Site 4, Alameda Point, California 52
Figure 3-26. Average Dissolved Ethene, Ethane, and Methane Concentrations at Site 4, Alameda Point, California 53
Figure 3-27. Average Organic Acid Concentrations at Site 4, Alameda Point, California 53
Figure 3-28. Average Field pH and Alkalinity Concentrations at Alameda Point, California 55
Figure 3-29. Average Dissolved Oxygen and Ferrous Iron Concentrations at Site 4, Alameda Point, California 55

Figure 3-30. Average Nitrate, Nitrite, and Ammonia Concentrations at Site 4, Alameda Point, California 56
Figure 3-31. Average Sulfate Concentrations at Site 4, Alameda Point, California 56
Figure 3-32. Average Chloride Concentrations at Site 4, Alameda Point, California 57
Figure 3-33. Average Dissolved Organic Carbon Concentrations at Site 4, Alameda Point, California 58
Figure 3-34. Average Redox Potential and Groundwater Temperature at Site 4, Alameda Point, California 59
Figure 3-35. Map Showing Location of the East Gate Disposal Yard Site at Fort Lewis, Washington 60
Figure 3-36. Results from Fort Lewis Microcosm (6-I) Fed 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} 66
Figure 3-37. Plan View of RABITT Demonstration Site at the EGDY, Fort Lewis, Washington 68
Figure 3-38. Bromide Tracer Testing Results from the EGDY, Fort Lewis, Washington 69
Figure 3-39. Suspected Alignment of Testing Zone with Respect to Background Groundwater Movement Illustrated by Bromide Tracer Concentration Contours 70
Figure 3-40. TCE Injection Concentration at the EGDY, Fort Lewis, Washington 73
Figure 3-41. TCE Concentration Contours at the EGDY, Fort Lewis, Washington 74
Figure 3-42. *cis*-DCE Concentration Contours at the EGDY, Fort Lewis, Washington 76
Figure 3-43. VC Concentration Contours at the EGDY, Fort Lewis, Washington 78
Figure 3-44. Average Methane, Ethane, and Ethene Concentrations at the EGDY, Fort Lewis, Washington 79
Figure 3-45. Average Organic Acid Concentrations at the EGDY, Fort Lewis, Washington 81
Figure 3-46. Average pH and Alkalinity Concentrations at the EGDY, Fort Lewis, Washington 82
Figure 3-47. Average Dissolved Oxygen and Ferrous Iron Concentrations at the EGDY, Fort Lewis, Washington 82
Figure 3-48. Average Nitrate, Nitrite, and Ammonia Concentrations at the EGDY, Fort Lewis, Washington 83
Figure 3-49. Average Sulfate Concentrations at the EGDY, Fort Lewis, Washington 83
Figure 3-50. Average Chloride Concentrations at the EGDY, Fort Lewis, Washington 84
Figure 3-51. Average Dissolved Organic Carbon Concentration at the EGDY, Fort Lewis, Washington 86
Figure 3-52. Average Redox Potential and Temperature at the EGDY, Fort Lewis, Washington 86
Figure 3-53. Dechlorination and Methanogenesis in a Camp Lejeune Microcosm (6-III) Amended with 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} 93
Figure 3-54. Fate of Added Donor and Appearance of VFAs in a Camp Lejeune Microcosm (6-III) Amended with 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} 94

Figure 3-55. Plan View of RABITT Demonstration at Site 88, Camp Lejeune, North Carolina 96
Figure 3-56. Bromide Tracer Testing Contours from Site 88, Camp Lejeune, North Carolina 98
Figure 3-57. PCE Concentration in Injected Groundwater at Site 88, Camp Lejeune, North Carolina 101
Figure 3-58. PCE Concentration (μM) Contour Plots at Site 88, Camp Lejeune, North Carolina 102
Figure 3-59. TCE Concentration (μM) Contour Plots at Site 88, Camp Lejeune, North Carolina 103
Figure 3-60. *cis*-DCE Concentration (μM) Contours at Site 88, Camp Lejeune, North Carolina 105
Figure 3-61. Vinyl Chloride Concentration (μM) Contours at Site 88, Camp Lejeune, North Carolina 107
Figure 3-62. Ethene Concentration (μM) Contours at Site 88, Camp Lejeune, North Carolina 108
Figure 3-63. Average Dissolved Ethene, Ethane, and Methane Concentrations at Site 88, Camp Lejeune, North Carolina 109
Figure 3-64. Average Organic Acid Concentrations at Site 88, Camp Lejeune, North Carolina 111
Figure 3-65. Average Field pH and Alkalinity Concentrations at Site 88, Camp Lejeune, North Carolina 111
Figure 3-66. Average Dissolved Oxygen and Ferrous Iron Concentrations at Site 88, Camp Lejeune, North Carolina 112
Figure 3-67. Average Nitrate, Nitrite and Ammonia Concentrations at Site 88, Camp Lejeune, North Carolina 113
Figure 3-68. Average Sulfate Concentrations at Site 88, Camp Lejeune, North Carolina 114
Figure 3-69. Average Chloride Concentrations at Site 88, Camp Lejeune, North Carolina 115
Figure 3-70. Average Dissolved Organic Carbon Concentrations at Site 88, Camp Lejeune, North Carolina 116
Figure 3-71. Average Redox Potential and Groundwater Temperature at Site 88, Camp Lejeune, North Carolina 117
Figure 4-1. Results from Butyrate-Amended Camp Lejeune Microcosm (6-I) 123
Figure 4-2. Results from Yeast Extract-Amended Camp Lejeune Microcosm (4-I) 123
Figure 5-1. Revised Technical Approach 127
Figure 5-2. Schematic Diagram of Extract-Inject Field Testing System 133
Figure 5-3. Schematic Diagram of an Aboveground Circulation Field Testing System 134
Figure 5-4. Schematic Diagram of an In Situ Circulation Field Testing System 134

Tables

Table 3-1. RABITT Site Rating System Score Summary for Facility 1381, Cape Canaveral Air Station, Florida 13
Table 3-2. Bottle Sets for Microcosm Studies at Facility 1381, Cape Canaveral Air Station, Florida 14
Table 3-3. Summary of Microcosm Results from the Second Set of Bottles After 60 Days of Incubation 15
Table 3-4. Well Construction Details at Facility 1381, Cape Canaveral Air Station, Florida 18
Table 3-5. Tracer Testing Flowrates and Concentrations at Facility 1381, Cape Canaveral Air Station, Florida 20
Table 3-6. System Operating Parameters at Facility 1381, Cape Canaveral Air Station, Florida 23
Table 3-7. Sampling Dates and Sample Types at Facility 1381, Cape Canaveral Air Station, Florida 24
Table 3-8. Analytes Listed by Sample Type at Facility 1381, Cape Canaveral Air Station, Florida 24
Table 3-9. RABITT Site Rating System Score Summary for Site 4, Alameda Point, California 35
Table 3-10. Initial Characterization of Soil and Groundwater at Site 4, Alameda Point, California 36
Table 3-11. Primary Dechlorination Products in the Donor-Fed Alameda Point Microcosms 37
Table 3-12. Well Installation Details at Site 4, Alameda Point, California 39
Table 3-13. Tracer Testing Flowrates and Concentrations at Site 4, Alameda Point, California 41
Table 3-14. Stock Solution Pumping Rates, Concentrations and Target In Situ Concentrations at Site 4, Alameda Point, California 43
Table 3-15. Sampling Dates and Sample Types at Site 4, Alameda Point, California 44
Table 3-16. Analytes Listed by Sample Type at Site 4, Alameda Point, California 45
Table 3-17. RABITT Rating System Score Summary for the East Gate Disposal Yard at Fort Lewis, Washington 62
Table 3-18. Initial Characterization of EGDY Soil and Groundwater 63
Table 3-19. Primary Dechlorination Products in the Donor-Fed EGDY Microcosms 65
Table 3-20. RABITT System Well Specifications at the EGDY, Fort Lewis, Washington 67
Table 3-21. Sampling Schedule at the EGDY, Fort Lewis, Washington 71
Table 3-22. Laboratory Analytes at the EGDY, Fort Lewis, Washington 72
Table 3-23. Dissolved Hydrogen Concentrations at the EGDY, Fort Lewis, Washington 80
Table 3-24. Correlation of Dissolved Hydrogen Concentrations with Terminal Electron-Accepting Process 80
Table 3-25. RABITT Rating System Score Summary for Site 88, Camp Lejeune, North Carolina 90
Table 3-26. Initial Characterization of Camp Lejeune Soil and Groundwater 91

Table 3-27. Dechlorination Products in Camp Lejeune Microcosms Seeded with Material from 45 to 49 ft bgs 92
Table 3-28. Well Construction Details at Site 88, Camp Lejeune, North Carolina 95
Table 3-29. Tracer Testing Flow Rates and Concentrations at Site 88, Camp Lejeune, North Carolina 96
Table 3-30. Sampling Schedule at Site 88, Camp Lejeune, North Carolina 100
Table 3-31. Field and Laboratory Analytes at Site 88, Camp Lejeune, North Carolina 100
Table 3-32. Dissolved Hydrogen Concentrations at Site 88, Camp Lejeune, North Carolina 110
Table 4-1. Overview of Field Results 119
Table 4-2. Overview of Microcosm Results – Dechlorination Endpoints and Molar Conversions after 6 Months 122
Table 4-3. Comparison of Microcosm and Field Results at the Four Demonstration Sites 125
Table 5-1. Analyses Retained in the Revised Protocol 137
Table 6-1. Estimated Cost of Microcosm Testing Option 138
Table 6-2. Estimated Cost of Field Testing Option 139

ABBREVIATIONS AND ACRONYMS

AST	aboveground storage tank
atm	atmosphere(s)
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CCAS	Cape Canaveral Air Station
cis-DCE	*cis*-dichloroethene
CMS	corrective measures study
DO	dissolved oxygen
DOC	dissolved organic carbon
DoD	(U.S.) Department of Defense
DP	drive point
EBRD	enhanced biological reductive dechlorination
EGDY	East Gate Disposal Yard
ESTCP	Environmental Security Technology Certification Program
ETH	ethene
FDEP	Florida Department of Environmental Protection
fpd	feet per day
GPW	Geoprobe® well
GW	gradient well
HDPE	high-density polyethylene
HRT	hydraulic retention time
I.D.	inner diameter
IRP	Installation Restoration Program
ITRC	Interstate Technology Regulatory Cooperation (Work Group)
IW	injection well
MCL	maximum contaminant level
MNA	monitored natural attenuation
MP	monitoring probe
mV	millivolts
MW	monitoring well
MWR	Morale, Welfare and Recreation

NAPL	nonaqueous-phase liquid
NAS	Naval Air Station
NCWQS	North Carolina Water Quality Standards
ND	nondetect
PCE	perchloroethene
PES	Parsons Engineering Service
POL	petroleum, oil and lubricant
ppb	parts per billion
ppm	parts per million
PVC	polyvinyl chloride
PZ	piezometer
RABITT	reductive anaerobic biological in situ treatment technology
RCRA	Resource Conservation and Recovery Act
RFI	RCRA Facility Investigation
RI	Remedial Investigation
SVOC	semivolatile organic compound
SW	supply well/system well
TCA	trichloroethane
TCE	trichloroethene
U.S. EPA	United States Environmental Protection Agency
UIC	Underground Injection Control
UST	underground storage tank
VC	vinyl chloride
VOC	volatile organic compound
YE	yeast extract

1.0 Introduction

1.1 Background

The chemical properties of the chlorinated solvents perchloroethene (PCE) and trichloroethene (TCE) make them particularly difficult groundwater contaminates to remediate. Both are relatively insoluble and hydrophobic; consequently, these compounds tend to form ganglia of nonaqueous-phase liquid (NAPL) and sorb to subsurface organic material. Their oxidized nature makes them resistant to aerobic biodegradation. Conventional pump-and-treat systems are ineffective because they are limited by the slow dissolution of these contaminants into the aqueous phase. The difficulty in pumping PCE and TCE to the surface for treatment has resulted in a search for an effective in situ treatment alternative. One promising alternative is enhanced in situ biologically catalyzed reductive dechlorination.

Laboratory research and field observations have shown that PCE and TCE may be reductively dechlorinated to ethene by microorganisms indigenous to contaminated environments (DiStefano et al. 1991; Major et al. 1991). These findings led to the rapid development of a variety of cleanup technologies that seek to exploit the remedial capabilities of these microorganisms. Although each of these technologies has distinguishing features, they all attempt to stimulate the dechlorination of chloroethenes by supplying electron-donating substrate to indigenous anaerobic microorganisms. There may be differences in the selected electron donor or how it is applied, but the underlying process is fundamentally the same.

Although enhanced biological reductive dechlorination (EBRD) shows great potential to effectively treat chlorinated solvent plumes, it is seldom employed. Often, those responsible for implementing site cleanups do not have a complete understanding of the reductive dechlorination process, and individuals that do are frequently left with uncertainty regarding the outcome of such a remedial strategy. Even at sites with laboratory and/or field data that strongly suggest a positive outcome, the best method to apply this type of in situ approach has not been clear.

Despite concerns regarding its application, EBRD still promises to be a very cost-effective tool for remediating sites contaminated with chloroethenes. It was envisioned that a standardized protocol might serve to alleviate concerns and foster its use at favorable sites while preventing its implementation at inappropriate sites. This led to the development of a draft technical protocol entitled, "*A Treatability Test for Evaluating the Potential Applicability of the Reductive Anaerobic Biological In Situ Treatment Technology (RABITT) to Remediate Chloroethenes*" (Battelle, 1997). This document, which would become more commonly known as the RABITT protocol, presents detailed instructions for assessing the applicability of in situ enhanced biological reductive dechlorination at a specific site.

The RABITT protocol was written by a multidisciplinary team of scientists and engineers and underwent a detailed peer review. To assess the utility of various protocol components and its overall effectiveness, the protocol was field-tested at four sites. The results of those

demonstrations and their ramifications for the draft technical protocol are the subject of this report.

1.2 Official DoD Requirement Statements

The U.S. Department of Defense (DoD) has identified groundwater contaminated with chlorinated solvents as a significant environmental problem affecting its installations. The need for more cost-effective groundwater treatment technologies is described in six official DoD requirement statements. The statements, which are listed below, can be found in their entirety on the CD-ROM that accompanies this report.

1. Improved Remediation of Groundwater with Chlorinated Hydrocarbons and Other Organics
2. Solvents in Groundwater
3. Organics in Groundwater
4. Alternatives to Pump and Treat
5. Need for Development of In Situ Treatment Using Anaerobic Bacteria for TCE Degradation
6. Methods and Remedial Techniques are Needed to More Effectively Treat Groundwater Contaminated with Chlorinated Solvents Such as TCE, trichloroethane (TCA), and PCE.

The scope of the DoD's need and its ability to tap into large allocations of funding have led a diverse group of environmental vendors offering a wide variety of remedial technologies to heavily market the DoD at all levels. Many vendors offer recently developed technologies with lofty and sometimes questionable claims of treatment performance, but only limited cost-performance data. This, combined with the fact that many technologies are heavily influenced by site-specific conditions, makes the selection of the best remedial approach a challenging task.

The screening of promising technologies for overall cost-effectiveness and site-specific treatment performance can be accomplished through treatability testing, but the quality of results necessarily depends upon the quality of the test design. In many cases, treatability tests are designed, if not run, by the environmental vendor, which may introduce an undesirable conflict of interest. In addition, inconsistencies between testing methodologies can create large differences in the cost of testing and may make comparisons to other tests of the same technology very difficult. In light of these limitations, the DoD surmised that a well-developed standardized testing methodology may produce higher quality results with more predictable costs.

EBRD is a technology that showed a great deal of promise for efficiently treating groundwater contaminated with chlorinated solvents, but demonstration sites around the country were producing mixed results. The limitations of the technology were not clear, so its applicability at any given site was unknown. The DoD opted to invest in the development of a standardized

protocol for testing the technology's effectiveness at any site where it could be considered it as a remedial alternative.

Each of the six DoD requirement statements describes a need for the development of a more cost-effective method to remediate groundwater contaminated with chlorinated solvents. This project was designed to provide guidance and a screening process to determine the site-specific applicability of in situ biological treatment.

Most DoD personnel responsible for environmental cleanup are aware that in situ biological treatments are available, but these methods are used infrequently due to uncertainty about site-specific treatment performance. This project attempts to bridge that gap by providing DoD personnel with guidance on performing a relatively inexpensive, site-specific treatability test designed to determine the effectiveness of in situ biological treatment. DoD personnel would use test results to either select or reject in situ biological treatment based on an evaluation of its treatment effectiveness. Because in situ biological treatment regularly outperforms more commonly used techniques, an increase in the use of in situ biological treatment may represent a substantial advance in the remediation of chlorinated-solvent-contaminated groundwater at DoD facilities across the country.

1.3 Objectives of the Demonstration

This project consisted of three specific objectives. First, develop a draft technical protocol that describes in detail how to conduct a treatability test for enhanced anaerobic dechlorination. Second, apply the draft protocol at four sites contaminated with chlorinated ethenes. Third, finalize the draft protocol based on the site-specific test results.

The writing of the draft RABITT treatability test protocol was completed following a thorough peer review on February 23, 1998. The four sites selected for field demonstrations are listed below in the order that testing was performed.

1. Cape Canaveral Air Station, Florida
2. Alameda Point, California
3. Fort Lewis, Washington
4. Marine Corps Base Camp Lejeune, North Carolina.

The objective of each of the four individual demonstrations was to use the draft RABITT treatability test protocol to evaluate whether appropriate microbial populations and geochemical conditions existed or could be produced in situ to support the biological reduction of chloroethenes to ethene. To the extent possible, treatability testing was performed in accordance with the procedures outlined in the draft RABITT treatability test protocol.

1.4 Regulatory Issues

In 1976, the United States Environmental Protection Agency (U.S. EPA) designated PCE and TCE as priority pollutants. The Safe Drinking Water Act Amendments of 1986 strictly regulate both of these compounds; each has a maximum contaminant level (MCL) in drinking water of 5

parts per billion (ppb) (U.S. EPA, 1996). When concentrations of these compounds at a contaminated site are too high, remedial action is required to lower the concentration and reduce the risk to human health and the environment.

1.5 Previous Testing of the Technology

The EBRD process has been extensively researched over the past two decades, but the implementation of the process as a technology for site remediation is only in the developmental stages. More pilot-scale tests/demonstrations have been conducted where the dechlorination efficiency has been the focus of the efforts, with scale-up to full-scale implementations lagging. This is in part due to the attention given to monitored natural attenuation (MNA), a technology that earlier was thought to be more widely applied than is proving to be true. Once the realization was made that MNA was not applicable at all chlorinated solvent sites, the attention was refocused back onto engineered approaches.

The RABITT protocol describes a laboratory-based and a field-based test methodology that is used to screen sites for application of engineered EBRD. The draft protocol has been tested at four sites to collect the data needed to finalize the approach(es) described in the final version, and although in situ EBRD has been applied at several other sites, it is still considered an innovative approach.

2.0 The Draft Protocol – Technology Description

2.1 Overview

The draft RABITT protocol is an 84-page document that describes a multiple step process for examining the potential for achieving in situ enhanced biological reductive dechlorination at a site. The protocol includes laboratory microcosm and field test methods designed to evaluate the response of indigenous microorganisms to the addition of soluble electron donating substrates. Increased rates of degradation and/or a furthering in the extent of dechlorination demonstrate the enhancement of the reductive dechlorination process. The draft protocol was not written to describe a pilot-test that would yield scale-up data for application of the reductive dechlorination process in full-scale implementation. Such testing would require extensive aquifer characterization and modeling for effective electron donor delivery and in situ mixing, which is technology specific and beyond the scope of the protocol. Instead, the draft protocol was developed to determine if reductive dechlorination can be achieved by simply engineering a system to add electron donor, or if an alternative technical approach is required, such as bioaugmentation or a physical/chemical removal/destruction technology.

The draft protocol begins with a brief review of in situ biodegradation approaches and then provides a slightly more detailed discussion about microbially catalyzed reductive dechlorination. A description of a proposed treatability testing process follows the introductory material. The testing process includes five specific areas: a preliminary site assessment, testing preparations, microcosm testing, field testing, and data analysis. A final section discusses scale-up considerations. A complete version of the draft RABITT protocol is available on the Environmental Security Technology Certification Program (ESTCP) Web site at: http://www.estcp.org/documents/techdocs/ Rabitt_Protocol.pdf.

The draft protocol was developed based on the monitoring of all aspects of reductive dechlorination and, as such, is more expansive than necessary to evaluate the potential for in situ process enhancement. The intent of the protocol developers was to list all of the methods used by practitioners of technologies such as MNA, and then screen this list down to methods/ procedures that provided value for evaluating the potential for successful reductive dechlorination enhancement. It was assumed that it would be easier to justify the exclusion of specific elements based on collected data than it would be to incorporate new untested elements into the final protocol. For example, both laboratory microcosm and field testing were included in the draft protocol, even though it was understood that including both would result in a very expensive test. The objective of including both was to evaluate the strengths and weaknesses of each test as well as to make a comparison between the two approaches at the four sites and determine what value each test provided. The goal was to determine if one test was superior in all cases, or if elements of both were needed to assess the potential for successful enhancement of the reductive dechlorination process. The results from implementation of the draft protocol at four sites would be used to specify exactly which methods should be included in the final protocol.

Similarly, the draft protocol was written with a heavy dose of monitoring requirements that included the collection of groundwater samples every two weeks. At the time the protocol was drafted, it was assumed that this level of monitoring would not be required in the final version, but it was necessary in the draft version to ensure sufficient data was collected. Although this approach allowed a more thorough testing of the protocol itself, it did serve to considerably raise the costs of conducting the test described in the draft protocol.

The draft protocol was applied at four DoD sites with different hydrogeologies and contaminant profiles. The four sites included Facility 1381 at Cape Canaveral Air Station, Florida; Site 4 at Alameda Point, California; the East Gate Disposal Yard at Fort Lewis, Washington; and Site 88 at Marine Corps Base Camp Lejeune, North Carolina. The expansive nature of the draft protocol and the four sites resulted in the generation of a tremendous amount of data that were used to refine the draft protocol into a final version for implementation at DoD sites which have chlorinated solvent contamination and which for one or more reasons cannot achieve cleanup using MNA.

2.2 Strengths and Weaknesses

The main strength of the protocol is that it provides an inexpensive method for screening sites for application of enhanced reductive dechlorination. Unlike petroleum hydrocarbon degradation, reductive dechlorination is not guaranteed at all sites because of more "specialized" microbial and geochemical requirements. Application of the RABITT protocol precedes the more extensive and expensive procedures required for designing a full-scale technology that applies enhanced reductive dechlorination to prevent misapplication of reductive-based technologies at sites where complete reductive dechlorination cannot be achieved. It is inappropriate to select and design an in situ enhanced reductive dechlorination technology based on the hydraulics of electron donor delivery and mixing alone. The costs for aquifer testing, modeling, system design, and installation can be a significant portion of the remedial cost. Finding out that reductive dechlorination cannot be stimulated as required after the system has been installed would be unfortunate, especially when the application of the RABITT protocol would have provided this information prior to moving ahead with the technology at that site.

The main weakness of the RABITT protocol is the lack of scale-up data collected during testing. Although the draft protocol was originally written to provide only a yes/no decision to proceed with the application of enhanced reductive dechlorination, the tests also provide some useful information on lag times and degradation kinetics. The tests do not provide any of the aquifer characteristics data required to design a full-scale system. Obtaining such data is technology- and site-specific and requires experienced groundwater professionals to design and implement the tests to ensure that high-quality data is collected as needed to accurately model and design an effective remedial system.

3.0 Application of the Draft Protocol

3.1 Technical Approach

The technical approach used for this project consisted of three fundamental tasks. The first task was to identify and select candidate demonstration sites. The second task was to apply the draft protocol at each of the four selected demonstration sites. The third task was to evaluate the performance of the draft protocol at each of the four sites and revise the protocol based on those results.

3.1.1 Site Selection. The selection of candidate demonstration sites was influenced primarily by technical considerations, but regulatory and political factors also played a role. Candidate sites were initially evaluated based on information supplied by Base personnel in questionnaires. The questionnaires consisted of 33 questions that requested information on a variety of subjects including the contaminant profile, geochemistry, geology, logistics, and the regulatory environment.

3.1.1.1 Technical Considerations. Because it was desired to test the protocol under a variety of field conditions ranging from promising to more challenging, only a few technical requirements were imposed on candidate demonstration sites, and most of those involved cost or feasibility considerations. The imposed technical requirements are listed below.

1. Parent compound – only sites with PCE or TCE as the parent compound were considered because *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC) presumably would be formed.
2. Level of contamination – the concentration of the parent compound had to be greater than 1 ppm. This was required both to ensure that the disappearance of the parent compound could be tracked with a high degree of certainty, and to increase the probability of observing daughter products.
3. Hydraulic conductivity – the hydraulic conductivity at the site had to be sufficient to allow the manipulation of groundwater in situ ($\geq 10^{-4}$ cm/sec).
4. Depth to contamination – sites with shallow (<50 ft bgs) contaminant plumes were preferred to reduce drilling costs.
5. Geochemistry – the groundwater pH at a site had to fall within a range suitable for microorganisms. No specific range was imposed, but sites with a pH in the range from 5 to 9 were preferred.
6. Geology – relatively homogeneous areas with well-defined stratigraphy were preferred to ensure that the movement of injected fluids could be tracked and results accurately recorded.

7. Cocontaminants – sites with commingled radioactive contamination were excluded from consideration. Sites also were screened for high concentrations of heavy metals that might have affected microbial activity.

3.1.1.2 Regulatory Considerations. The field test described in the draft protocol specifies the extraction, amendment, and subsequent injection of nutrient-amended groundwater that is contaminated with chlorinated ethenes. This approach was selected after careful consideration of several alternatives because it allows mixing of added nutrients with the groundwater and prevents the simple displacement of contaminated groundwater with a clean injection solution. Although the technical arguments for conducting the demonstration in this manner may be strong, it was assumed that the regulatory community would have concerns regarding the injection of contaminated groundwater.

At the time the draft protocol was written, there was no consensus among regulators regarding the issue of reinjection. Although there appeared to be concessions in the federal regulations, which would allow the reinjection of contaminated groundwater as part of a remedial action, there was certainly no guarantee that the regulations would be interpreted in this way. For the protocol to function as a standardized document it had to be applicable to the entire United States, so an effort was made to conduct demonstrations in different U.S. EPA regions and under the jurisdiction of different state regulators. Conducting demonstrations in different parts of the country would provide precedents for this type of approach and hopefully pave the way for future uses of the technology.

The candidate site questionnaire contained several questions about the local regulatory environment. Base personnel were asked if regulators were open to demonstrations of innovative technologies and if the reinjection issue had been addressed. The underlying goal was to apply the protocol in different regulatory jurisdictions, but not in a location where protracted regulatory negotiations would be necessary.

The protocol was applied in four states (Florida, California, Washington, and North Carolina) and under the jurisdiction of three U.S. EPA Regions (4, 9, and 10). The greatest regulatory obstacles were encountered in the State of Florida, which has a statute banning the injection of contaminated fluids. After considerable regulatory negotiation it became clear that the protocol could not be applied as written, and the standardized testing design would need to be redesigned to comply with state law.

3.1.1.3 Political Considerations. In addition to demonstrating the protocol under various regulatory jurisdictions, it was considered important to attempt to interact with each of the four branches of the military to provide a precedent within each and help foster technology transfer. Army, Air Force, Navy and Marine Corps installations around the country were contacted and asked if they would be interested in hosting a demonstration. Assuming all technical and regulatory considerations were met, preference was given to Bases representing a branch of the military that had not yet hosted a demonstration. By the end of the project, the

protocol had been demonstrated successfully at installations operated by each of the four military branches.

3.1.2 The Process: Implementing the Draft Protocol. The step-by-step process described in the draft RABITT protocol was followed at each of the demonstration sites. The process consists of four basic phases, the preliminary site assessment, test preparations, microcosm testing, and field testing, with each phase separated by a decision point. Figure 3-1 shows the decision flowchart presented in the draft protocol, which outlines the basic procedure.

The first phase in the process was the preliminary site assessment, which makes up the first four steps in the decision flowchart, and consists of defining project goals, collecting and reviewing existing site data, developing a conceptual model, and evaluating the potential for stimulating reductive dechlorination based on project goals and collected information. Subsequent sections of this report present selected information collected during the preliminary site assessment for each of the four demonstration sites.

The draft protocol contains a site rating system that was used to classify sites based on their contaminant, hydrogeologic, and geochemical profiles. The system uses a standardized scoring system that assigns point values for specific objective parameters, such as the presence of daughter products and hydraulic conductivity. Resulting scores are ranked on a scale that ranges from the "highest potential for success" to "prohibitive." The site rating system was used at each of the four demonstration sites; the outcomes of each are presented in subsequent sections of this document.

The second phase in the process, test preparations, involved selecting a specific field-testing location, writing a site-specific demonstration plan, seeking regulatory approval, and performing any additional site characterization that may be necessary to fill in data gaps. During this phase, the generic field-testing system described in the draft protocol (see Figure 3-2) was customized to address site-specific conditions. For example, the length and alignment of the test zone were specified based on the speed and direction of groundwater flow to achieve a hydraulic retention time of approximately 30 days. Elements of the site-specific demonstration plans developed for each of the four demonstration sites, including the customized system designs and operational parameters, are included in subsequent sections of this document. Full versions of each of the demonstration plans are contained on the CD-ROM supplied with this report.

The third phase in the testing process was microcosm testing. It involved the collection and characterization of aquifer core material and groundwater from the specific field-testing location identified during the test preparation phase. Collected core material and groundwater were used to construct microcosms and screen electron donors for their ability to stimulate reductive dechlorination. Microcosms provided insight into the rate and extent of reductive dechlorination and the fate of added reducing equivalents for each electron donor tested. Results were used to select an electron donor for use in the field.

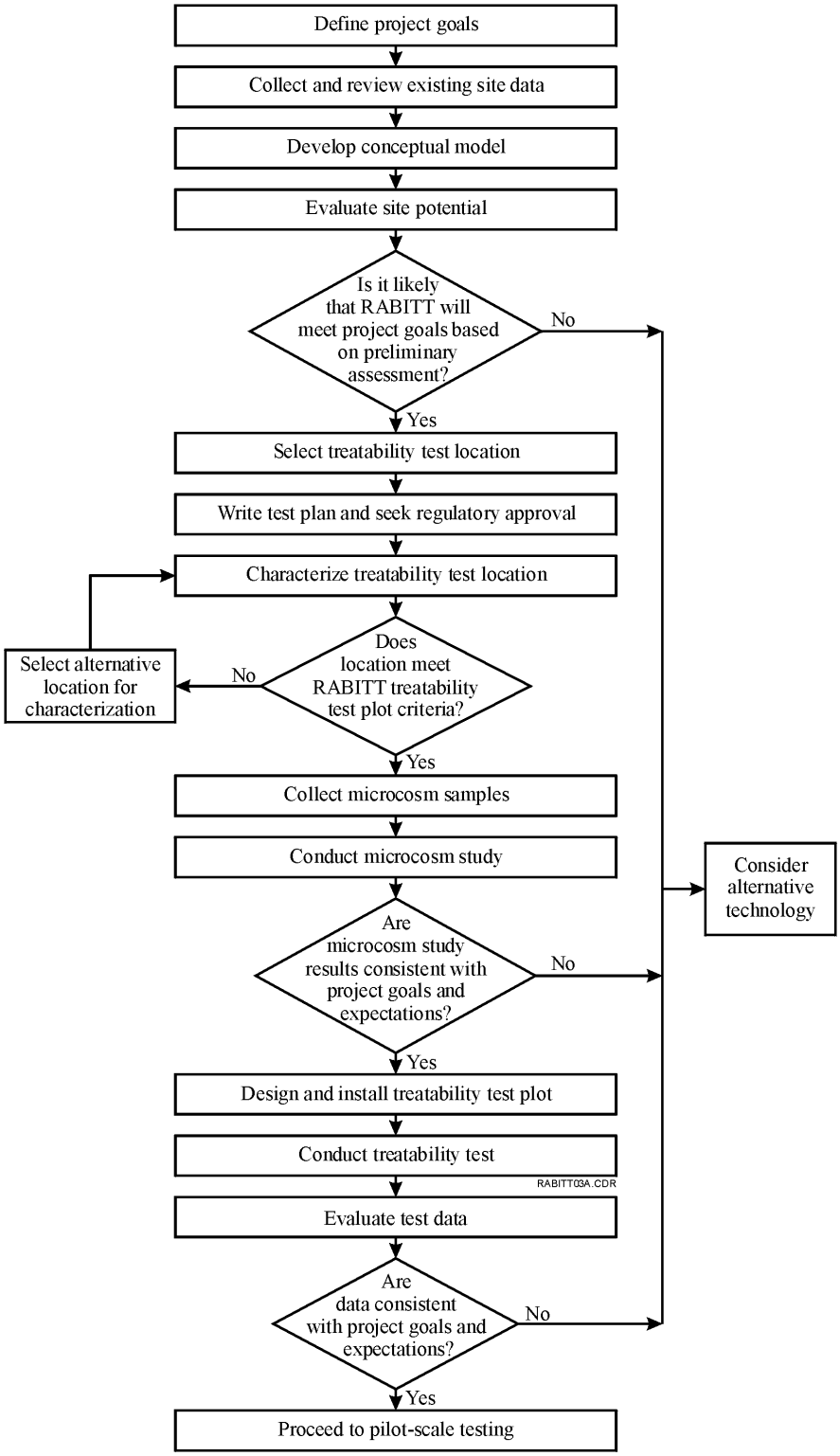


Figure 3-1. RABITT Decision Flowchart

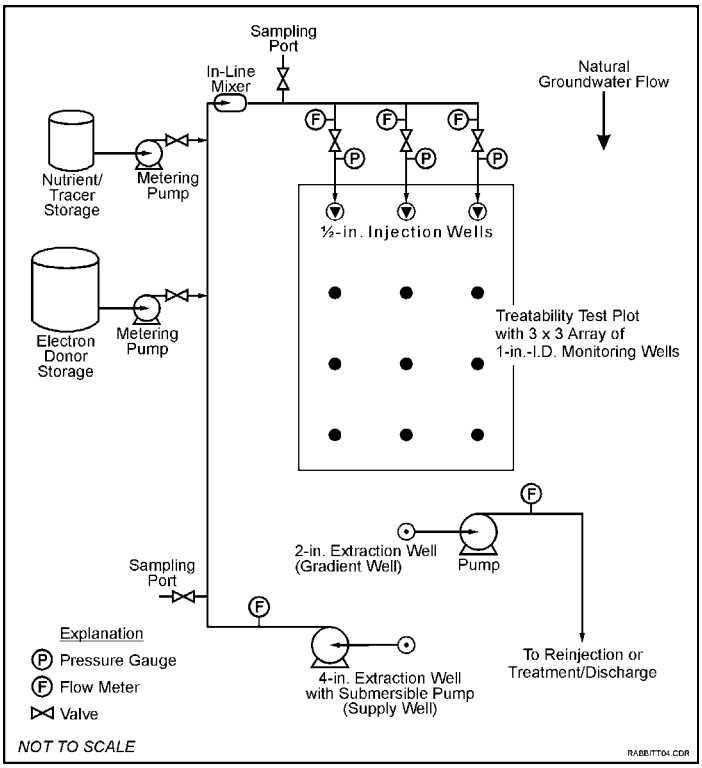


Figure 3-2. Generic RABITT System Design

The final phase in the draft protocol's implementation was field testing. It included installation of the field system, tracer testing and treatability testing. The drilling methods used to install subsurface components varied from site to site based on site-specific conditions. After all field system components had been installed, a round of groundwater samples was collected to determine baseline contaminant and geochemical conditions in the aquifer. Bromide tracer testing marked the beginning of fluid injection at each of the sites. The tracer test was used to determine an appropriate injection flowrate and to ensure injected fluids could be monitored in the subsurface. Once tracer testing established that injected fluid was moving through the testing location as predicted, electron donor injection could begin. Target in situ amendment concentrations were selected based on concentrations used in the microcosm study. Groundwater samples were collected approximately every two weeks for the duration of each field test. Site-specific installation and testing details are provided in Sections 3.2 through 3.5 of this report.

3.1.3 Assessment and Revision of the Protocol. The performance of the draft protocol at the four demonstration sites and its implications for the final version of the protocol are the subject of this report. The results from each demonstration are presented and subsequently used to explain proposed protocol revisions. The report answers fundamental questions such as:

1. Is it necessary to perform both microcosm and field testing, and if not, which method is preferable?
2. How often does a field test need to be monitored?
3. Which parameters should be monitored?

3.2 Cape Canaveral Air Station – Facility 1381

The first RABITT demonstration was conducted on the eastern coastline of central Florida at Cape Canaveral Air Station (CCAS). The demonstration system was installed just outside the fence line of Facility 1381, the Ordnance Support Facility, which is a somewhat isolated single-story building located approximately ¼ mile from the nearest permanent structure.

3.2.1 Site Description – Facility 1381. Facility 1381 was constructed in 1958 and operated from 1958 to 1968 as the Guidance Azimuth Transfer Building. An aerial photograph of the site dated March 13, 1967 shows two tanker trucks parked and numerous drums stored around the periphery of the facility (PES, 1997). An employee familiar with past operations at the facility stated that tanker trucks used to dump solvents in the woods around the site (PES, 1997).

From 1968 to 1977, Pan Am operated Facility 1381 as the In-Place Precision Cleaning Lab. Activities at the site included the cleaning of metal components in acid and solvent dip tanks, resulting in the generation of approximately 3,300 gallons of waste TCE per year from one parts dip tank (PES, 1997).

Since 1977 the U.S. Coast Guard has been operating the site as the Ordnance Support Facility (PES, 1997).

In 1997, PES completed a Resource Conservation and Recovery Act (RCRA) Facility Investigation (RFI) at Facility 1381. The results of this and previous investigations revealed a shallow 110-acre volatile organic compound (VOC) plume consisting primarily of TCE, DCE, and VC (PES, 1997). There is evidence that dechlorination of TCE to DCE and subsequently VC is occurring naturally; however, VOCs have been detected in a surface water body adjacent to the site (PES, 1997). This prompted the Florida Department of Environmental Protection (FDEP) and the U.S. EPA to require a corrective measures study (CMS) of various remedial options.

3.2.2 Site Assessment/Selection – Facility 1381. The selection of Facility 1381 for a RABITT demonstration was based on several criteria. First, the average concentration of TCE at the site was significantly greater than its detection limit, so contaminant reduction could be easily measured and documented. Second, the presence of *cis*-DCE and VC, daughter products of TCE degradation, indicated that microbially catalyzed dechlorination was already occurring at the site. This provided an opportunity to examine the potential for accelerating the process with a high probability of success. It also provided a positive control for microcosm testing results. Third, the subsurface at Facility 1381 was composed almost exclusively of sands, ideal for the

delivery of electron donor in situ. Fourth, both the water table and contamination were found at shallow subsurface depths. This minimized drilling and sampling costs. Fifth, the site's climate helped to maintain relatively warm groundwater temperatures and allowed fieldwork to be conducted throughout the year. Sixth, a project being conducted at Pinnellas Naval Air Station (NAS) in Florida provided a regulatory precedent in the state and U.S. EPA Region for the injection of electron-donating substrate into the subsurface.

The site rating system described in the draft RABITT protocol was applied to Facility 1381 to assess the site's potential for success and to allow the rating system to be evaluated after completing the demonstration. As expected, the rating system indicated that the conditions at Facility 1381 were favorable for enhancing microbial catalyzed reductive dechlorination. Average site conditions obtained during preliminary site characterization work were compared against criteria in the rating system and results are listed in Table 3-1 along with the corresponding rating score.

Table 3-1. RABITT Site Rating System Score Summary for Facility 1381, Cape Canaveral Air Station, Florida

Rating Parameter	Conditions at Facility 1381	Score
Contaminant Profile	Ethene present	25
Hydraulic Profile	$K = 10^{-3}$ cm/sec	25
Geochemical Profile		
Dissolved Oxygen	< 0.5 mg/L	3
Nitrate	Data not available	0
Hydrogen Sulfide	Data not available	0
Sulfate	> 20 mg/L	0
Redox potential	200 mV to –200 mV	0
Temperature	> 15°C	3
Dissolved Organic Carbon	< 10 mg/L	0
Bicarbonate Alkalinity	< 1 g/L	-1
pH	6.5-7.5	3
Methane	> 0.1 mg/L	3
Total Point Value		61

Facility 1381 scored a total point value of 61 out of 69 total possible points. The maximum total point value is typically 75, but the lack of nitrate and hydrogen sulfide data prevented the assignment of scores for those parameters, so they were given the default value of zero. The score of Facility 1381 fell into the range considered "Promising" in the RABITT protocol.

3.2.3 Microcosm Testing – Facility 1381

3.2.3.1 Setup. Two sets of microcosms were set up using groundwater and aquifer material from Facility 1381. Cores collected between February 23, 1998 and February 26, 1998

were used to assemble the first set of microcosms. Eleven soil cores were collected between existing wells GPW09 and GPW10 from a depth of 13 to 17 ft bgs in acetate sleeves. When microcosm results from this first set were essentially negative for dechlorination activity, a second set was prepared using material from a more promising location. The second set of microcosms was assembled from a second group of cores collected on 15 September 1998 and 17 September 1998 along a line between wells GPW06 and GPW11, and in an area bounded by wells GPW06, GPW07, GPW02, and GPW03. The second set of cores was collected from 15 to 17 ft bgs.

Microcosms were prepared in an anaerobic glovebox, using 50 g dry weight of aquifer material and 100 g of site groundwater amended with 0.8 mg resazurin/L. Typical VOC contents of the second set of microcosms upon setup were: TCE, 5 µmol/bottle; *cis*-1,2-DCE , 10 µmol/bottle; *trans*-1,2-DCE, trace or not detected; 1,1 DCE, 0.1 µmol/bottle; VC, 0.4 µmol/bottle; ETH, 0.03 µmol/bottle; and methane, 4.5 µmol/bottle. Neat TCE was added to result in a TCE content of approximately 23 µmol/bottle. Bottles were shaken overnight after TCE addition, analyzed to get a Day 0 value, assigned to their respective bottle sets, then donors and amendments were added in the amounts described in the protocol (Table 3-2). Bottles were incubated inverted in the dark at 24°C.

Table 3-2. Bottle Sets for Microcosm Studies at Facility 1381, Cape Canaveral Air Station, Florida

Bottle Set	Donor	Yeast Extract (20 mg/L)	Vitamin B_{12} (0.05 mg/L)
0	None (Autoclaved Groundwater 100 mL)	No	No
1	None (Autoclaved, Abiotic Control)	No	No
2	None (Biotic Control)	No	No
3	None	Yes	Yes
4	Yeast Extract (200 mg/L)	No	Yes
5 (A)	Lactate (3 mM)	No	No
5 (B)	Lactate (3 mM)	Yes	No
5 (C)	Lactate (3 mM)	No	Yes
5 (D)	Lactate (3 mM)	Yes	Yes
6	Butyrate (3 mM)	Yes	Yes
7	Lactate/Benzoate Mixture (1.5 mM each)	Yes	Yes
8	Propionate (1.5 mM)	Yes	Yes

3.2.3.2 Results. After 78 days of incubation, only two bottles in the first set of microcosms had begun exhibiting dechlorination. Of the two bottles exhibiting dechlorination, one was amended with 1.5 mM lactate, 1.5 mM benzoate, yeast extract, and vitamin B_{12}, and the other contained 3 mM lactate and vitamin B_{12}. Both bottles had reduced all TCE to *cis*-1,2-DCE but no other dechlorination products were produced. Disappointed with these results and suspicious that the cores had not been taken from a particularly promising location, plans were made to take a second set of cores from an alternative location.

In contrast with the first set of microcosms, the second set showed dechlorination from TCE to *cis*-1,2-DCE in every electron donor-amended bottle after only 60 days of incubation. Conversion of *cis*-1,2-DCE to VC and ethene depended on the electron donor added. Table 3-3 below summarizes some of the observations made after 60 days of incubation.

Table 3-3. Summary of Microcosm Results from the Second Set of Bottles After 60 Days of Incubation

Microcosm Amendments	Extent of Dechlorination
Yeast Extract (200 mg/L)	All TCE converted to *cis*-DCE with trace VC production
Propionate (1.5 mM)	All TCE converted to *cis*-DCE with trace VC production
Lactate (3 mM)	All TCE converted to *cis*-DCE and more than half of *cis*-DCE converted to VC
Butyrate (3 mM)	Complete conversion of TCE to VC and an order of magnitude increase in ethene concentration
Lactate/Benzoate mixture (1.5 mM each)	Complete conversion of TCE to VC and an order of magnitude increase in ethene concentration
Live Controls (no donor)	One bottle has converted TCE to *cis*-DCE
Killed Controls	No dechlorination or significant losses

The earlier onset and more complete dechlorination observed in the second set of microcosms persuaded team members to situate the center of the testing location just northwest of existing well GPW06. Although more complete dechlorination of TCE was observed with butyrate and a lactate/benzoate mixture, lactate alone was selected for use as the in situ electron donor because it exhibited dechlorination in both the first and second set of microcosms.

Figure 3-3 depicts results from a representative lactate-fed microcosm (Bottle 5D-I), which also received yeast extract (20 mg/L) and vitamin B_{12}. Note the reasonably good equivalents balance between lactate fed and products formed (principally acetate and propionate - methane, sulfide, and reduction products from TCE were minor by comparison). Neither sulfate reduction (ca. 40 µmol/bottle) nor methanogenesis (ca. 3 µmol/bottle) represented a significant sink for reducing equivalents supplied by lactate in these microcosms. Sulfide was measured at the end of the microcosm study, and the sulfide formed (ca. 60 µmol/bottle = 480 µeq/bottle) is shown as a vertical bar to the right of the equivalents-balance graph. The amount of sulfide formed was about 75% of the amount of sulfate measured in the microcosms at setup (ca. 80 mg/L sulfate = 80 µmol/bottle).

3.2.4 Field Testing – Facility 1381

3.2.4.1 System Design/Installation. Installation of the RABITT demonstration system at Facility 1381 began on February 3, 1999. It was not possible to use the standardized treatability test system described in the draft protocol because Underground Injection Control (UIC) legislation in the State of Florida prohibits the extraction and subsequent reinjection of contaminated groundwater. As a result, the field system was redesigned.

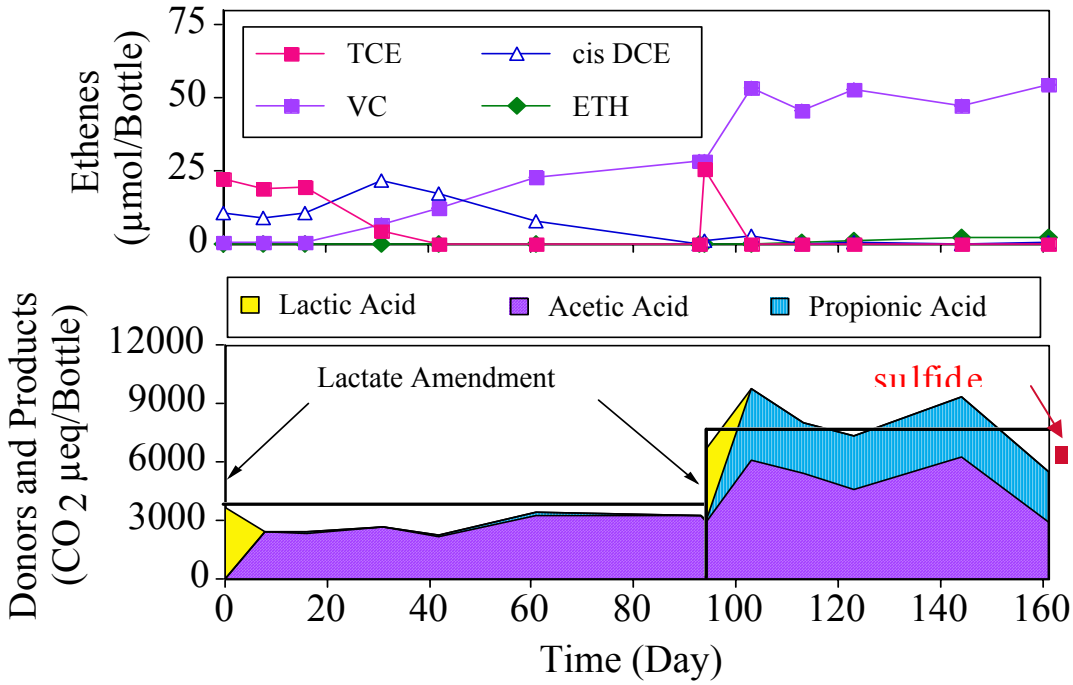


Figure 3-3. Results from CCAS Microcosm Set 2, for A Bottle (5D-I) Fed 3mM Lactate + 20 mg/L YE + 0.05 mg/L B_{12}

The modified system design had to reliably deliver electron donor solution and achieve subsurface mixing without displacing contaminated groundwater with "clean" injection solution or pumping contaminated groundwater from the aquifer. The system also needed to provide for extensive monitoring and hydraulic control.

The final modified system design was similar to that described by Kawakami et al., 1998. The system consisted of two 2-inch-diameter communicating system wells, a series of 13 trilevel groundwater monitoring probes, and six 1-inch monitoring wells. The relative locations of subsurface system components are shown in Figure 3-4.

A Geoprobe® rig was used to install the 13 trilevel groundwater-monitoring probes. Each probe consisted of a steel anchor point, a 6-inch-long, 1/2-inch-diameter stainless steel screen, and 1/8-inch stainless steel tubing, which extended from the probe to the surface. Groundwater samples were withdrawn from the probe through the stainless steel tubing. Figure 3-5 illustrates the vertical position of monitoring probes relative to other subsurface system components.

The communicating system wells had a dual screen design, with one operating in an upflow mode and the other in a downflow mode (see Figure 3-6). A hollow-stem auger was used to install the two system wells. The wells were placed close enough to affect each other with the effluent from one well feeding the influent of the other. This resulted in groundwater circulation

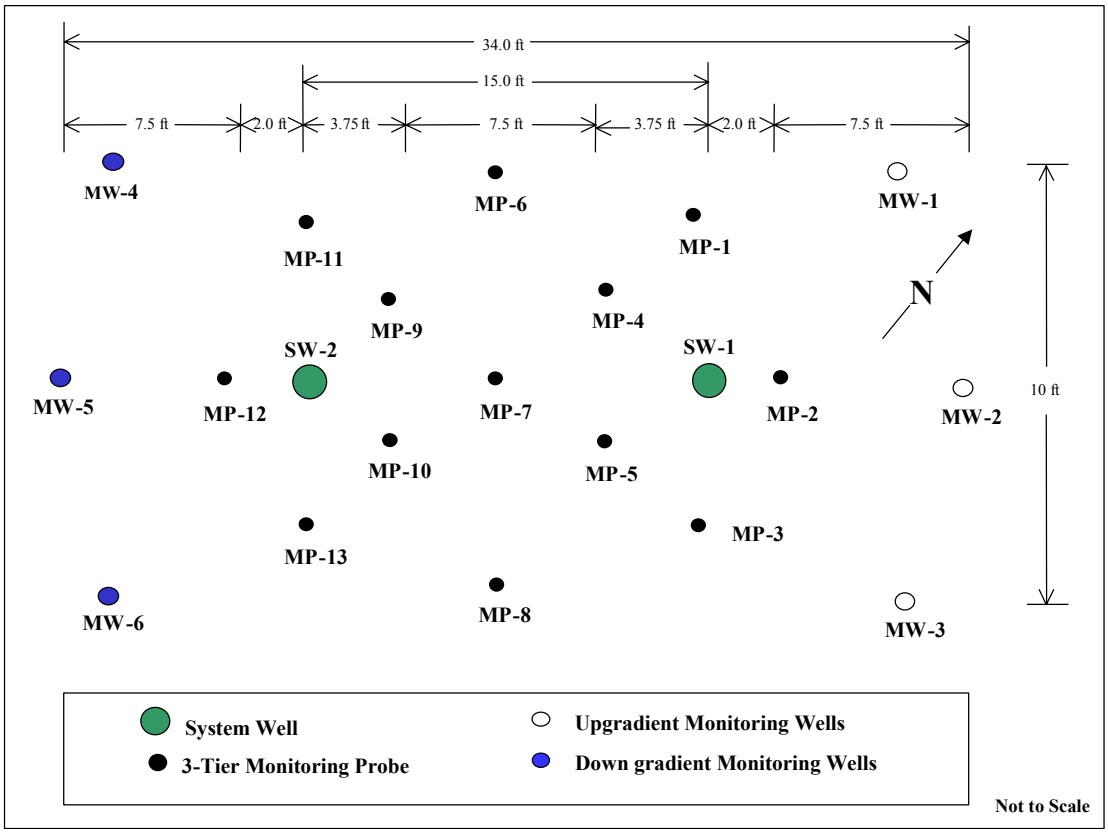


Figure 3-4. Plan View of RABITT Demonstration Site at Facility 1381, Cape Canaveral Air Station, Florida

that could be used to mix and distribute the electron donor/nutrient formulation. The trilevel groundwater monitoring probes were positioned around the treatment cell to provide the three-dimensional data required to track the tracer and added donor/nutrients, calculate mass reductions during treatment, and evaluate gains and losses from the cell through background groundwater migration.

The six monitoring wells were 1-inch-diameter, Schedule 40 polyvinyl chloride (PVC) wells with a 5-ft-long, 0.010 slot screen sections. These wells were driven into the ground at the indicated locations using a Geoprobe® rig. Table 3-4 provides the well construction details for all subsurface system components.

Once all subsurface system components had been installed and developed, a complete round of groundwater samples was collected and field measurement taken to examine baseline conditions within the testing zone. After sampling was completed, the fluid injection system was plumbed and brought on line to check for leaks and allow for general troubleshooting.

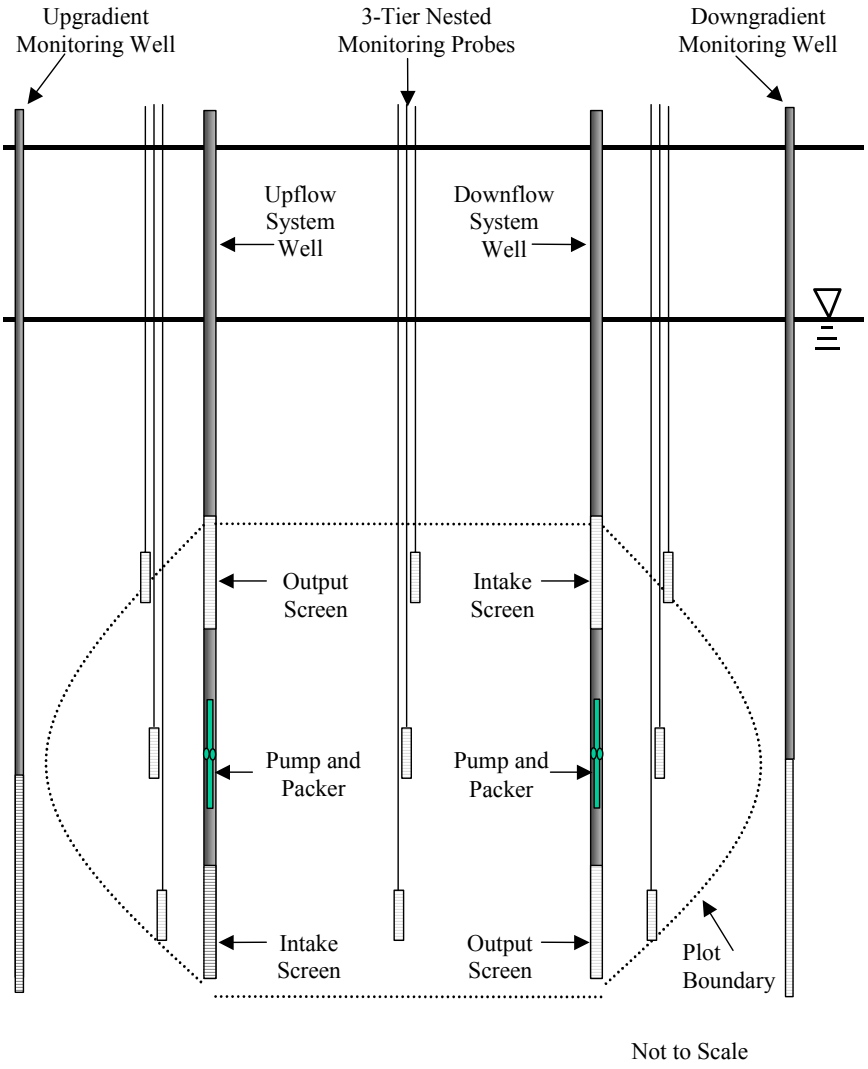


Figure 3-5. Cross-Sectional View of the Subsurface RABITT Test System Components at Facility 1381, Cape Canaveral Air Station, Florida

Table 3-4. Well Construction Details at Facility 1381, Cape Canaveral Air Station, Florida

Parameter	System Wells	Monitoring Wells	Groundwater Monitoring Probes
Diameter	2-inch	1-inch	½-inch
Screen Intervals (ft bgs)	10 ft to 12.5 ft 17.5 ft to 20 ft	15 ft to 20 ft	11 ft to 11.5 ft 14.75 ft to 15.25 ft 18.5 ft to 19 ft
Slot Size (inches)	0.010	0.010	0.0057
Material	PVC	PVC	Stainless Steel

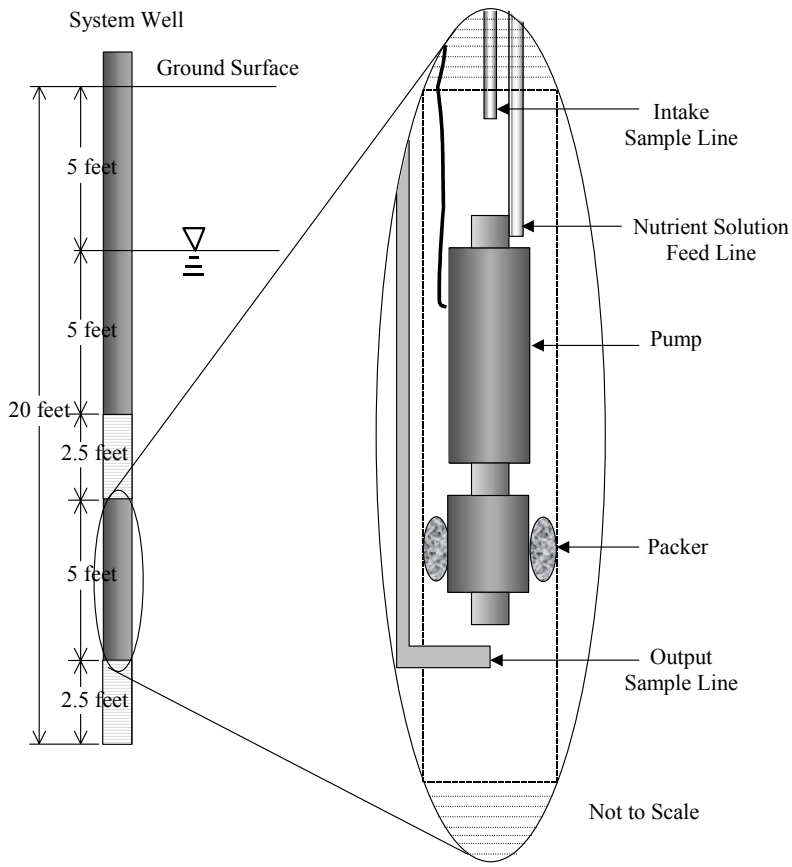


Figure 3-6. Facility 1381 System Well Design Schematic; Cape Canaveral Air Station, Florida

3.2.4.2 Tracer Testing. The modified system design employed at Facility 1381 required that tracer testing be conducted using concentrated slugs to prevent the accumulation of tracer in the testing zone. Ideally, the gradual loss of tracer from the system could be used to assess the rate of fluid exchange between the treatment volume and the surrounding area. The two dual screened system wells were used to add the slugs of tracer solution to the subsurface. Each system well had a dedicated metering pump that fed stock tracer solution to the intake side of the installed submersible pump.

Two slugs of a concentrated sodium bromide tracer solution were injected into the testing zone at Facility 1381. The first was added on February 17, 1999, and the second was added three days later when it became evident that the treatment volume would be considerable larger than expected. Table 3-5 outlines specific details from tracer testing operations such as flowrates and concentrations. Field measurements of subsurface bromide concentrations were taken using an ion-specific electrode.

Table 3-5. Tracer Testing Flowrates and Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

Operational Parameter	Initial Injection (February 17, 1999)	Second Injection (February 20, 1999)
System well pumping rate (each well)	3.8 L/min	3.8 L/min
Bromide stock solution feed rate	13 mL/min	13 mL/min
Bromide stock solution concentration	370 g NaBr/L	609.7 g NaBr/L
Total volume of stock solution injected	2 liters	4.85 liters
Total mass of bromide added	575 g Br^-	2,296 g Br^-
Delivery time	77 minutes	187 minutes
Wells used for injection	SW-1, SW-2	SW-1, SW-2

Figure 3-7 shows a three-dimensional time series of bromide concentration contours, which illustrate the movement of bromide through the testing zone. The contours shown have been sliced down the longitudinal axis of the testing zone to show the concentration profile at the center of the testing zone. System wells are illustrated by blue columns, and monitoring probes are identified by thin yellow lines. The small colored boxes indicate the sampling locations and the concentration range that was observed during that sampling event. Note that low concentration contours (below 10 mg/L) were excluded from the figure so the three-dimensional movement of tracer could be observed. Lower concentrations can be gauged by examining the small colored boxes that represent individual sampling locations. The data show the circulation of fluid through the testing zone and suggest that that the system wells achieve effective communication within two days of startup.

3.2.4.3 Treatability Testing

System Operation

Treatability testing at Facility 1381 involved the continuous injection of electron donor (lactic acid) into the subsurface for six months. Injection began on February 24, 1999 and ended on August 11, 1999. Lactic acid stock solutions (1.25 M) were prepared in two covered 15-gallon high-density polyethylene (HDPE) tanks using concentrated lactic acid and distilled water. Each solution was fed into its respective system well by a dedicated metering pump at approximately 1 mL/min. The feed line led directly into the intake of the submersible Grunfos™ pump installed in each system well to ensure that system well effluent was well mixed. Specific system operating parameters are outlined in Table 3-6.

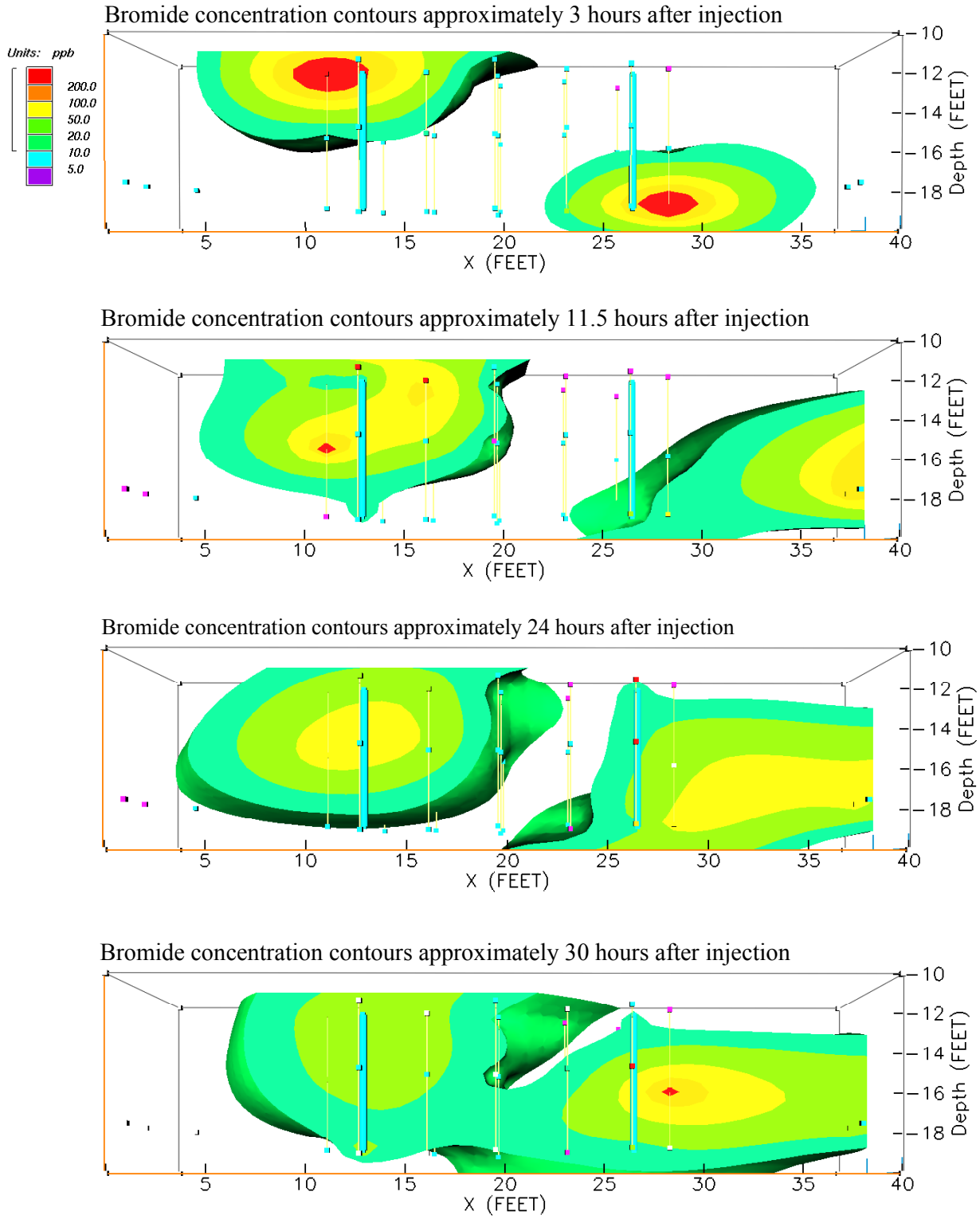
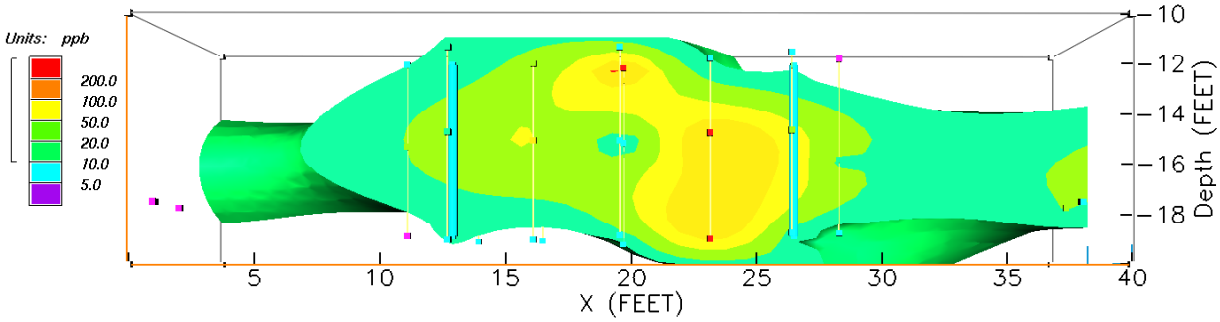
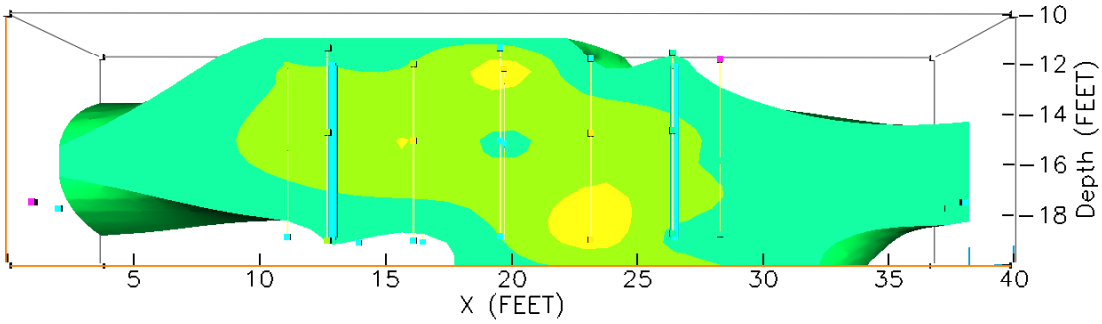


Figure 3-7. Bromide Tracer Testing Results from Facility 1381, Cape Canaveral Air Station, Florida

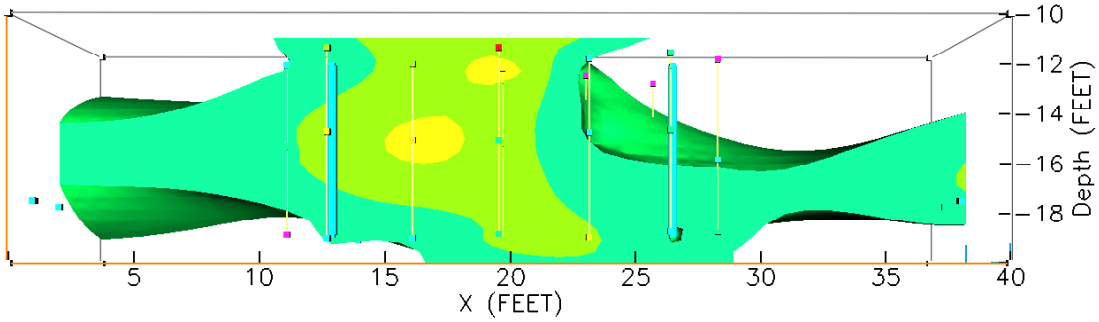
Bromide concentration contours approximately 45 hours after injection



Bromide concentration contours approximately 51 hours after injection



Bromide concentration contours approximately 72.5 hours after injection



Bromide concentration contours approximately 97 hours after injection

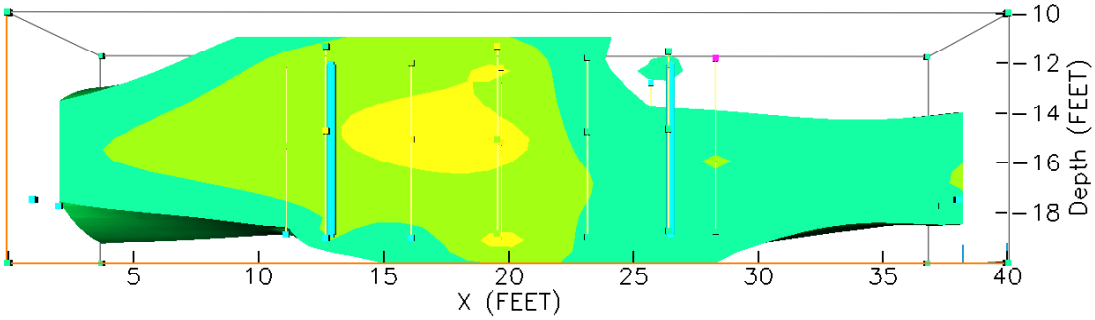


Figure 3-7. Bromide Tracer Testing Results from Facility 1381, Cape Canaveral Air Station, Florida (Continued)

Table 3-6. System Operating Parameters at Facility 1381, Cape Canaveral Air Station, Florida

Operational Parameter	Value
Total Initial System Pumping Rate	7.6 L/min
Each System Well	3.8 L/min
Electron Donor: Lactic Acid	
Target In Situ Concentration	2-6 mM
Stock Solution Concentration	1.25 M
Stock Solution Feed Rate	~1 mL/min

Neither yeast extract nor vitamin B_{12} were added to the injected electron donor solution. In addition, bromide tracer was not added during treatability testing.

System operation continued uninterrupted until system shutdown on August 11, 1999.

The RABITT demonstration at Facility 1381 included a very heavy load of sampling and analysis. Groundwater samples were collected every two weeks from each of 49 individual monitoring locations. Table 3-7 shows the specific sampling dates and sample types collected at Facility 1381, and Table 3-8 lists the specific analytes for each sample type. Additional information regarding analytical methods, container types, sample preservatives, and holding times can be found in the Cape Canaveral Demonstration Plan (Battelle and Cornell U., 1999a).

A peristaltic pump was used to pump groundwater from individual monitoring locations and into a flowthrough cell without exposing it to the atmosphere. The flowthrough cell was instrumented with probes which measured pH, temperature, redox potential, DO, and the bromide ion concentration. Groundwater was allowed to flow through the cell and into a waste container until redox potential and DO measurements stabilized. Once these measurements stabilized, all field measurements were recorded and groundwater samples were collected and prepared for shipment to the appropriate analytical laboratory.

3.2.4.4 Results. The RABITT demonstration at Facility 1381 generated a sizeable amount of data. Consider that 49 sampling locations were sampled on 14 occasions for up to 27 different parameters, yielding almost 14,000 individual data points. Consequently, overall system performance was assessed by constructing graphs of average data from the treatment zone. The data presented in these graphs represent the average total concentration from each of the 39 groundwater-monitoring probes and the 6 groundwater-monitoring wells. Data from inlet and outlet ports on the system wells are not included.

Table 3-7. Sampling Dates and Sample Types at Facility 1381, Cape Canaveral Air Station, Florida

Date	Elapsed Time (Weeks)	Field Data	Laboratory Analytes				
			VOCs	Dissolved Gases	Organic Data	Inorganic Data	DOC
Feb 11-16, 1999	0 (preinjection)	X	X	X	X	X	X
Feb 22-23, 1999	1 (injection begins)	X	X	X	X	X	X
Mar 10-11, 1999	3	X	X				
Mar 24-25, 1999	5	X	X	X	X	X	X
Apr 7-8, 1999	7	X	X				
Apr. 26-27, 1999	10	X	X	X	X	X	X
May 11-12, 1999	12	X	X				
May 18-19, 1999	13	X	X	X	X	X	X
Jun 1-2, 1999	15	X	X				
Jun 16-18, 1999	18	X	X	X	X	X	X
Jun 29-Jul 1, 1999	19	X	X				
Jul 14-15, 1999	21	X	X	X	X	X	X
Jul 27-28, 1999	23	X	X				
Aug 10-11, 1999	25	X	X	X	X	X	X

Table 3-8. Analytes Listed by Sample Type at Facility 1381, Cape Canaveral Air Station, Florida

Field Data	Laboratory Analytes				
	VOCs	Dissolved Gases	Organic Data	Inorganic Data	DOC
Water Level Redox potential pH Temperature Bromide DO Fe(II)	PCE TCE *cis*-DCE VC	Ethene Ethane Methane	Lactic acid Acetic acid Propionic acid	pH Conductivity Alkalinity Nitrate Nitrite Ammonia Chloride Sulfate Bromide	Dissolved organic carbon

DO = dissolved oxygen.
DOC = dissolved organic carbon.

A complete set of the raw data from the demonstration conducted at Facility 1381 is available on the CD-ROM supplied with this report.

Chloroethene Concentration Profiles

Figure 3-8 shows the average molar concentrations of TCE, *cis*-DCE, VC, and ethene within the testing zone at Facility 1381. Baseline samples were collected on Day 0, just prior to tracer testing. A second round of samples was collected on Day 7, one day prior to the initiation of electron donor injection. Although TCE, VC and ethene concentrations remained stable during tracer testing, *cis*-DCE concentrations dropped by 22%, from 113 µM to 88 µM. The reason for this change remains unknown.

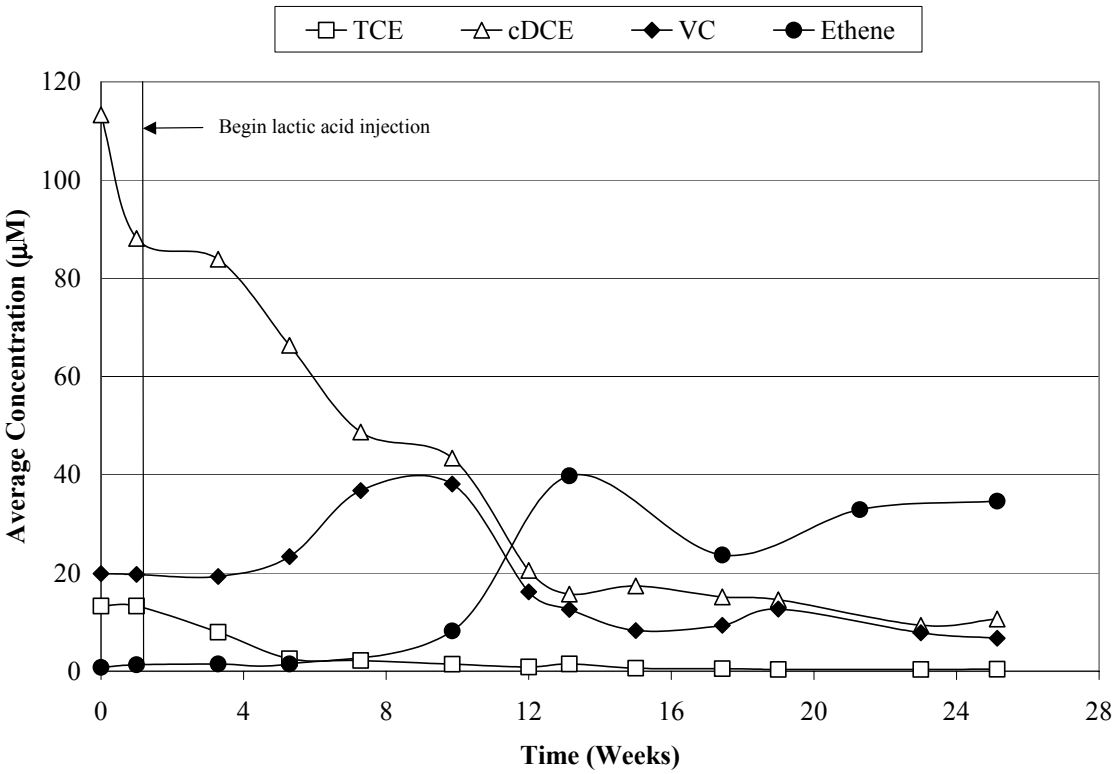


Figure 3-8. Average Chloroethene and Ethene Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

Once electron donor injection was initiated, TCE and *cis*-DCE concentrations dropped by 97% and 88%, respectively, and VC showed a transient increase indicative of biologically catalyzed reductive dechlorination. Ethene, which initially accounted for only 1% of the total molar concentration of ethene species, accounted for 66% of the total moles by the end of the demonstration. The overall changes in the contaminant profile provide strong evidence that reductive dechlorination had been stimulated and that the native microbiology was capable of converting TCE to the nonhazardous ethene endpoint.

The production of VC and ethene was not sufficient to account for the loss of the TCE and *cis*-DCE, resulting in a net loss of target compounds from the treatment volume. The average molar concentration of ethenes on Day 7 was 122.4 μM, but this had dropped to 52.4 μM by the end of the demonstration (Week 25). This corresponds to a molar concentration recovery of only 42.8%. Ethane was not produced in significant amounts. It was not expected that a mass balance would be retained within the treatment volume since hydraulic containment could not be assured. The conversion of TCE and *cis*-DCE to the lighter, more mobile, and more volatile gases VC and ethene is probably responsible for the marginal recovery, because VC and ethene could have escaped the treatment volume considerably faster than TCE or *cis*-DCE would have been introduced.

Dissolved Gases

The dissolved gases ethene, ethane, methane, and oxygen were monitored during the field demonstration to determine the extent of chloroethene degradation and assess microbiological conditions within the testing zone. Results from ethene, ethane, and methane samples are shown in Figure 3-9. Dissolved oxygen results are presented with other electron accepting species in a following section.

Ethene levels began to rise by Week 10, indicating that the conversion chloroethenes to the nonhazardous ethene endpoint was occurring. Ethene production began prior to the onset of methanogenesis, which started sometime after Week 13.

The average ethane concentration remained very low throughout the demonstration, indicating that reduction of ethene was not a significant process at the site. Low levels of ethane were occasionally observed at a few sampling locations within the heart of the testing zone.

Methane concentrations remained relatively stable for the first 13 weeks of the demonstration, indicating that methanogenesis was not initially the predominant terminal electron accepting process at the site. The steady increase in the average methane concentration that began midway through the demonstration corresponds to the depletion of sulfate from several sampling points within the core of the testing zone and signals a shift from sulfate reduction to methanogenesis. The levels of methane observed within the testing zone did remain relatively low (< 10 mg/L in all sampling points) indicating that high-rate methanogenesis was not consuming an excessive portion of added reducing equivalents.

Organic Acids

The concentrations of acetic, lactic, and propionic acids were tracked during the field demonstration to ensure that sufficient lactic acid was being injected and to examine the fate of added reducing equivalents. Figure 3-10 shows the average concentration of each of these acids within the testing zone. The injection concentration of lactic acid was approximately 3,000 μM throughout the demonstration.

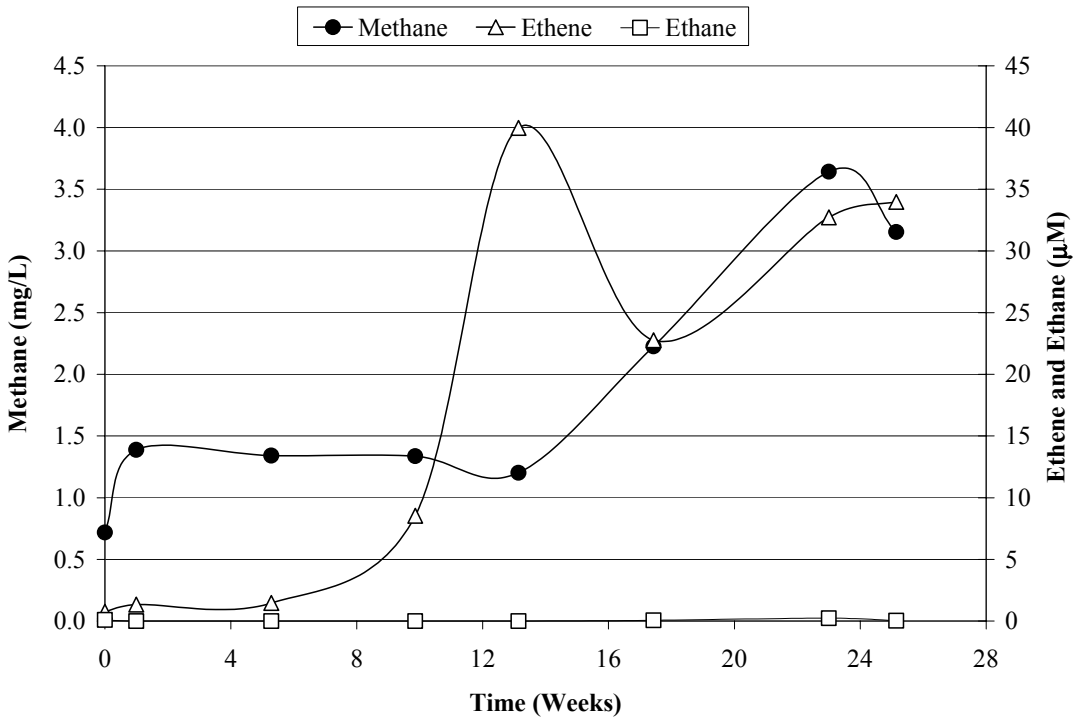


Figure 3-9. Average Dissolved Gas Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

Figure 3-10 shows that lactic acid was quickly consumed in the subsurface and that both acetic and propionic acids were produced and began to accumulate. These observations correlate well with the results from the microcosm study, which also showed that lactic acid was quickly consumed and that acetic acid and propionic acid were the primary fermentation products.

The concentration of lactic acid in the testing zone generally remained below detectable levels, but was apparently sufficient to drive the reductive dechlorination process without generating high levels of methane. The unusually high average lactic acid concentration observed during Week 23 resulted from very high levels found in four monitoring points located near the system well effluent screens. Monitoring points MP 12-19 and MP 5-11 had lactic acid concentrations of 22,800 µM and 12,200 µM, respectively. This was in stark contrast to most other monitoring points, which were typically below detection limits. It is unclear why lactic acid appeared to accumulate in some locations.

Inorganic Species

Several inorganic species were tracked throughout the field demonstration, including: pH, alkalinity, nitrate, nitrite, ammonia, sulfate, and chloride. Data for each of these species is described in the following subsections and is presented in Figures 3-11 through 3-15.

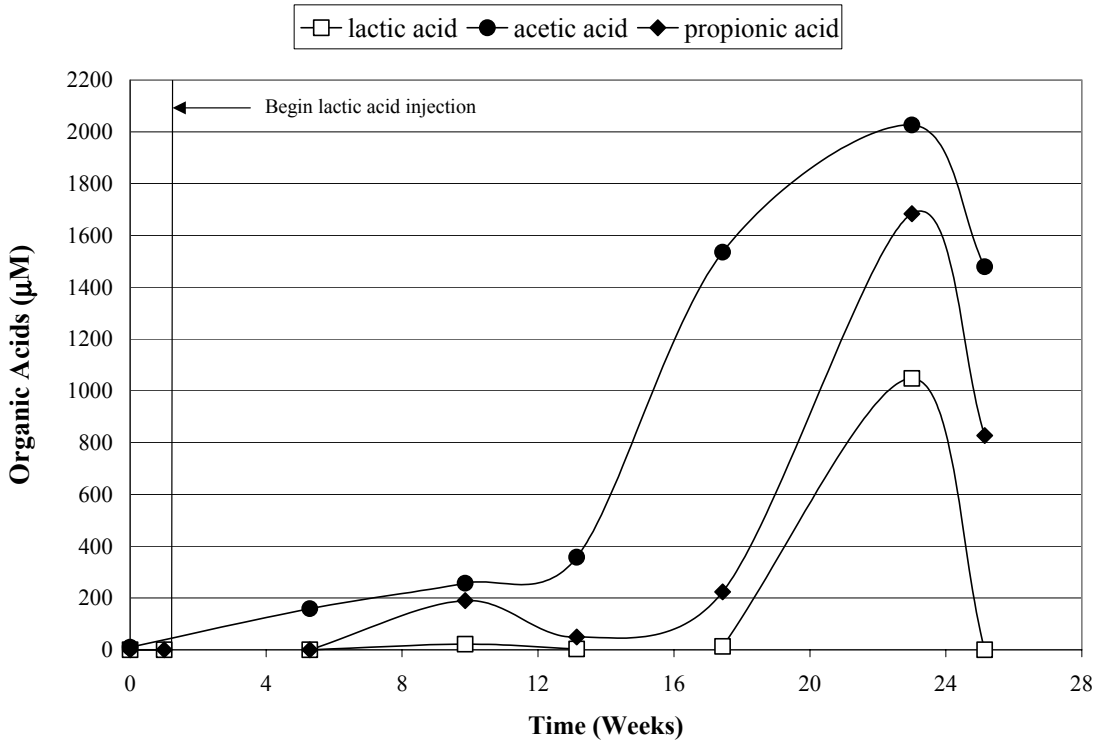


Figure 3-10. Average Organic Acid Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

pH and Alkalinity

There was initially some concern that the continuous injection of lactic acid into the testing zone might impact the local groundwater pH, but Figure 3-11 shows that the average groundwater pH within the testing zone remained relatively neutral throughout the demonstration. High levels of natural alkalinity in the aquifer, which increased as the demonstration proceeded, helped to buffer the groundwater from pH changes.

Dissolved Oxygen and Ferrous Iron

Figure 3-12 shows the average dissolved oxygen and ferrous iron concentrations in groundwater samples collected from monitoring points and wells at Facility 1381. Measurements were made at the wellhead using a dissolved oxygen probe and a ferrous iron colorimetric test kit. The data show that the groundwater at Facility 1381 initially had relatively low levels of DO and relatively high levels of ferrous iron, suggesting that anaerobic microorganisms, including iron-reducing bacteria, were prevalent at the site. Subsequent measurements showed a continued depression of DO levels and a gradual increase in the average ferrous iron concentration. Although increases in ferrous iron indicate that iron-reduction was occurring in or around the testing zone, it was not the predominant terminal electron acceptor process at the site.

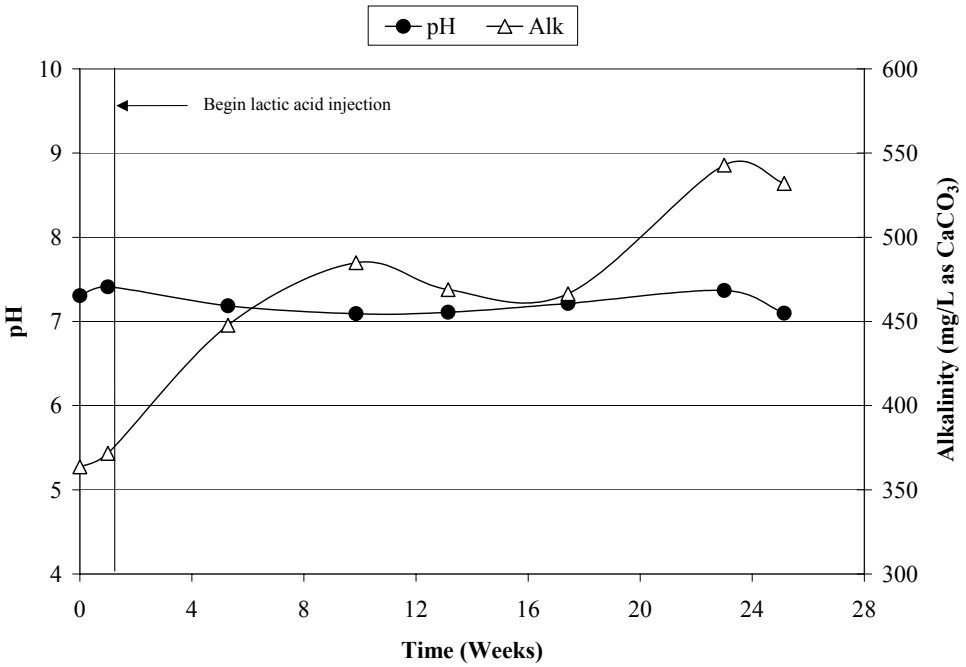


Figure 3-11. Average pH and Alkalinity Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

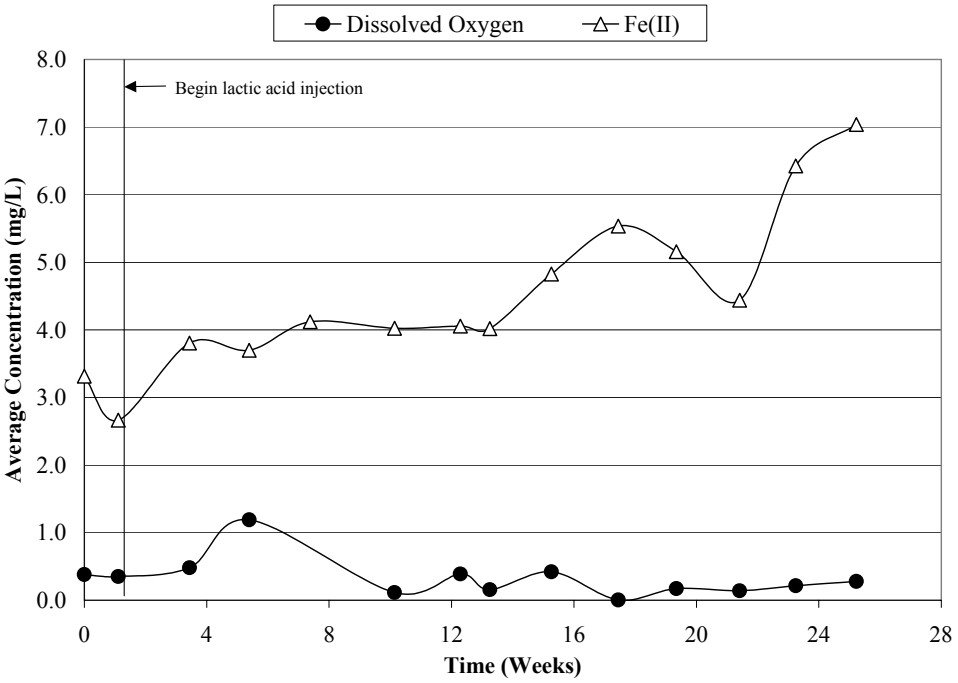


Figure 3-12. Average Dissolved Oxygen and Ferrous Iron Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

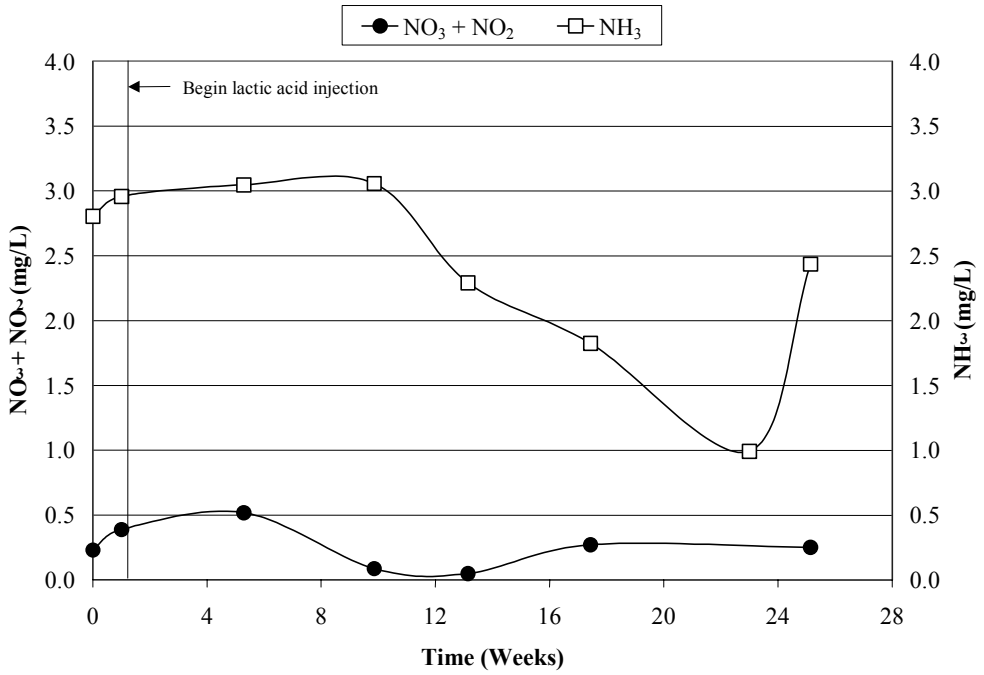


Figure 3-13. Average Nitrate, Nitrite, and Ammonia Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

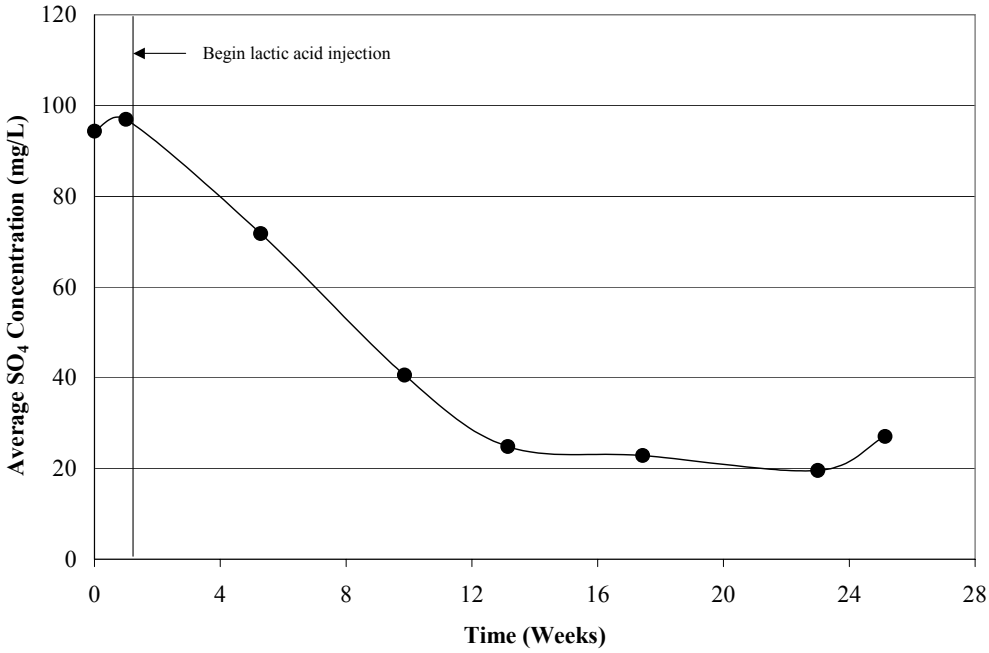


Figure 3-14. Average Sulfate Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

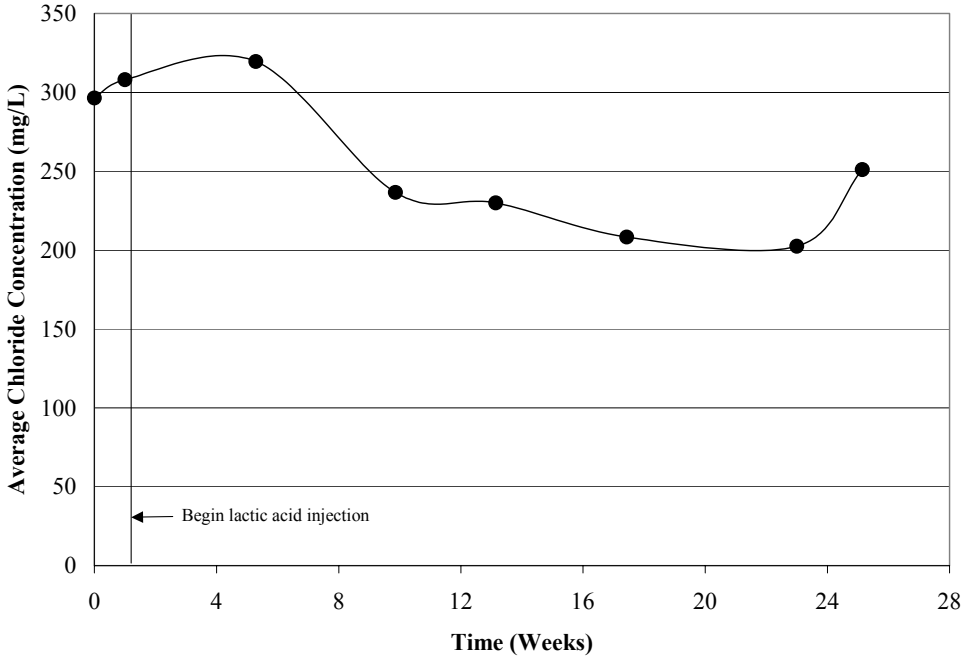


Figure 3-15. Average Chloride Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

Nitrate, Nitrite, and Ammonia

The groundwater at Facility 1381 contained relatively low levels (<0.5 mg/L) of nitrate and nitrite, but significantly higher levels of ammonia (see Figure 3-13). This observation coupled with average redox potential measurements consistently below -150 mV strongly suggest that nitrate reduction had essentially run to completion at this site prior to initiating the treatability test. The reason for the significant drop in ammonia concentrations towards the end of the demonstration is not known.

Sulfate

A steady and significant drop in the average sulfate concentrations over the first 13 weeks of the demonstration suggest that sulfate reduction was the predominant terminal electron accepting process during this period (see Figure 3-14). By Week 13, several sampling points began to show sulfate levels below the 0.5 mg/L detection limit. By the end of the demonstration, the vast majority of sampling points had sulfate levels below the detection limit, but levels in monitoring points on the periphery of the treatment zone remained high and prevented the average sulfate concentration from falling below 20 mg/L.

Chloride

At some sites the reductive dechlorination process causes observable increases in local chloride levels as chlorine atoms are sequentially removed from parent chloroethene compounds, but the high levels of chloride present in the groundwater at Facility 1381 made this impossible. Figure

3-15 shows that the average chloride concentration fluctuated considerably from 200 to 350 mg/L. Many factors likely contributed to this fluctuation, but regardless of the cause it would be impossible to observe the relatively minor increase that would result from the reductive dechlorination of chloroethenes at the site. Consider that the complete dechlorination of all chloroethenes initially present in the testing zone would increase the average chloride concentration by only 8.4 mg/L.

Dissolved Organic Carbon

Dissolved organic carbon measurements were made to determine their value as a surrogate parameter for the more costly organic acid analysis. Figure 3-16 shows that the DOC concentration curve provides a reasonable estimation of the total organic acids (shown as DOC equivalents) present in the testing zone. Although the DOC measurement cannot differentiate the various organic acids, it does show that organic carbon concentrations were significantly increased and sustained by the addition of lactic acid.

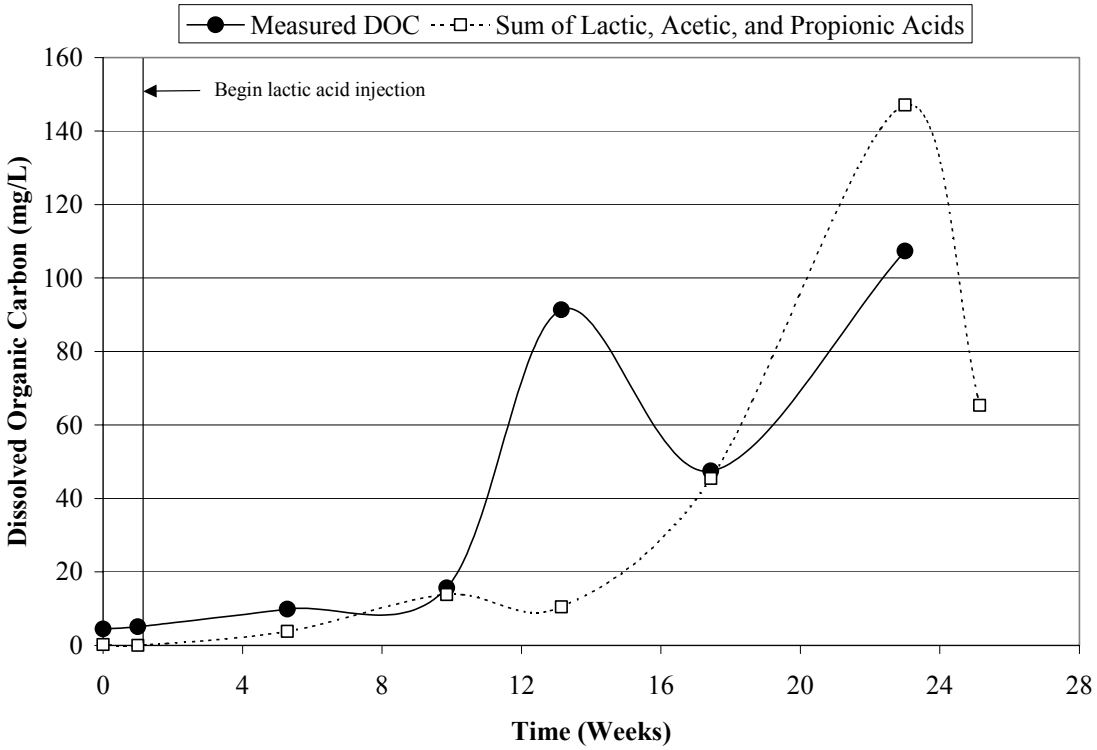


Figure 3-16. Average Dissolved Organic Carbon Concentrations at Facility 1381, Cape Canaveral Air Station, Florida

Redox Potential and Temperature
The average redox potential and temperature of groundwater collected from sampling points and monitoring wells at Facility 1381 are shown in Figure 3-17. Redox potential measurements at the site were consistently below -150 mV, which correlates well to the observed trends in electron acceptor species. The slow but steady increase in groundwater temperature reflects the seasonal change in temperature. The demonstration began in late February and was completed in early August.

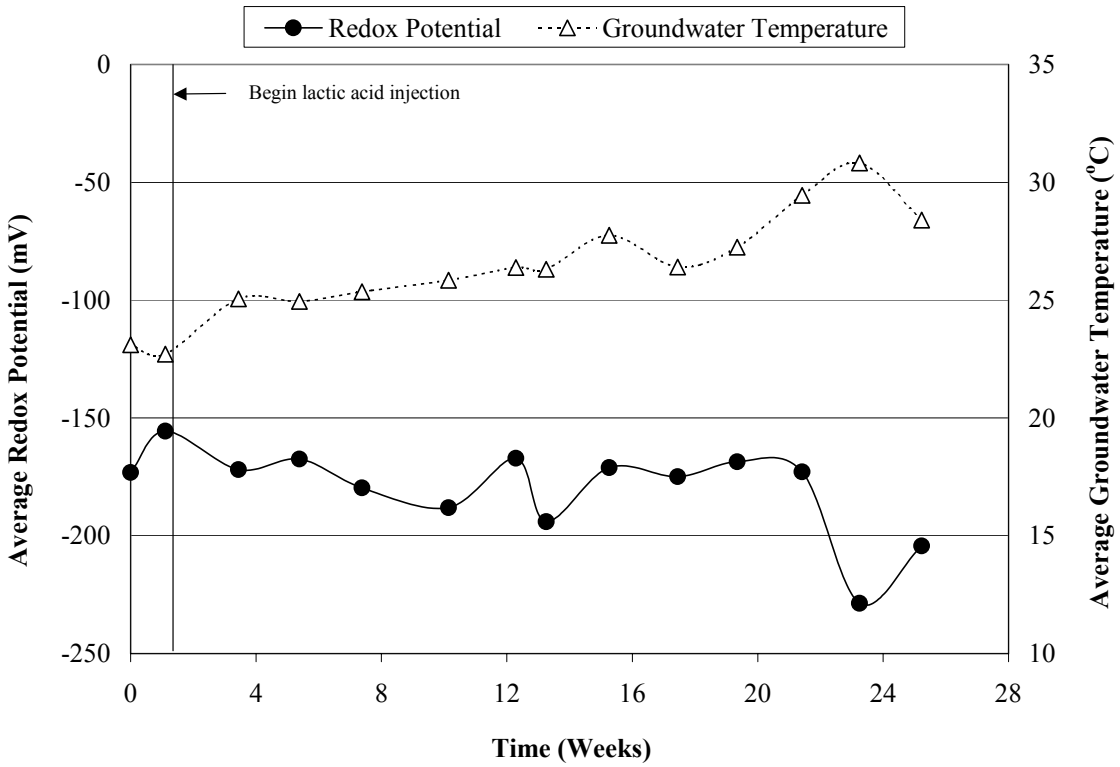


Figure 3-17. Average Redox Potential and Groundwater Temperature at Facility 1381, Cape Canaveral Air Station, Florida

3.2.4.5 Conclusions. Results from the RABITT field demonstration at Cape Canaveral Air Station show that native subsurface microbial populations are capable of sequentially reducing TCE to ethene. Results showed the characteristic contaminant profile shift, from TCE and *cis*-DCE to VC and finally ethene, but microcosm results suggest that this capability may be highly localized. Nonetheless, it appears that localized capabilities can be extended and enhanced by creating suitable subsurface conditions.

Although the modified RABITT system design did provide effective treatment of chloroethenes, it did not permit the formulation of a mass balance or allow the rigorous analysis of reaction kinetics. It was difficult to gauge the actual size of the treatment volume and impossible to

maintain complete hydraulic control. Because the size of the treatment volume was much larger than anticipated and impacted all peripheral wells, it was not possible to collect background samples and verify that observed changes resulted from treatment.

The overall impact of the demonstration on the natural subsurface geochemistry was mild. The addition of the lactic acid caused depletion of sulfate, an increase in DOC and the eventual production of methane at relatively low levels. The addition of lactic acid did not affect the average pH in the testing zone, which was buffered by naturally high levels of alkalinity present in the aquifer.

Chloride concentration measurements could not be used at this site as evidence of reductive dechlorination because background levels were too high.

3.3 Alameda Point – Site 4

3.3.1 Site Description – Site 4. The second RABITT demonstration was conducted at Alameda Point's Site 4, which is located less than ½ mile from the San Francisco Bay. Site 4 is associated with Building 360, which is located near the eastern perimeter of the Alameda Point off of Eleventh Street.

Building 360 was used as an aircraft engine repair and testing facility, and consisted of former machine shops, and cleaning areas, as well as plating, painting and welding shops and parts assembly areas. In the former plating shop, activities included paint stripping by blasting, metal stripping, etching and plating. Solvents used in the cleaning shop of Building 360 have included a mixture of 55% PCE and other chemicals such as dichlorobenzene, methylene chloride, toluene and 30-70% solutions of sodium hydroxide (Tetra Tech EM, Inc., 1997a).

In May of 1997, OSIGO Environmental prepared a report summarizing a geochemical profiling investigation of grab groundwater samples collected by the Navy at Site 4 (OSIGO, 1997). The results of this and previous investigations at this site revealed elevated levels of chlorinated solvents, primarily TCE (24,000µg/L), DCE (8,600 µg/L) and VC (2,200 µg/L), detected between 5.5 and 15.5 ft bgs (Tetra Tech EM, Inc., 1997a). Other contaminants detected at Site 4 from previous soil and groundwater investigations include metals (chromium, copper, lead, and nickel), semivolatile organic compounds (SVOCs) (fluoranthene), and cyanide (Tetra Tech EM, Inc., 1997a).

3.3.2 Site Assessment/Selection – Site 4. The contaminant profile at Site 4 had been well defined. A previous site investigation produced by OSIGO Environmental (OSIGO, 1997) delineated both the horizontal and vertical extent of chloroethene contamination. This report showed that the average concentration of TCE at the site was significantly greater than its detection limit, so contaminant reduction would be easily measured and documented. In addition, the report detailed the presence of the TCE daughter products *cis*-DCE and VC, suggesting that reductive dechlorination was already occurring at the site. Finally, the contaminants were found at relatively shallow depths, which reduced drilling and sampling costs.

The site appeared to be somewhat heterogeneous, but was not expected to present problems with the subsurface delivery of electron donor. No existing geochemical data could be found for Site 4. Although the lack of geochemical data increased the risk of an unsuccessful demonstration, team members agreed that the other factors (e.g., the presence of daughter products) overrode potential problems with the geochemistry. Baseline sampling of geochemical parameters was conducted during system installation.

The Base facility showed an enthusiastic willingness to support the demonstration, and the regulators in the region did not raise any objections to the proposed system design. Furthermore, no logistical impediments were discovered at the site.

The site rating system found in the RABITT protocol was applied to Site 4 to assess the site's potential for success and to allow the rating system to be evaluated in retrospect after completing the demonstration. Average site conditions obtained from existing site characterization work were compared against criteria in the rating system and results are listed in Table 3-9 along with the corresponding rating score. In several instances existing data were not available to complete the rating system score summary table; in these cases a default value of 0 was assigned to the parameter.

Table 3-9. RABITT Site Rating System Score Summary for Site 4, Alameda Point, California

Rating Parameter	Conditions at Site 4	Score
Contaminant Profile	Vinyl chloride present	15
Hydraulic Profile	2×10^{-3} cm/sec	25
Geochemical Profile		
Dissolved Oxygen	Data not available	0
Nitrate	Data not available	0
Hydrogen Sulfide	Data not available	0
Sulfate	Data not available	0
Redox potential	Data not available	0
Temperature	Data not available	0
Dissolved Organic Carbon	Data not available	0
Bicarbonate Alkalinity	Data not available	0
pH	6.9 - 7.1	3
Methane	Data not available	0
Total Point Value		43

Site 4 scored a total point value of 43 out of 75 total possible points. As mentioned previously, the lack of geochemical data prevented the assignment of scores for several parameters, so they were given the default value of zero. Despite this disadvantage, the score of Site 4 fell into the range considered "Satisfactory" in the RABITT protocol.

3.3.3 Microcosm Testing – Site 4

3.3.3.1 Microcosm Setup. Core material was collected from Site 4, Alameda Point on November 9, 1998. Cores (1.7-inches inside diameter [I.D.], 13 to 19 ft bgs depth interval) were obtained from three separate locations near a previous sampling point, 2D-C. Cores were taken along a line that runs approximately east to west (parallel with the railroad tracks) just to the south of 2D-C. These coring locations were denoted R-1, R-2, and R-3. In general, R-1, R-2, and R-3 were approximately 9 to 15 ft from 2D-C and 10 ft from each other. Groundwater was obtained from R-2 via a temporary well screened from 15 to 19 ft bgs.

For microcosm preparation, core material from the following locations and depths were mixed: R-1: 14-14.5 ft, 15-15.5 ft; R-2: 14-14.5 ft, 15-15.5 ft; and R-3: 15.5-16 ft, 17-17.5 ft. Some characteristics of the sediment and groundwater are shown in Table 3-10.

The microcosms were set up in the anaerobic chamber using 50 g dry core mixture and 100 g groundwater which had been amended with 0.8 mg resazurin/L. Alkalinity in the groundwater was increased by 0.035 eq/L through the addition of $NaHCO_3$. Microcosms were not purged, but rather retained the N_2 headspace of the anaerobic chamber, which contained approximately 2% H_2. The resulting microcosm pH (by probe) was 7.4. The typical VOC content of the microcosms was: TCE, 21 µmol/bottle; *cis*-1,2-DCE, 4 µmol/bottle; trans-1,2-DCE, trace or not detected; 1,1-DCE, 0.03 µmol/bottle; VC, 1.2 µmol/bottle; ETH, 0.2 µmol/bottle; and CH_4, 0.9 µmol/bottle. No additional TCE was added. Bottles were shaken overnight to ensure equilibrium, analyzed to get a Day 0 value, and assigned to their respective bottle sets. Donors and amendments then were added in the amounts described earlier for CCAS microcosms (Table 3-2), except that propionate was employed at 3 mM (instead of 1.5 mM) in Alameda microcosms. Bottles were incubated inverted in the dark at 24°C.

Table 3-10. Initial Characterization of Soil and Groundwater at Site 4, Alameda Point, California

Mixed Core Moisture Content (% moisture)	13.7
Groundwater pH	6.9-7.1
Groundwater Sulfate (mg/L)	965
Groundwater Total Alkalinity (eq/L)	0.013
Groundwater Conductivity (mS/cm)	14.4
Soil/Groundwater Mixture[(a)] pH	6.9-7.2
Soil/Groundwater Mixture[(a)] Total Alkalinity (eq/L)	0.015

(a) At ratio used in microcosm construction.

3.3.3.2 Microcosm Results. Table 3-11 summarizes dechlorination results over the first 90 days of microcosm operation. With a few exceptions noted in the table, all donors appeared to stimulate dechlorination, though not to the same degree. High yeast extract (YE) (bottle set 4) and butyrate (bottle set 6) gave the most complete conversion to ethene.

Table 3-11. Primary Dechlorination Products in the Donor-Fed Alameda Point Microcosms

Bottle Set/Donor	Triplicate I	Triplicate II	Triplicate III
4 (200 mg/L Yeast Extract)	ETH	ETH	ETH
5A (Lactate only)	—	*cis*-DCE, VC	*cis*-DCE, VC
5B (Lactate + 20 mg/L Yeast Extract)	ETH	ETH	*cis*-DCE, VC
5C (Lactate + B_{12})	*cis*-DCE, VC	—	*cis*-DCE, VC
5D (Lactate + 20 mg/L Yeast Extract + B_{12})	*cis*-DCE, VC	*cis*-DCE, VC	ETH
6 (Butyric Acid + 20 mg/L Yeast Extract + B_{12})	ETH	ETH	ETH
7 (Lactate/Benzoate + 20 mg/L Yeast Extract + B_{12})	—	—	ETH
8 (Propionic Acid + 20 mg/L Yeast Extract + B_{12})	ETH	—	*cis*-DCE, VC

— = no significant dechlorination activity at this time.
ETH – ethene.

Figures 3-18 and 3-19 show more detailed performance of representative microcosms fed lactate and butyrate, respectively (plus 20 mg/L YE and 0.05 mg/L B_{12}).

Unlike results obtained with CCAS microcosms, Alameda Point microcosms fed lactate evidenced a comparatively huge loss of reducing equivalents to processes other than methanogenesis (which was extremely insignificant, with levels typically less than 1 µmol/bottle methane), reductive dechlorination, and fermentation products. This is evident from the large gap in the equivalents balance of Figure 3-18; lactate disappears, without corresponding appearance of monitored products. The explanation appears to be the presence of significant sulfate-reduction in lactate-fed, Alameda Point microcosms. At the end of the study, sulfide was found to be ca. 360 µmol/bottle (2,880 µeq/bottle) in lactate-fed, Alameda Point microcosms, accounting for most of the "gap" in the equivalents balance (recall that sulfate concentrations in Alameda groundwater are very high [965 mg/L = 1,000 µmol/bottle]). It is likely that lactate was being used directly by sulfate reducers at Alameda Point, constituting a significant competitive demand for added lactate.

It is also worth noting that benzoate, unlike at CCAS, apparently was not fermented in Alameda Point microcosms. This illustrates the site-specific differences in microbial capabilities that can be ascertained through use of microcosms.

Sulfate reduction was also evident in butyrate-fed microcosms. However, the data (Figure 3-19) indicate that sulfate reducers at Alameda Point were not using butyrate directly. Note that a considerable gap in the equivalents balance did not occur until acetate began to be utilized (after Day 92), suggesting that acetate was the donor most significantly used by sulfate reducers. Thus, at Alameda Point, butyrate offered a significant advantage (relative to lactate) in the lack of demand for butyrate by sulfate reducers. Butyrate's slower degradation rate (i.e., its persistence) and lack of sulfate-reducer demand for it, probably accounted for it being the superior donor in Alameda Point microcosms. On this basis, butyrate was selected for subsequent field testing.

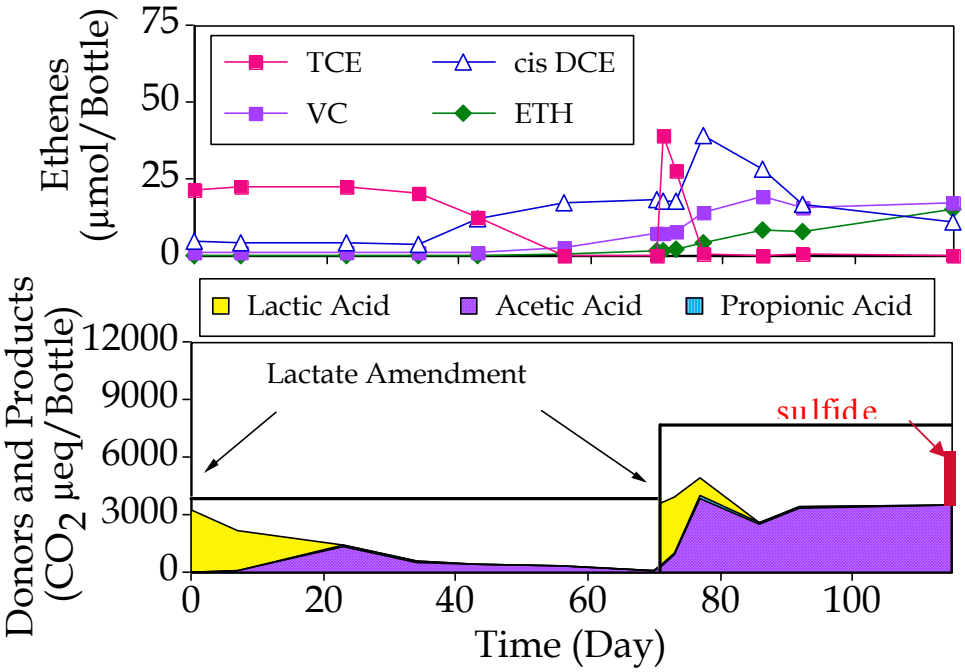


Figure 3-18. Results from Alameda Microcosm (5D-II) Fed 3mM Lactate + 20 mg/L YE + 0.05 mg/L B_{12}

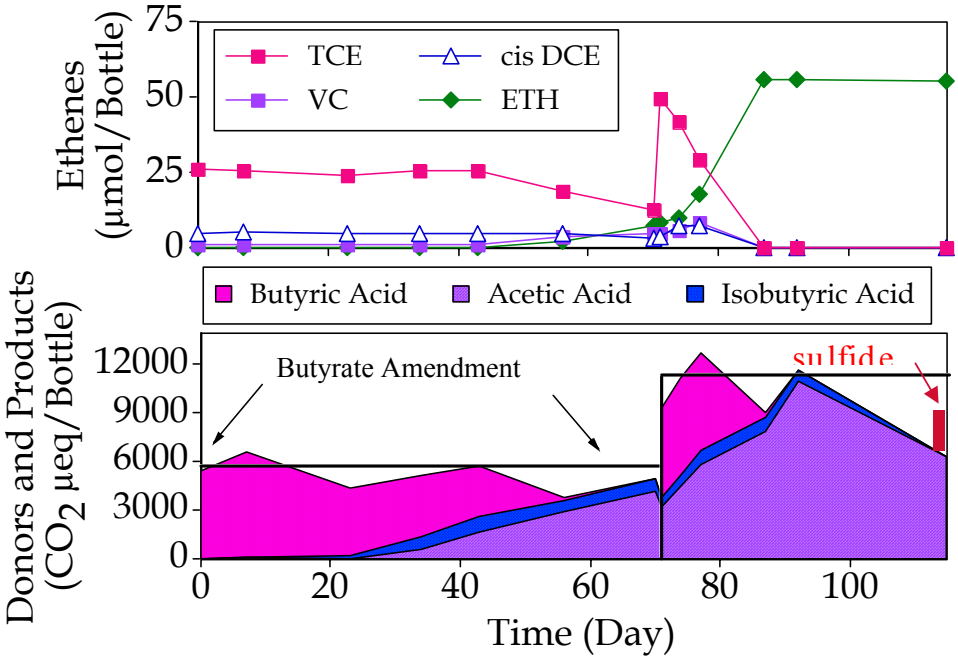


Figure 3-19. Results from Alameda Microcosm (6-III) Fed 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12}

3.3.4 Field Testing – Site 4

3.3.4.1 System Design/Installation. The installation of the RABITT demonstration system at Alameda Point began on May 11, 1999. The system was installed approximately 150 feet to the north/northwest of Building 360 in the proximity of the groundwater sampling location identified as 2D-C. A total of 15 wells were installed with screened intervals ranging from 13 to 16 ft bgs. Difficulties producing water during development of these wells prompted the installation of a second set of wells in a deeper, more hydraulically conductive layer. Installation of these wells began on May 18, 1999. New wells were installed immediately adjacent to existing wells, but were screened over the range from 24 to 27 ft bgs. Well installation details are provided in Table 3-12 and the relative well locations are shown in Figure 3-20.

Table 3-12. Well Installation Details at Site 4, Alameda Point, California

Parameter	Injection Wells	Monitoring Wells	Supply Well	Gradient Well	Background Well
Diameter (inches)	½	1	2	2	1
Screened Interval (ft bgs)	24 to 27	24¾ to 26¼	13 to 16	13 to 16	24¾ to 26¼
Slot Size (inches)	0.01	0.01	0.01	0.01	0.01
Material	PVC	PVC	PVC	PVC	PVC

Once all subsurface system components had been installed and developed, a complete round of groundwater samples was collected and field measurement taken to examine baseline conditions within the testing zone. After sampling was completed, the fluid injection system was plumbed and brought on line to check for leaks and allow for general troubleshooting.

3.3.4.2 Tracer Testing. Following the installation of the RABITT system wells, a bromide tracer test was initiated on June 5, 1999 to determine the direction of groundwater flow through the monitoring well array and its approximate hydraulic retention time. A review of existing groundwater potentiometric contour maps led us to believe that the general movement of groundwater in this area would be parallel to the longitudinal axis of the monitoring well array.

Groundwater was continuously pumped from the supply well and amended with a concentrated sodium bromide solution in the on-site field trailer. A calibrated metering pump was used to add a consistent amount of bromide stock solution to the groundwater flow. After amendment with bromide stock solution, the flow was evenly split and injected into injection wells IW-1, IW-2, and IW-3. The target bromide concentration for injected water was 100 mg/L, but groundwater extracted from the supply well contained approximately 90 mg/L of bromide ion, so at least initially, the actual average bromide injection concentration was about 190 mg/L.

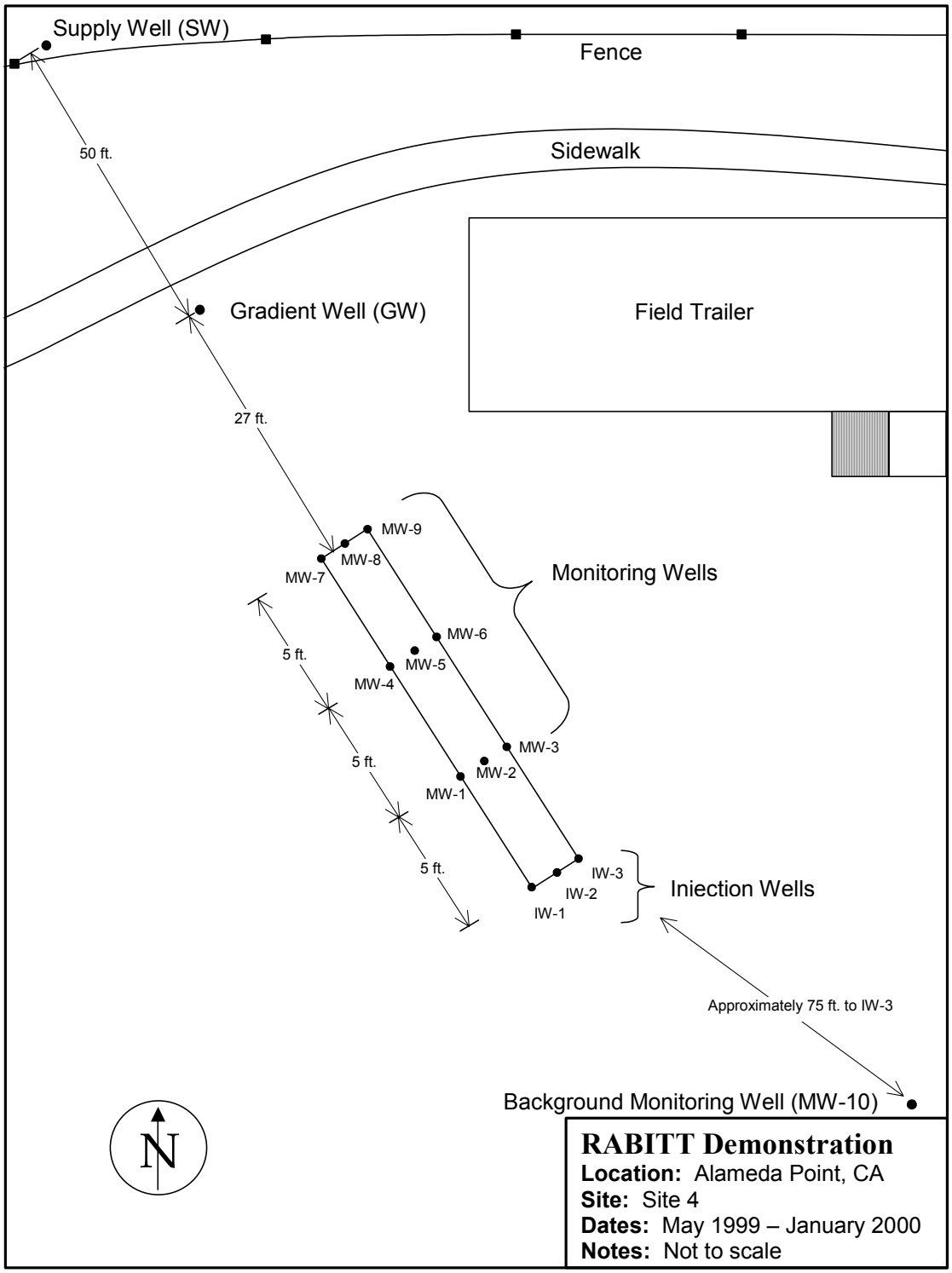


Figure 3-20. Plan View of RABITT Demonstration at Site 4, Alameda Point, California

Tracer injection was briefly interrupted sometime during the evening of June 7 (Day 2) or the morning of June 8 (Day 3) when a circuit breaker in the field trailer tripped and caused the metering pump and bladder pumps to shut down. The system was restarted on June 8, but then encountered a second interruption on June 13 (Day 8) when the metering pump responsible for regulating the flow of the NaBr solution failed. The pump was replaced and testing resumed on June 23 (Day 18) with a few modifications. First, the concentration of the tracer solution was reduced from 160 g NaBr/L to 62 g NaBr/L. To compensate for the lower tracer solution concentration the tracer flowrate was increased to 1 mL/min. The resulting bromide ion injection concentration was variable due to fluctuations in concentration from the supply well, but remained generally in the vicinity of 200 mg/L. System flowrates and concentrations for both the initial and modified tracer testing setup are presented in Table 3-13. The system operated normally under these injection conditions until June 30 (Day 25) when electron donor injection was initiated.

Table 3-13. Tracer Testing Flowrates and Concentrations at Site 4, Alameda Point, California

Operational Parameter	Initial Design (June 5)	Modified Design (June 23)
Total pumping rate from the supply well	630 mL/min	630 mL/min
Bromide stock solution feed rate	0.5 mL/min	1.0 mL/min
Bromide stock solution concentration	124,237 mg/L as [Br^-]	48,142 mg/L as [Br^-]
Bromide concentration of extracted water	~ 90 mg/L	~ 90 mg/L[(a)]
Bromide concentration of injected water	~188 mg/L	~166 mg/L[(b)]
Wells used for injection	IW-1, IW-2, IW-3	IW-1, IW-2, IW-3

(a) Initial measurements were approximately 90 mg/L but this value ranged widely.
(b) Calculated value based on initial measurements, variability in the bromide concentration of extracted water caused the injection concentration to fluctuate.

Figure 3-21 shows a time series of contour plots, which illustrate the movement of bromide through the testing zone. The first in the series of contours (Day 0) shows that bromide was present prior to tracer injection. The impact of tracer injection became evident in the first row of monitoring wells by Day 5 as bromide concentrations doubled. As testing continued, concentration contours circled around MW-2, suggesting that the well was located in a less hydraulically conductive zone. This observation would hold during treatability testing, which showed that activity at MW-2 consistently lagged behind nearby monitoring wells. By Day 23 bromide concentrations in the second row of monitoring wells had increased significantly and concentrations in the third row were beginning to rise. These observations convincingly indicated that the 630 mL/min injection flowrate would provide a hydraulic retention time of approximately 30 days, so electron donor injection was initiated the following day.

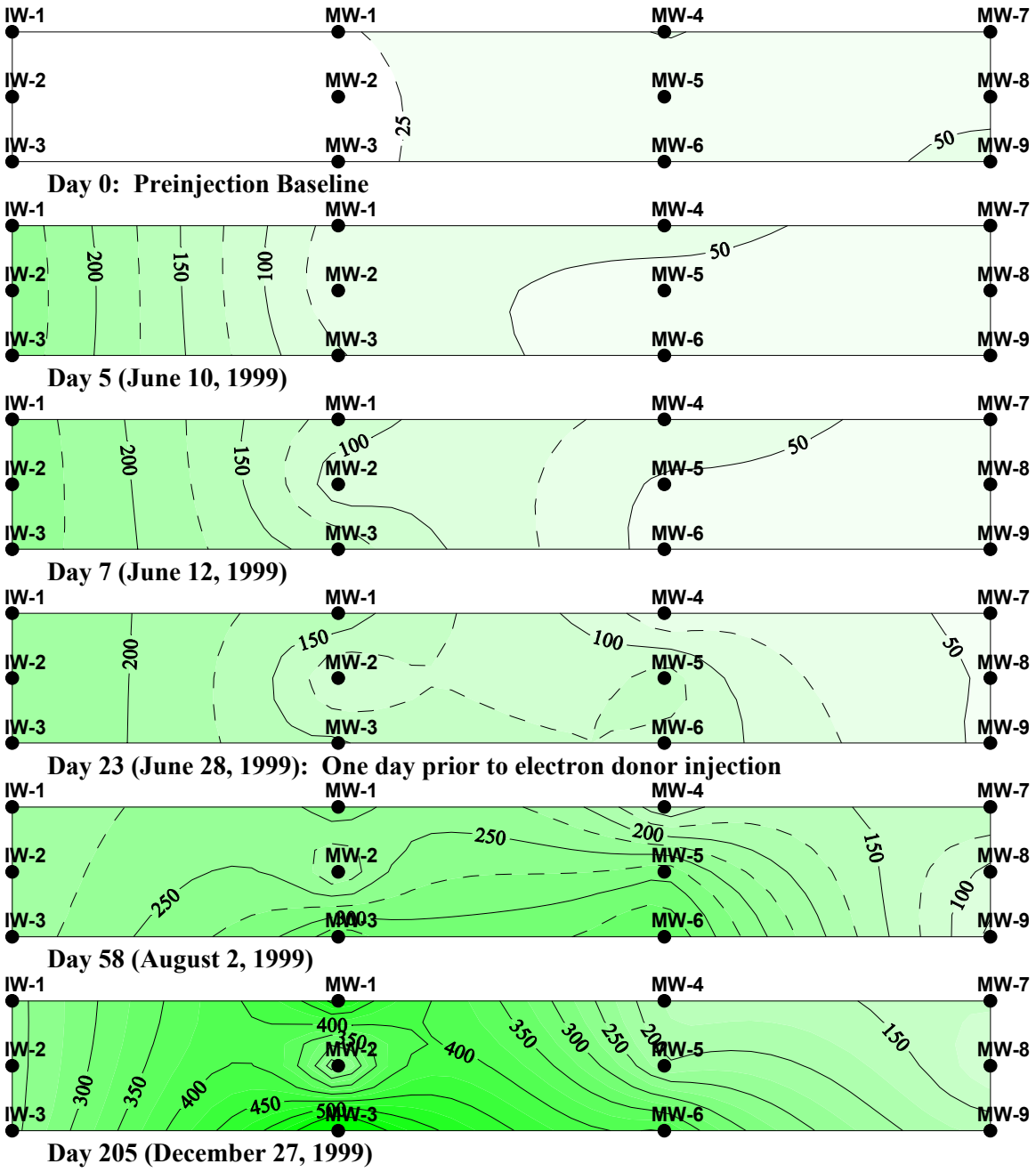


Figure 3-21. Bromide Tracer Testing Results from Site 4, Alameda Point, California

Four weeks after electron donor injection had begun, bromide concentrations within the testing zone began to exceed injection concentrations. This unexpected observation seemed to indicate that the bromide-specific electrode was malfunctioning. It soon was discovered that several reduced ionic species, such as sulfide and ammonia, would interfere with the electrode at

relatively low concentrations. Groundwater samples were never analyzed for sulfide, but they were analyzed for ammonia. Results showed that ammonia was present in the more highly reduced zones of the plot, which incidentally is where bromide concentrations were exaggerated. Based on these observations, it was concluded that ionic interference probably caused the unusual bromide measurements.

3.3.4.3 Treatability Testing

System Operation

Treatability testing at Site 4 involved the continuous injection of an electron donor solution containing butyric acid and YE into the subsurface for seven months. In addition, a second solution, containing sodium bicarbonate (pH buffer) and sodium bromide (tracer) also was continuously injected. Injection began on June 29, 1999 and ended on January 10, 2000.

A bladder pump was used to extract groundwater from the supply well and into the field trailer where two dedicated metering pumps added amendments. The first metering pump fed a solution containing sodium bicarbonate (65 g/L) and NaBr (7.85 g/L) at 8 mL/min, and the second metering pump added a solution containing butyric acid (1.25 M) and YE (8.3 g/L) at 1.5 mL/min. Specific system operating parameters are outlined in Table 3-14. After the groundwater had been amended with nutrients in the field trailer, it was evenly split into the three injection wells. The total injection flowrate was approximately 630 mL/min, resulting in approximately 210 mL/min down each injection well.

Groundwater injection frequently was interrupted by problems associated with the bladder pump, most of which were related to air compressor failures.

Table 3-14. Stock Solution Pumping Rates, Concentrations and Target In Situ Concentrations at Site 4, Alameda Point, California

Amendment	Stock Solution Concentration	Stock Solution Feed Rate	Target In Situ Concentration
Sodium bicarbonate	65 g/L	8 mL/min	828 mg/L
Sodium bromide	7.85 g/L		100 mg/L
Butyric acid	1.25 M	1.5 mL/min	3 mM
Yeast extract	8.3 g/L		20 mg/L

The butyric acid-YE stock solution was prepared in a covered 15-gallon HDPE tank using concentrated butyric acid, YE and tap water. Similarly, the sodium bicarbonate-sodium bromide solution was prepared in a covered 55-gallon HDPE tank using sodium bicarbonate, sodium bromide, and tap water.

The gradient well, which was installed as a precautionary measure to ensure that groundwater would flow through the monitoring well array, was never used. Groundwater flowed through the array without imposing an artificial gradient.

Sampling

The RABITT demonstration at Site 4 required the frequent sampling and analysis of a variety of groundwater parameters. Groundwater samples were collected every two weeks from each of 12 individual monitoring locations. Table 3-15 shows the specific sampling dates and sample types collected at Site 4, and Table 3-16 lists the specific analytes for each sample type. Additional information regarding analytical methods, container types, sample preservatives, and holding times can be found in the Alameda Point Demonstration Plan (Battelle and Cornell U., 1999b).

Table 3-15. Sampling Dates and Sample Types at Site 4, Alameda Point, California

Date	Elapsed Time (Weeks)	Field Data	Laboratory Analytes				
			VOCs	Dissolved Gases	Organic Data	Inorganic Data	DOC
03-Jun-99	0 (preinjection)	X	X	X	X	X	X
29-Jun-99	4 (injection begins)	X	X	X	X	X	X
13-Jul-99	6	X	X				
02-Aug-99	8	X	X	X	X	X	X
16-Aug-99	10	X	X				
31-Aug-99	12	X	X	X	X	X	X
15-Sep-99	14	X	X				
28-Sep-99	16	X	X	X	X	X	X
12-Oct-99	18	X	X				
26-Oct-99	20	X	X	X	X	X	X
09-Nov-99	22	X	X				
22-Nov-99	24	X	X	X	X	X	X
07-Dec-99	26	X	X				
13-Dec-99	28	X	X	X	X	X	X
27-Dec-99	30	X	X				
10-Jan-00	32	X	X	X	X	X	X

A peristaltic pump was used to pump groundwater from monitoring wells and into a flowthrough cell without exposing it to the atmosphere. The flowthrough cell was instrumented with probes, which measured pH, temperature, redox potential, and DO. Groundwater was allowed to flow through the cell and into a waste container until redox potential and DO measurements stabilized. Once these measurements stabilized, all field measurements were recorded and groundwater samples were collected and prepared for shipment to the appropriate analytical laboratory. Additional groundwater samples were collected and used to measure the bromide ion and ferrous iron concentrations in the field.

Table 3-16. Analytes Listed by Sample Type at Site 4, Alameda Point, California

Field Data	Laboratory Analytes				
	VOCs	Dissolved Gases	Organic Data	Inorganic Data	DOC
Water Level Redox potential pH Temperature Bromide DO Fe(II)	PCE TCE *cis*-DCE VC	Ethene Ethane Methane	Lactic acid Acetic acid Propionic acid Benzoic acid Butyric acid	pH Conductivity Alkalinity Nitrate Nitrite Ammonia Chloride Sulfate Bromide	Dissolved organic carbon

3.3.4.4 Results. Results from the RABBIT demonstration at Alameda Point are presented in the following subsections. Concentrations of TCE and its primary dechlorination products, *cis*-DCE, VC, and ethene, are presented in a series of contour plots showing the spatial distribution of contaminant in the test plot over time. The remaining analytical parameters are presented in graphs that show their average concentration in the test plot over time. The data presented in these graphs represent the average total concentration from monitoring wells MW-1 to MW-9. Data from the supply, injection, gradient, and background wells were not included.

A complete set of the raw data from the demonstration conducted at Site 4 is available on the CD-ROM supplied with this report.

Chloroethene Concentration Profiles
The results for TCE, *cis*-DCE, VC, and ethene are presented from selected VOC sampling events. Contour plot concentration units are in µM to allow for direct comparison between the four compounds on an equivalent basis. Results for *trans*-DCE, 1,1-DCE and other VOCs are included on the CD-ROM supplied with this report.

Trichloroethene
The disappearance of TCE within the test plot is illustrated in Figure 3-22, which shows a time series of TCE concentration contours. The figure shows that preinjection TCE concentrations (Week 0) ranged across the test plot from 5 µM (657 ppb) to 25 µM (3,285 ppb). The elevated TCE levels observed near injection wells IW-1, IW-2, and IW-3 illustrate the constant influx of TCE-contaminated groundwater. Injected groundwater contained an average TCE concentration of 84.2 µM (11,063 ppb) and ranged from 61.5 µM (8,080 ppb) to 97.4 µM (12,800 ppb).

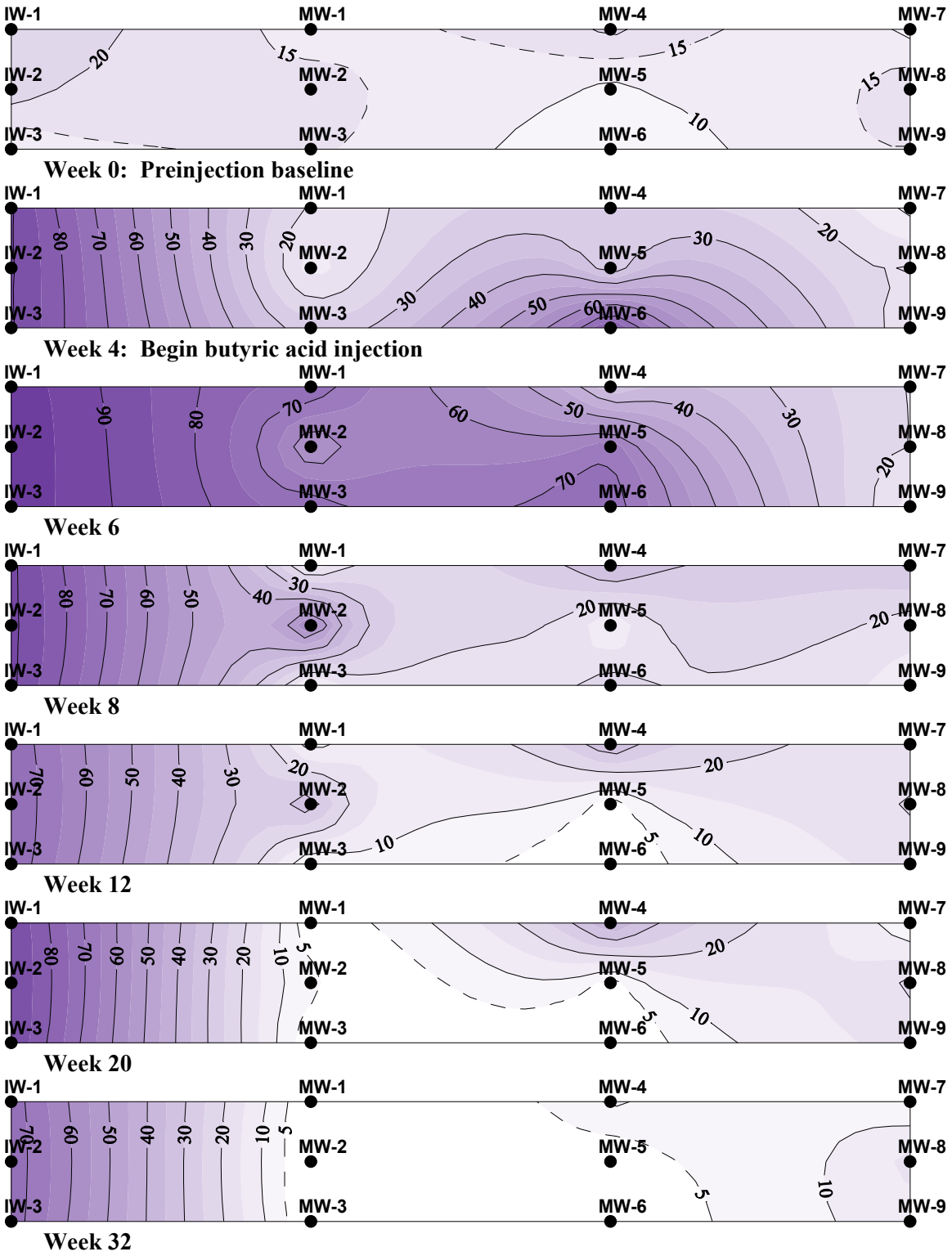


Figure 3-22. TCE Concentration Contours at Site 4, Alameda Point, California

After eight weeks of butyric acid injection, TCE concentrations began to decrease in the first row of monitoring wells, indicating the onset of reductive dechlorination. Note that TCE concentrations in MW-2 lagged behind those observed in MW-1 and MW-3, supporting results from tracer testing that indicated MW-2 was in a less hydraulically conductive area. After 20 weeks 97% of the injected TCE was degraded prior to reaching the first row of monitoring wells. By the end of the demonstration that figure exceeded 99%. Applying pseudo-first-order kinetics to the data and assuming a seven-day travel time to the first row of monitoring wells, the half-life of the injected TCE was approximately 20 hours.

The concentration of TCE in the background well remained consistent throughout the demonstration. It ranged between 1.9 and 4.1 μM (252-540 ppb) with no apparent trend.

***cis*-Dichloroethene**

cis-DCE was not initially present within the test plot (see Figure 3-23), but it was in the injected groundwater that was obtained from the supply well. The average *cis*-DCE concentration in injected water was about 6.5 μM (632 ppb), with values ranging from 1.5 μM (152 ppb) to 8.1 μM (790 ppb).

The Week 8 sampling event revealed that *cis*-DCE concentrations within the test plot had begun to exceed injection concentrations and indicated that reductive dechlorination was occurring. This observation correlates well with the TCE data, which show TCE concentrations beginning to decline in Week 8. The data show an approximately proportional transformation with the greatest activity occurring near wells MW-3, MW-5, and MW-6. By Week 20, *cis*-DCE concentrations began to drop throughout most of the testing zone, suggesting that conversion to VC had begun.

The concentration of *cis*-DCE in the background well remained consistent during the demonstration, ranging between 0.1 and 0.2 μM (1-24 ppb). No trend was evident from the data.

Vinyl Chloride

VC was not initially present within the testing zone at appreciable levels (see Figure 3-24), but low levels were in the injected groundwater obtained from the supply well. The average VC concentration in injected water was about 3.4 μM (210 ppb), with values ranging from 0.2 μM (12 ppb) to 18.6 μM (1,160 ppb).

VC concentrations in the testing zone began to surpass those in the injected water after 12 weeks, suggesting that *cis*-DCE dechlorination had begun. VC levels continued to rise until Week 32, when they began to subside slightly.

The concentration of VC in the background well remained very low throughout the demonstration. Most samples were below the 1.0 ppb detection limit. The highest concentration found was 0.008 μM (2.5 ppb). No trend was evident from the data.

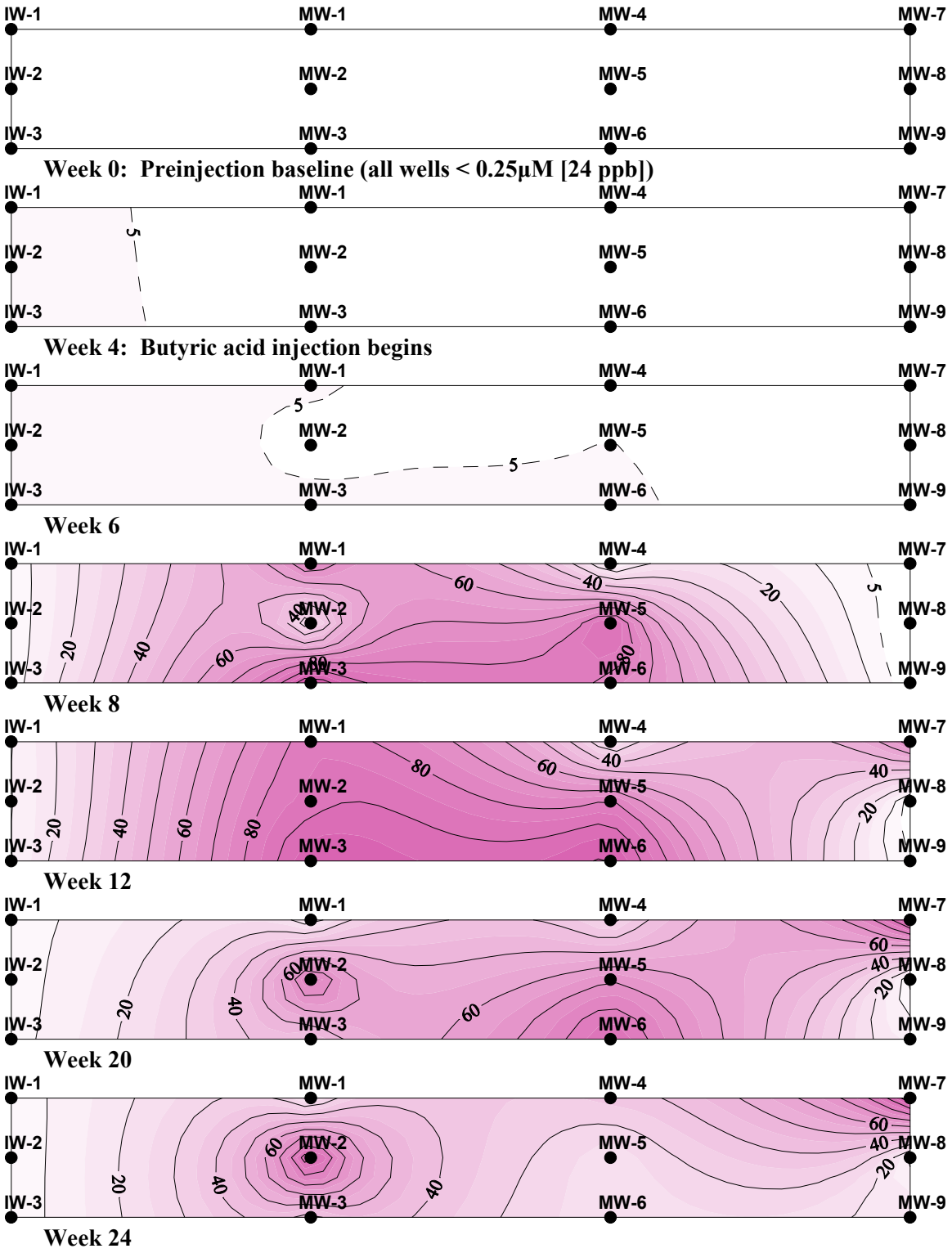
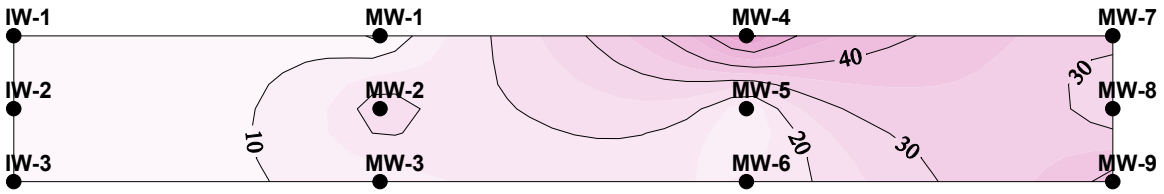


Figure 3-23. *cis*-DCE Concentration Contours at Site 4, Alameda Point, California



Week 32: End of demonstration

Figure 3-23. *cis*-DCE Concentration Contours at Site 4, Alameda Point, California (Continued)

Ethene

Ethene was not detected in groundwater samples collected from the testing zone for the first 12 weeks of the demonstration, and it was never present at significant levels in injected groundwater. Ethene was first observed in the testing zone four months after butyric acid began (Week 20). Surprisingly, the highest concentration occurred in MW-1 (see Figure 3-25), which had a relatively low level of VC at the time. As the demonstration continued, ethene was observed in relatively high concentrations across most of the test plot. At the end of the demonstration the average ethene concentration in the first row of monitoring wells (50.4 µM) accounted for 60% of the average influent TCE concentration (84.2 µM). The average first row concentrations of VC and *cis*-DCE can be added to construct a reasonable mass balance. VC and *cis*-DCE each accounted for about 16% of the total mass in the first row, yielding a total mass recovery of about 92%.

Ethene concentrations never exceeded 0.3 µM in the background monitoring well.

Dissolved Gases

The dissolved gases ethene, ethane, oxygen and methane were monitored during the field demonstration to determine the extent of chloroethene degradation and assess the microbiological conditions within the testing zone. Results from ethene, ethane, and methane are shown in this section. Dissolved oxygen results are presented with other electron accepting species in a subsequent section.

Figure 3-26 shows the average ethene, ethane, and methane concentrations across the test plot. As shown previously, ethene concentrations undergo a dramatic increase after 17 weeks. Ethane concentrations remained very low throughout the demonstration indicating that chloroethene reduction did not proceed past ethene. Similarly, methane concentrations remained low during the demonstration with only a slight increase in methane levels towards the end of the demonstration. This slight increase was probably due to small, localized pockets of methanogenesis. The consistently high levels of sulfate present at Site 4 would have made it very difficult for methanogens to compete with sulfate-reducing bacteria.

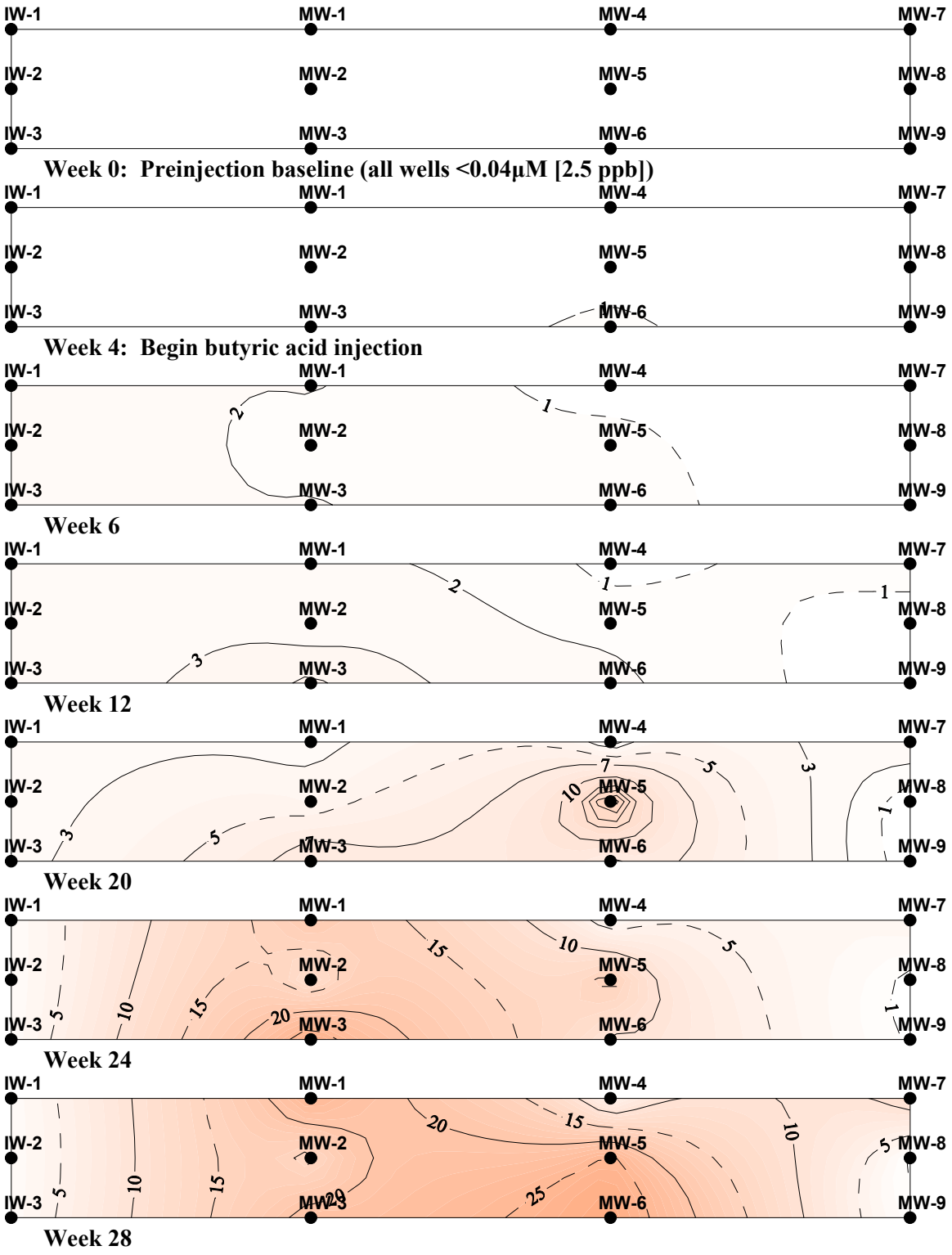
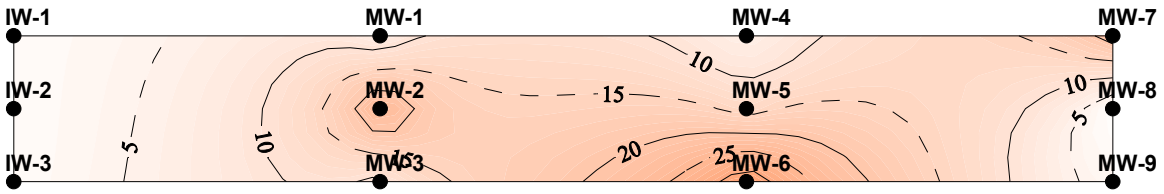


Figure 3-24. VC Concentration Contours at Site 4, Alameda Point, California



Week 32: End of demonstration

Figure 3-24. VC Concentration Contours at Site 4, Alameda Point, California (Continued)

Organic Acids

The concentrations of butyric, acetic, lactic, and propionic acids were tracked during the field demonstration to ensure that sufficient butyric acid was being injected and to examine the fate of added reducing equivalents. Unfortunately, the analytical laboratory did not report butyric acid results until Week 21 due to a miscommunication. Figure 3-27 shows the average concentration of each of these organic acids within the testing zone.

Although butyric acid data are not available for the first 20 weeks of the demonstration, the concentrations of organic acids that were measured were relatively low compared to the other demonstration sites. The injection concentration of butyric acid was approximately 3,000 μM throughout the demonstration, but a series of power disruptions at the site caused occasional interruptions in butyric acid injection and may have contributed to the relatively low levels of organic acids observed in the testing zone.

Acetic acid was present intermittently at the site, but at concentrations much less than expected. Microcosm studies showed that acetic acid was the primary fermentation product and that it tended to accumulate in the bottles. The field demonstration did not exhibit this accumulation. Perhaps the interruptions in butyric acid injection promoted the use of residual acetic acid.

Lactic and propionic acids were occasionally observed at low concentrations.

Organic acids were never detected in the background well.

Inorganics

Several inorganic species were tracked throughout the field demonstration, including pH, alkalinity, nitrate, nitrite, ammonia, sulfate, and chloride. Data for each of these species is described in the following subsections and is presented in Figures 3-28 through 3-32.

pH and Alkalinity

Figure 3-28 shows that the average groundwater pH within the testing zone remained relatively neutral despite the continuous addition of butyric acid. Undoubtedly, the high level of background alkalinity served as an effective pH buffer. The significant increase in alkalinity observed during the demonstration resulted from the addition of sodium bicarbonate solution, which was done in conjunction with the butyric acid injection.

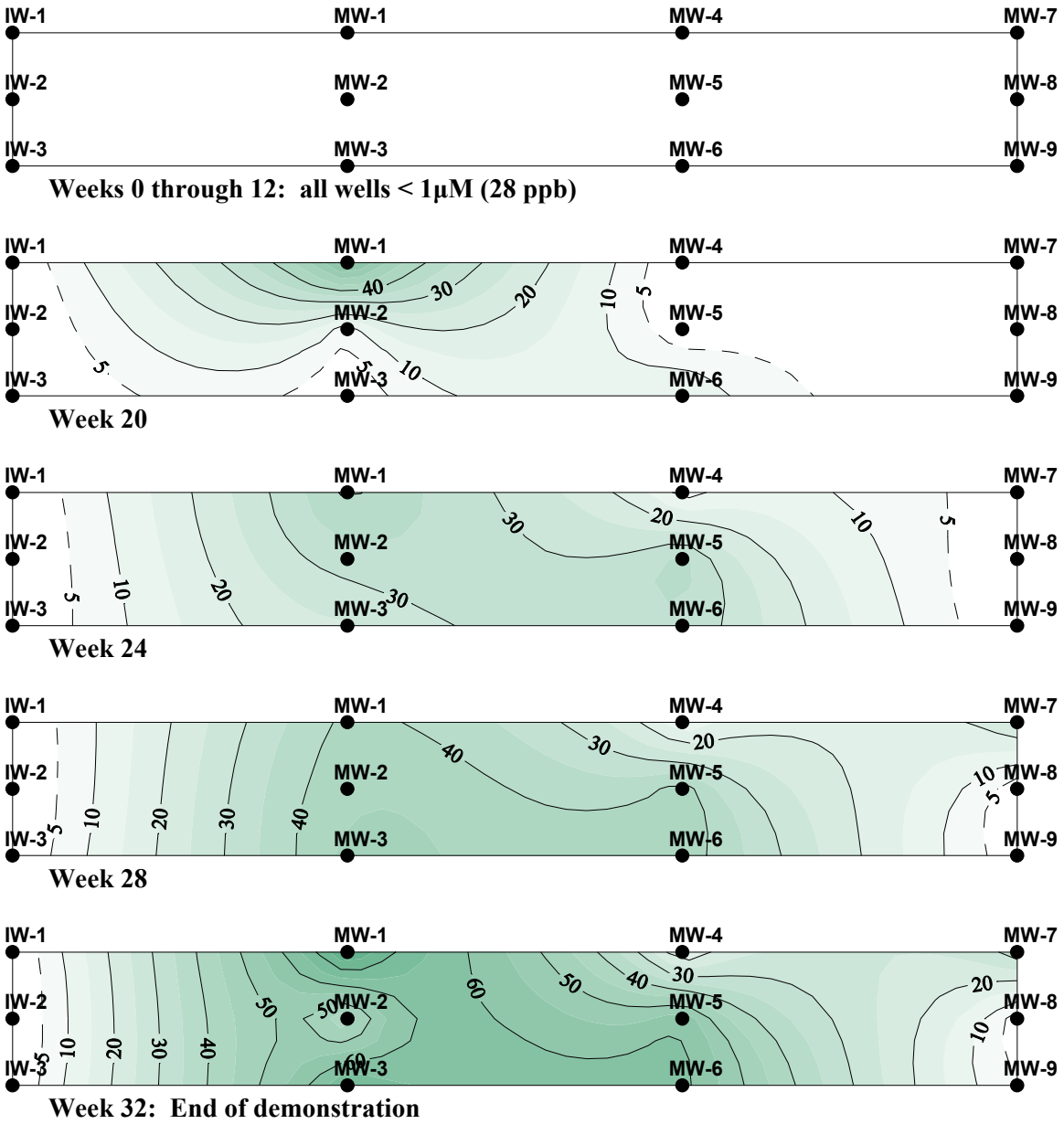


Figure 3-25. Ethene Concentration Contours at Site 4, Alameda Point, California

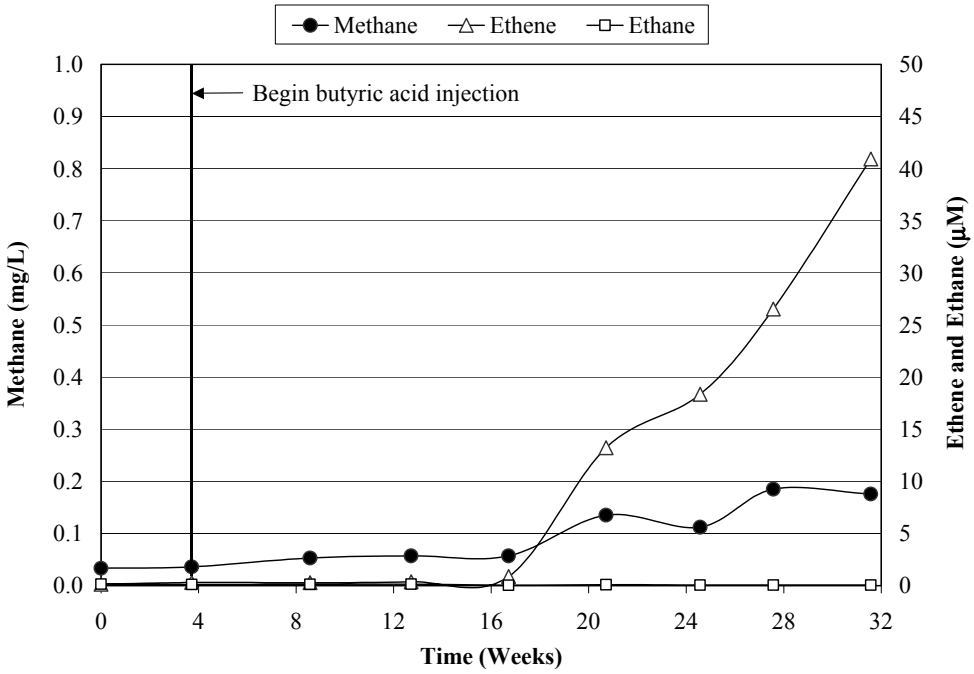


Figure 3-26. Average Dissolved Ethene, Ethane, and Methane Concentrations at Site 4, Alameda Point, California

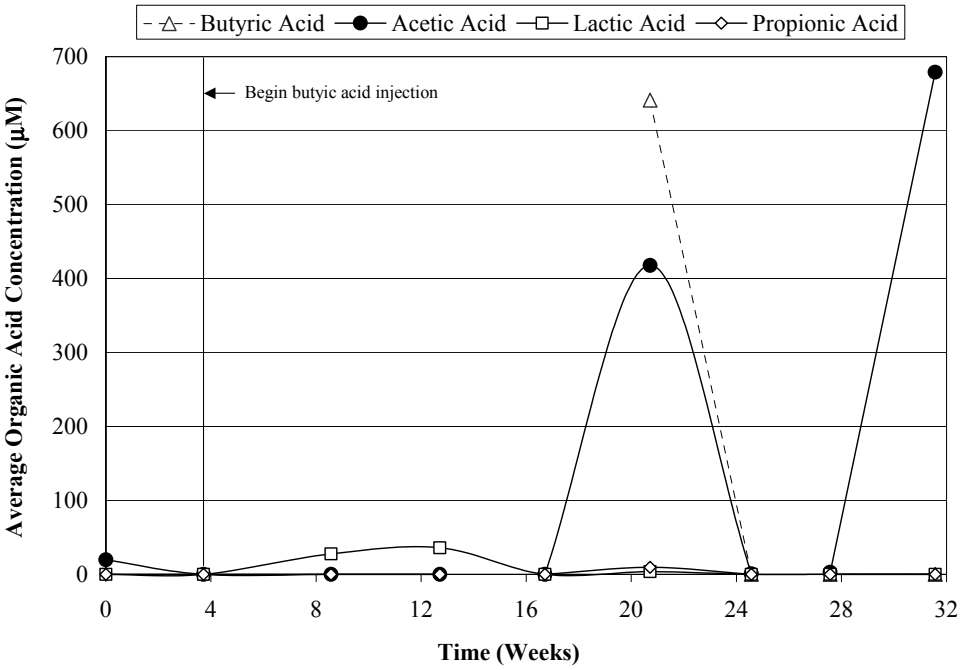


Figure 3-27. Average Organic Acid Concentrations at Site 4, Alameda Point, California

Dissolved Oxygen and Ferrous Iron
Dissolved oxygen and ferrous iron measurements were made to examine the terminal electron accepting process occurring at the site. Measurements were made at the wellhead using a dissolved oxygen probe and a ferrous iron colorimetric test kit.

Figure 3-29 shows that dissolved oxygen levels at the site remained low enough at the site to suppress aerobic microbial activity during the demonstration. The reason for the slight increase in dissolved oxygen levels towards the end of the demonstration is unknown.

A surge in the ferrous iron concentration occurred between the sixth and eighth week of the demonstration, suggesting that iron reduction was a significant terminal electron-accepting process during that period. Unexpectedly, a second surge in the ferrous iron level was observed between Weeks 20 and 22, suggesting that a second source of ferric iron became available mid-demonstration (perhaps from the supply well).

Ferrous iron was not detected in water samples collected from the background well or the supply well.

Nitrate, Nitrite, and Ammonia
The groundwater at Site 4 had the highest concentrations of nitrate and nitrite observed at the four RABITT demonstration sites. It was expected that the injection of butyric acid would stimulate the reduction of these compounds and perhaps generate ammonium (NH_4^+) as the site became highly reduced, but the decline in nitrate and nitrite levels observed over the first eight weeks of the study was probably largely the result of dilution (see Figure 3-30). The supply well, which was screened over a shallower interval than the testing zone, produced groundwater with significantly lower concentrations of nitrate and no nitrite. The initial concentration of nitrate in the supply well was 0.3 mg/L, and the average concentration over the course of the demonstration was 0.77 mg/L. The continuous injection of this water into the testing zone would certainly have lowered the average in situ nitrate and nitrite concentrations. This is particularly evident during the first four weeks of the demonstration, during which only bromide tracer was injected

Late in the demonstration, ammonia levels began to increase slightly, suggesting that nitrogen species were being reduced within the testing zone, but overall, nitrate was not a significant obstacle for stimulating reductive dechlorination at this site.

Sulfate
The groundwater at Site 4 contained high levels of sulfate, which is not surprising considering the site's proximity to the Pacific Ocean. Although data from the first 8 to 12 weeks of the demonstration show wild variability, the data do begin to settle down and show a steady decline within the testing zone (see Figure 3-31). This decrease in the average sulfate concentration indicates sulfate reduction was probably occurring at the site during the last 20 weeks of the demonstration.

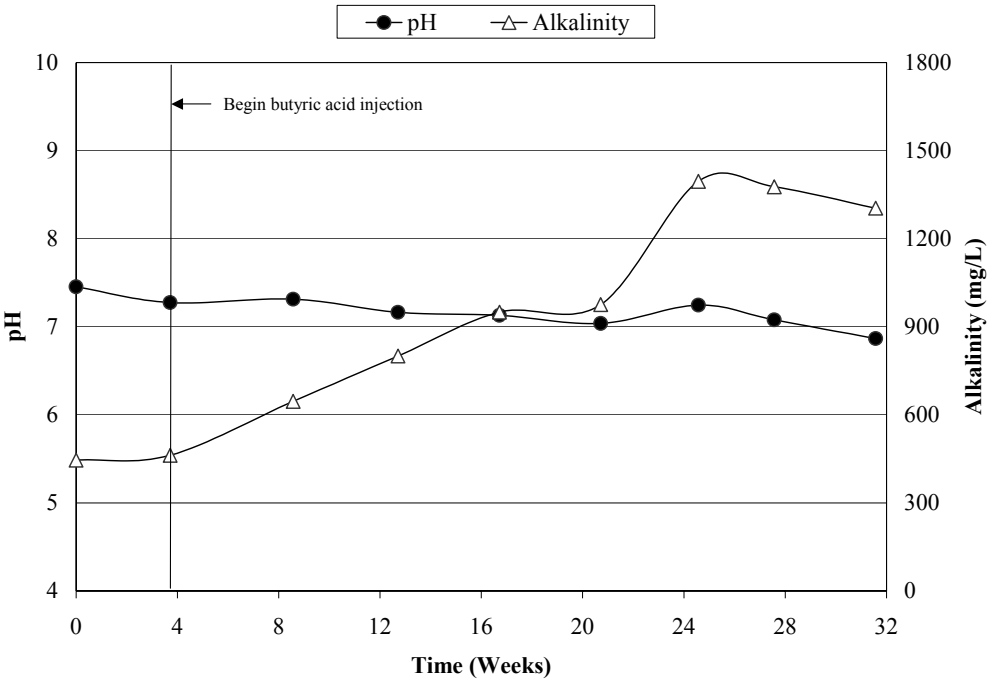


Figure 3-28. Average Field pH and Alkalinity Concentrations at Alameda Point, California

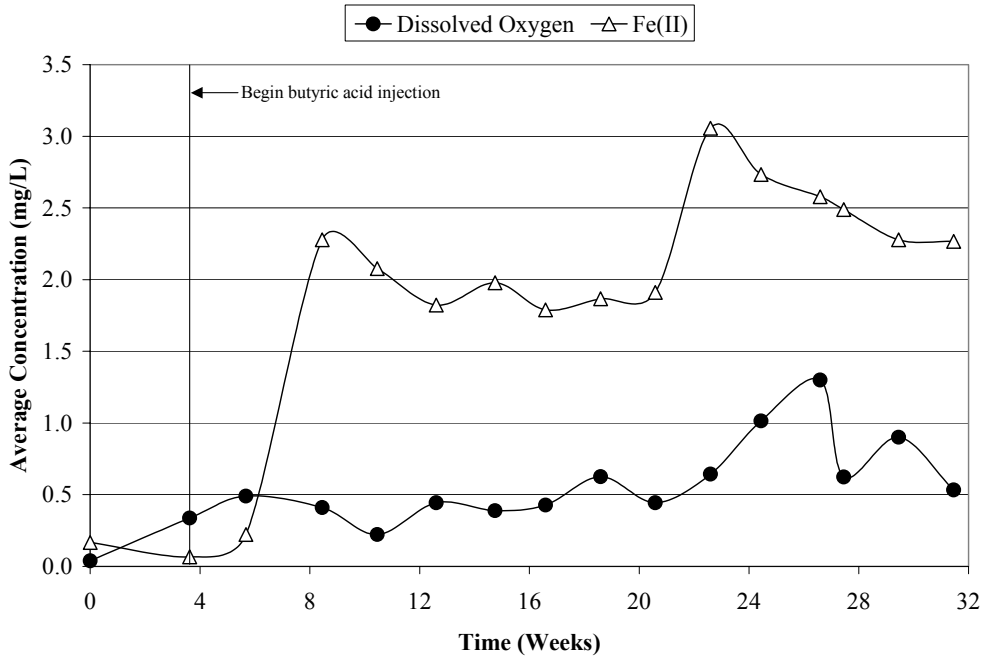


Figure 3-29. Average Dissolved Oxygen and Ferrous Iron Concentrations at Site 4, Alameda Point, California

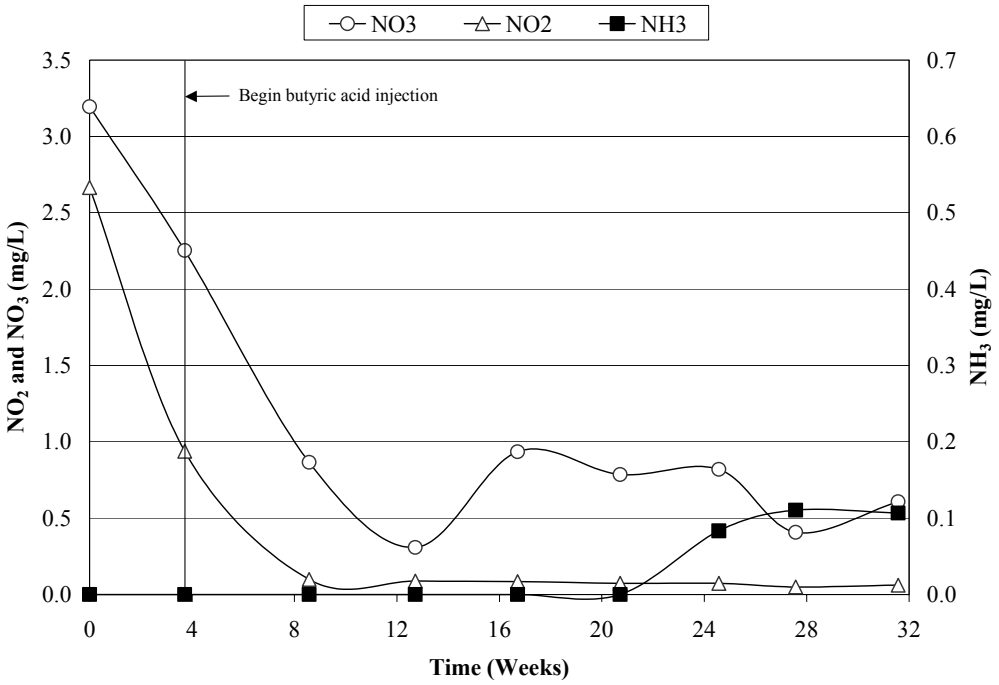


Figure 3-30. Average Nitrate, Nitrite, and Ammonia Concentrations at Site 4, Alameda Point, California

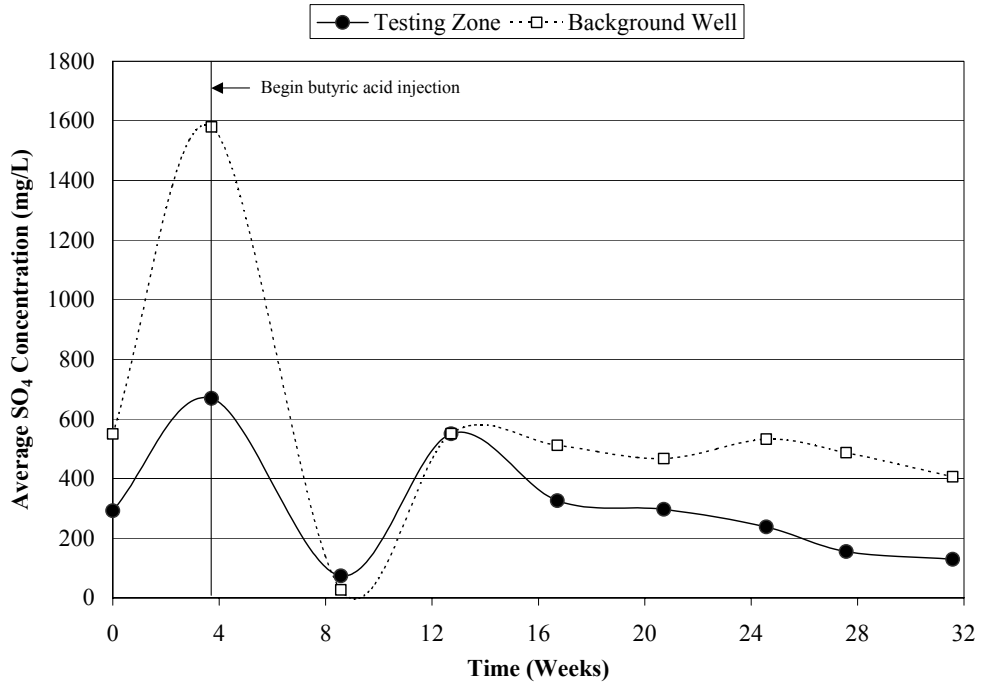


Figure 3-31. Average Sulfate Concentrations at Site 4, Alameda Point, California

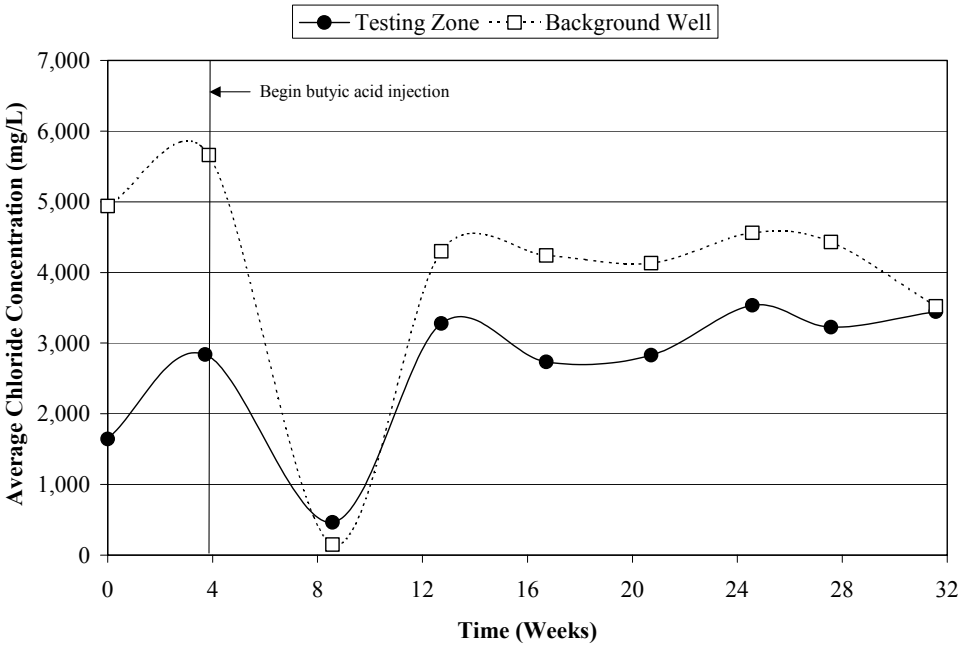


Figure 3-32. Average Chloride Concentrations at Site 4, Alameda Point, California

Chloride

Chloride levels in the groundwater at Site 4 were exceptionally high throughout the demonstration and prevented the observation of the relatively small (<10 mg/L) increases that might have resulted from reductive dechlorination. The high chloride levels were certainly related to the site's proximity to the San Francisco Bay.

Figure 3-32 shows that the average chloride concentration fluctuated considerably in both the testing zone and the background well, with concentrations ranging from 5,660 mg/L down to 150 mg/L. The dramatic dip in chloride concentrations during Week 8 also was seen in the sulfate data. An explanation for this unexpected observation was never found.

Dissolved Organic Carbon

The initial average DOC concentration in the testing zone was high at 120 mg/L, but surprisingly subsequent measurements, which were made after butyric acid injection began, remained below 20 mg/L. Figure 3-33 shows measured DOC values versus the total organic acid concentration represented as DOC equivalents. Unfortunately, it is somewhat difficult to assess how well DOC measurements correlated to the total organic acid concentration because butyric acid data were not generated until Week 20. In addition, DOC data was not reported during Week 20, which coincidentally, exhibited an unusual spike in the organic acid concentration. Nonetheless, only during Week 0 did the organic acid data differ from the DOC data by more than 10 mg/L.

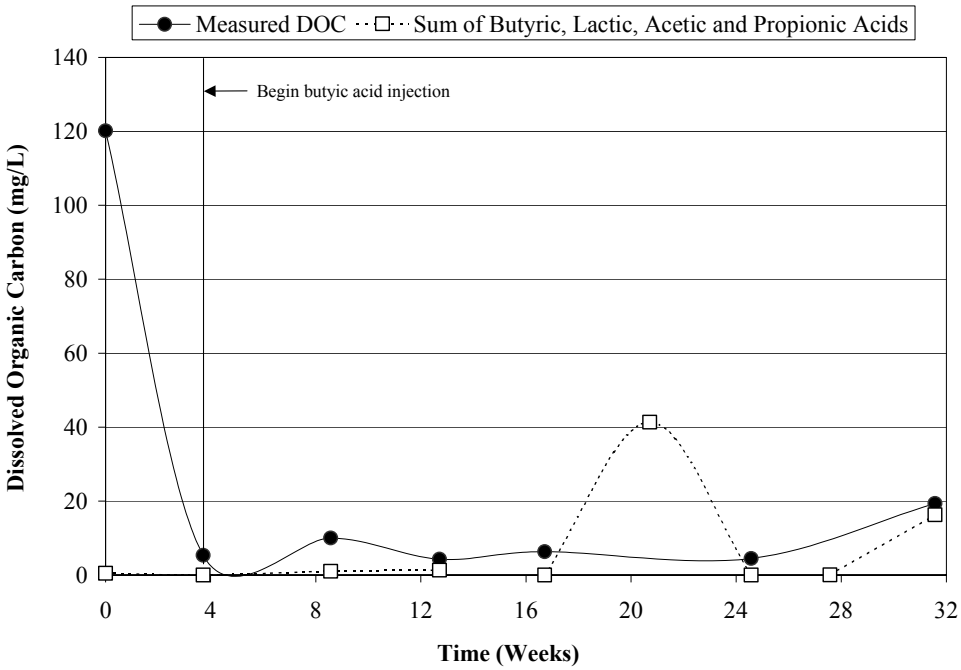


Figure 3-33. Average Dissolved Organic Carbon Concentrations at Site 4, Alameda Point, California

DOC levels in the background and supply wells closely resemble the average DOC concentrations observed in the testing zone (data not shown), so the dramatic decrease in DOC levels seen in the testing zone during tracer testing did not result from dilution.

Redox Potential and Temperature

Figure 3-34 shows the average redox potential and groundwater temperatures recorded at Site 4 during the RABITT demonstration. The figure shows that butyric acid injection lowered the average redox potential within the testing zone from an initial value of +27 mV to a final value of -66 mV with some fluctuation in between. As expected, redox potential measurements in monitoring wells closest to the injection wells were considerably lower than those observed at outlying wells, but they did not fall below -200 mV. The redox potential in the background well remained relatively stable; it ranged from +27 mV to +89 mV with no apparent trend.

The groundwater temperature at Site 4 was relatively stable over the course of the demonstration; it ranged from 18.4°C to 23.3°C. This is not surprising considering the temperate climate in the San Francisco Bay area.

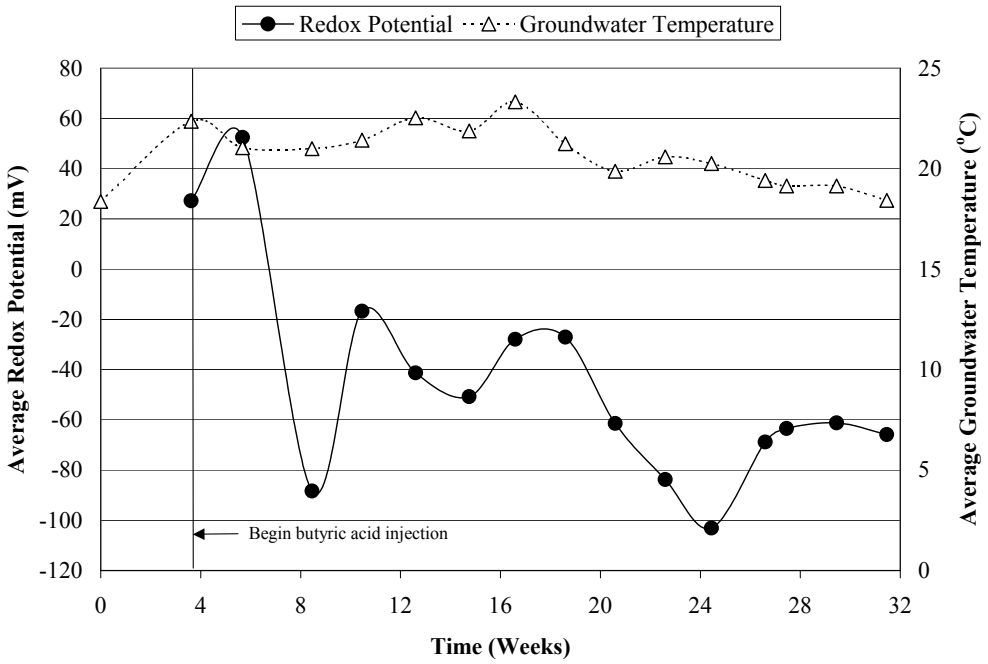


Figure 3-34. Average Redox Potential and Groundwater Temperature at Site 4, Alameda Point, California

3.3.4.5 Conclusions. Results from the RABITT field demonstration at Alameda Point show that native subsurface microbial populations effectively dechlorinated TCE to ethene at Site 4. Once the process was established, the conversion was both rapid and complete with no significant accumulation of intermediate products. Mass recovery of injected chloroethenes was 92% in the first row of monitoring wells and showed a 60% conversion to ethene.

The data show that the dechlorination process was not adversely affected by the relatively high concentrations of sulfate observed at the site. Dark-colored purge water and the unmistakable smell of hydrogen sulfide were present in monitoring wells MW-1 and MW-3, but no inhibition of microbial activity was evident. In addition, the depletion of sulfate and generation of methane was fairly steady and suggested that these microbial processes would not spiral out of control and consume an excessive portion of added reducing equivalents.

The overall impact of the demonstration on the natural subsurface geochemistry was mild and typically fell within expectations. The injection of the nutrient-amended groundwater did suppress the local redox potential and caused significant increases in alkalinity and the dissolved iron concentration. In addition, nitrate and nitrite concentrations were reduced through a combination of dilution and microbial reduction. DO and chloride levels remained largely unaffected, as did the in situ pH, which exhibited a very subtle decline. Perhaps the only surprise was the DOC data, which were initially very high, but then decreased following the initiation of nutrient injection.

Overall, results from Site 4 were very favorable and suggest that EBRD could be employed at this site.

3.4 Fort Lewis – East Gate Disposal Yard

3.4.1 Site Description – East Gate Disposal Yard. Fort Lewis is located at the southern end of Puget Sound between the cities of Olympia and Tacoma, Washington. The East Gate Disposal Yard (EGDY) is located in the northwest section of Fort Lewis, approximately 2 miles southeast of the town of Tillicum (see Figure 3-35).

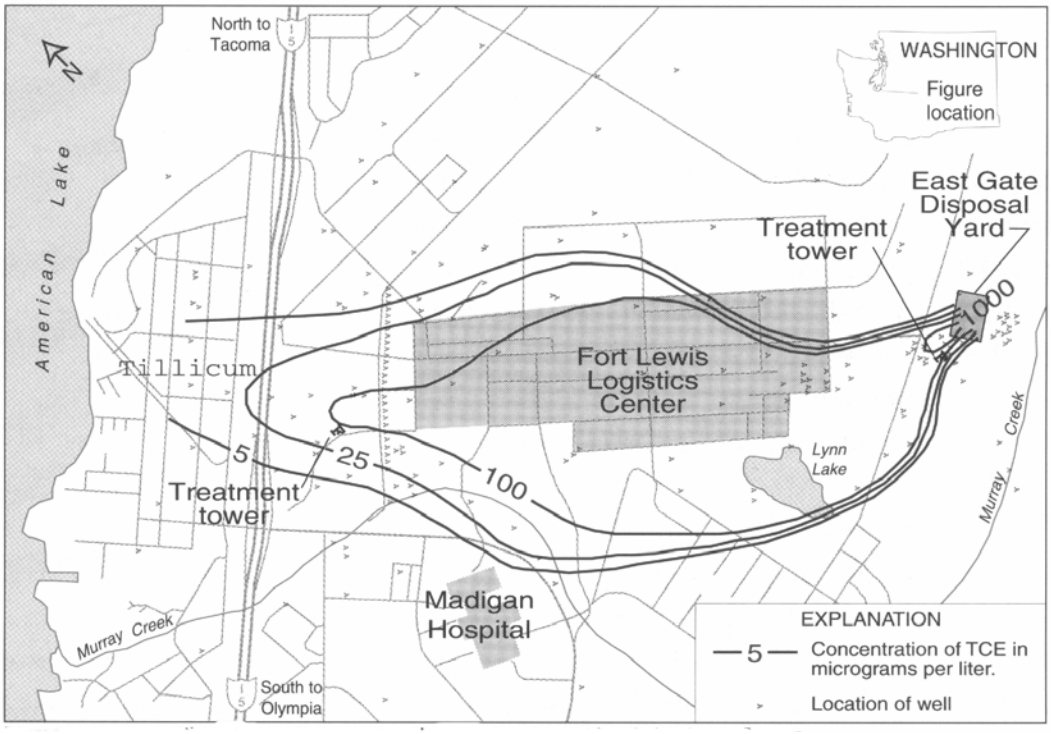


Figure 3-35. Map Showing Location of the East Gate Disposal Yard Site at Fort Lewis, Washington

The EGDY originally consisted of a 13.5-acre fenced waste disposal area; however, later investigation showed that waste was disposed outside the fenced area and that the site actually covered approximately 29 acres (Woodward-Clyde, 1997). Aerial photographs indicated that between 1940 and 1971 the EGDY was used as a storage and disposal site for various solid and liquid wastes (Woodward-Clyde, 1997). The photographic evidence shows that the wastes were disposed of in large trenches and pits, and that on occasion, the waste materials were burned. The majority of the liquid waste disposal activities occurred in trenches located on the western half of the EGDY site. Waste materials disposed of at the EGDY included TCE and petroleum, oil, and lubricant (POL) wastes from equipment cleaning and degreasing activities conducted at the Fort Lewis Logistics Center.

The results from a Remedial Investigation (RI) performed by Envirosphere delineated a contaminant plume in the Vashon Drift Aquifer that was more than 2 miles long, 3,000 to 4,000 feet wide, and 60 to 80 feet thick (Envirosphere, 1988). The primary contaminant was TCE, with *cis*-DCE at concentrations of up to 10% of the TCE concentrations. It was noted that *cis*-DCE was never used at the Fort Lewis Logistics Center, which sparked speculation that the *cis*-DCE was introduced as an impurity in the TCE or that it was the result of anaerobic biological transformation.

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) Record of Decision for the Fort Lewis Logistic Center specifies that pump and treat is used to prevent the further migration of the TCE plume. A system utilizing air stripping and reinjection through recharge galleries was installed and has been operating since 1995.

The geology at the site is typical of that of the Pleistocene glaciations that were predominant during depositional sequences of the Puget Sound Lowland area. The deposits of interest for the RABITT treatability test fall into the Vashon Drift, which represents the units deposited during the Vashon Stage of the Fraser Glaciation. In general, there are five distinctive units within the Vashon Drift including, in descending order, Steilacoom Gravel, Recessional Gravel, Vashon Till, Advance Gravel, and Colvos Sand. The Colvos Sand unit is not encountered at the EGDY site.

The uppermost soils at the EGDY site consist of recently deposited brown to black, alluvial sands and gravel, with localized lenses of silts and clay. The underlying Steilacoom Gravel unit is characterized with brown, loose to dense, well-graded, sandy, coarse gravel. The average thickness of this unit is approximately 13 ft throughout the EGDY site. The Vashon Till unit is encountered at an elevation of approximately 260 ft above mean sea level and consists of gray, dense, well-graded gravel in a matrix of sand, silt, and clay. This unit is characterized with low permeability and serves as an aquitard separating the upper shallow aquifer from the lower aquifer. Previous site investigations have shown that the contamination has been retained in the shallow aquifer.

The depth to groundwater at the EGDY site is approximately 10 ft bgs. The general direction of groundwater flow appears to be toward the west-northwest (Woodward-Clyde, 1997). Background groundwater velocities across the EGDY have been reported in the range of 2 to 3 ft per day. Both the direction and groundwater velocities in the area are influenced by the operation of the pump-and-treat system currently operating for plume control at the EGDY site. Preliminary modeling output using the Modflow™ groundwater simulation package estimated groundwater velocities in the area of interest approximately 3 to 3.5 ft per day.

3.4.2 Site Assessment/Selection – East Gate Disposal Yard. Previous site investigations delineated both the horizontal and vertical extent of chloroethene contamination at the EGDY site (USGS, 1999; Woodward-Clyde, 1997). These investigations indicated that the average TCE concentration at the site was significantly greater than its detection limit, which allowed contaminant reduction to be easily measured and documented. In addition, the

investigations delineated the presence of the TCE daughter products *cis*-DCE and VC, suggesting that microbially catalyzed dechlorination may already by occurring at the site. Finally, the contaminants were found at relatively shallow depths (10 to 35 ft bgs), so drilling costs would be reasonable and a peristaltic pump could be used for groundwater sampling.

Although the EGDY had been fairly well characterized with respect to contaminants, there were only limited geochemical data were available and the site was known to have considerable geological heterogeneity that could make injection tricky. In addition, an existing groundwater model suggested that the groundwater velocity through the site was on the order of 3 ft/day. Nonetheless, data from an existing sampling location (GD-18) showed the aquifer to be anoxic and within an acceptable pH range, and redox potential measurements and iron data suggested that the site was under iron-reducing conditions. Eventually, concerns regarding the geological heterogeneity, high groundwater velocities, and the lack of geochemical data were overridden by the desire to include more challenging sites to the overall project.

The site rating system described in the RABITT protocol was applied to the EGDY site to assess the site's potential for success and to allow the rating system to be evaluated after completing the demonstration. Average site conditions obtained from previously conducted site characterization work were compared against criteria in the rating system. The results from this comparison are listed in Table 3-17 along with the corresponding rating score. In several instances existing data were not available to complete the rating system score summary table; in these cases a default value of 0 was assigned to the parameter.

Table 3-17. RABITT Rating System Score Summary for the East Gate Disposal Yard at Fort Lewis, Washington

Rating Parameter	Conditions at the EGDY site	Score
Contaminant Profile	Vinyl chloride present	15
Hydraulic Profile	2×10^{-3} cm/sec	25
Geochemical Profile		
Dissolved Oxygen	0.70 mg/L	1
Nitrate	Data not available	0
Hydrogen Sulfide	Data not available	0
Sulfate	1.8 – 7.3 mg/L	2
Redox potential	-49.3 mV	0
Temperature	10.97°C	0
Dissolved Organic Carbon	0.2 - 1.9 mg/L	0
Bicarbonate Alkalinity	55-99 mg/L	-1
pH	6.9 - 7.1	3
Methane	Data not available	0
Total Point Value		45

The EGDY site scored a total point value of 45 out of 75 total possible points. As mentioned previously, the lack of geochemical data prevented the assignment of scores for several

parameters, so they were given the default value of zero. Despite this disadvantage, the score of the EGDY site fell into the range considered "Satisfactory" in the RABITT protocol.

3.4.3 Microcosm Testing – East Gate Disposal Yard

3.4.3.1 Microcosm Setup. Sediment and groundwater were collected from the EGDY on July 28 and 29, 1999. Cores were collected from three locations (PZ1, PZ2, and PZ3) within the probable test plot location. PZ1 and PZ3 were located on a line running northwest from drive point (DP) 18 to well LC134. PZ1 was approximately 10 ft from DP 18, and PZ3 was approximately 100 ft from DP 18. The third coring location (PZ2) was approximately 55 ft from DP18 and about 20 ft to the southeast of the line between DP 18 and well LC134. Cores were extracted from the 15- to 25-ft depth at PZ1, and at the 20- to 25-ft depth at PZ2 and PZ3.

Upon extraction from the ground, the split-spoon sampler was opened and the cores were immediately placed in a field glovebox that was then purged with argon gas for several minutes. Sleeves were capped with plastic caps, sealed with tape, placed in a cooler with a small amount of ice, and shipped to the laboratory the same day. Groundwater (10 L) was collected from PZ1 after limited development. Upon arrival at the laboratory the cores and groundwater were stored in a 4°C chamber.

The cores were composited for use in the microcosm study: autoclaved utensils and mixing dishes and a never-before-used disposable glovebag were utilized. Stones that exceeded 22 mm (the diameter of the opening of the vials used in this study) were removed from the sediment and discarded. Roughly 40-50% of the sediment was of a useable diameter.

The resulting sediment was mixed thoroughly and a sample was removed for moisture content analysis and alkalinity determination, and a small amount was placed in a sterile vial for later molecular characterization. The remaining mixed core material was packed tightly into autoclaved mason jars, sealed, and stored in a cooler 4°C.

Characterization of Fort Lewis (EGDY) composited sediment samples and groundwater is shown in Table 3-18

Table 3-18. Initial Characterization of EGDY Soil and Groundwater

Characterization Parameter	Value
Mixed Core Moisture Content (% moisture)	8.2 %
Groundwater pH	7.2
Soil/Groundwater Mixture[(a)] sulfate (mg/L)	35
Groundwater Total Alkalinity (eq/L)	0.0013 (65 mg $CaCO_3$/L)
Groundwater Conductivity (µS/cm)	148
Soil/Groundwater Mixture[(a)] pH	7.5
Soil/Groundwater Mixture[(a)] Total Alkalinity (eq/L)	0.00515 (258 mg $CaCO_3$/L)

(a) At ratio used in microcosm construction.

On August 14, 1999, the Fort Lewis microcosms were constructed. On the previous day, groundwater, mixed core, and sterile serum bottles, caps, and utensils were placed in the disposable glovebag. The glovebag was purged overnight with anoxic N_2 gas. Based on the alkalinity measurements and previous results with buffering microcosms, it was decided to add an additional 0.02 eq/L alkalinity to the groundwater through the addition of sterile $NaHCO_3$. Redox indicator (resazurin) also was added to the groundwater. Wet soil (54.5 g) and buffered groundwater (95.5 g) was added to an autoclaved serum bottle and the bottle was capped. Microcosms also were prepared that contained 119 g buffered groundwater alone (this volume mimicked the headspace volume of the sediment/groundwater microcosms). Upon setup, all the microcosms were purple tinted, indicating that the conditions were not fully reducing, but rapidly became reducing upon later addition of electron donor.

The bottles were quiescently incubated upside down at 15°C (the approximate prevailing in situ groundwater temperature at Fort Lewis) until August 20, 1999, when the autoclaving of the controls was finished. Also on that day, several bottles were analyzed to determine the background pollutant concentrations. The estimated levels in the groundwater were: TCE, 200 ppb; *cis*+*trans*-DCE, nondetect (ND); 1,1-DCE, ND; VC, ND; ethene, ND; methane, 20 ppb; and hydrogen, 30μM (10^{-3} atmosphere [atm] in the headspace). The lack of pollutant was troubling; however, it was decided to go forward with the test since the bottles were already constructed. The elevated hydrogen level likely was caused by abiotic production of hydrogen in the iron-rich sediments that have been sheared, crushed, and otherwise disturbed by the sonic drill (Steven Cox, USGS, personal communication).

On Day 0 (8/20/99), TCE (30 μmol/bottle) was added to each bottle and the bottles were shaken on a wrist action shaker for 36 hrs. The bottles were again analyzed and then donor and nutrients were added according to the protocol in Table 3-19, but with propionate at 3 mM and with the inclusion of a ninth set of bottles with 3 mM acetate + YE + B_{12}. After shaking on the wrist action shaker, hydrogen levels increased to as much as 10^{-2} atm. Thus, despite setup in a practically hydrogen-free disposable glovebag, the microcosm test commenced with each microcosm containing a significant dose of molecular hydrogen as electron donor.

3.4.3.2 Microcosm Results. The Fort Lewis microcosms were operated for 292 days. No significant dechlorination occurred in control bottles (biotic or autolaved). Lactate, butyrate, and high YE all stimulated dechlorination to ethene by the end of the period, with butyrate evidencing the earliest TCE transformation and ethene formation, and with lactate + 20 mg/L YE performing better than lactate alone. The other donors (lactate +benzoate, acetate, or propionate) performed less well, with conversion only to *cis*-DCE (but incomplete conversion to ethene in some replicates) (Table 3-19). Like the Alameda Point microcosms and unlike those at CCAS, Fort Lewis microcosms indicated little or no fermentation of benzoate. Methane was evident from buyrate-fed microcosms late in the study, seemingly from accumulated acetate.

Less than 10 mg/L sulfide was measured in any of the biotic reactors at the conclusion of the monitoring period. This concentration represents a maximum electron sink of less than 250 μeq/bottle, which is much less than the typical gaps observed in the electron equivalent

Table 3-19. Primary Dechlorination Products in the Donor-Fed EGDY Microcosms (292 Days After Microcosm Seeding)

Bottle Set/Donor	Triplicate I	Triplicate II	Triplicate III
4 (200 mg/L Yeast Extract)	ethene	ethene	*cis*-DCE
5A (Lactate only)	ethene	*cis*-DCE (19%) VC (81%)	VC (92%) ethene (8%)
5B (Lactate + 20 mg/L Yeast Extract)	*cis*-DCE	*cis*-DCE (94%) VC (6%) (after 163 days)[(a)]	ethene
5C (Lactate + B_{12})	VC (73%) ethene (27%)	*cis*-DCE (after 177 days)[(a)]	*cis*-DCE (3%) VC (90%) ethene (7%)
5D (Lactate + 20 mg/L Yeast Extract + B_{12})	*cis*-DCE	ethene	VC (23%) ethene (77%)
6 (Butyric Acid + 20 mg/L Yeast Extract + B_{12})	ethene	ethene	*cis*-DCE
7 (Lactate/Benzoate + 20 mg/L Yeast Extract + B_{12})	*cis*-DCE (30%) VC (70%)	*cis*-DCE (3%) VC (92%) ethene (5%)	ethene
8 (Propionic Acid + 20 mg/L Yeast Extract + B_{12})	*cis*-DCE (95%) VC (5%)	*cis*-DCE	*cis*-DCE
9 (Acetic Acid + 20 mg/L Yeast Extract + B_{12})	*cis*-DCE (52%) VC (48%)	*cis*-DCE	*cis*-DCE

(a) Replicate was accidentally broken on indicated date.

distribution graphs. The fact that such limited sulfide production was observed was not surprising given the low levels of sulfate present in these sediments; 35 mg/L of sulfate was found in Fort Lewis microcosms versus the 80 and 965 mg/L measured in CCAS and Alameda Point microcosms, respectively.

Dechlorination in the Fort Lewis microcosms was markedly slower than anticipated based on previous results with samples collected from Alameda Point and CCAS. While the initial dose of TCE was removed from all of the amended, biotic reactors, formation of VC and complete conversion to ethene occurred in only a few bottle sets after 292 days of monitoring. Lower temperature (15°C vs. 24°C) may partially explain the slower kinetics.

Another important factor influencing both lag and extent of dechlorination was probably the low, native levels of TCE in the materials from which these microcosm sets were created. Although the cores were selected from locations that appeared to contain significant contamination, there was no way of ensuring that there was TCE in the exact material used in the microcosms. And, in fact, initial analyses of the microcosms after setup showed no appreciable native TCE levels in them. Without prior exposure to TCE, there is little selective pressure for the growth of native microorganisms capable of dechlorination. Although this does not preclude the eventual growth of such organisms following extended acclimation to the chlorinated ethenes, it may have resulted in longer lag times as population shifts took place within the microcosms.

The lack of prior exposure to *cis*-DCE and VC likely influenced the dechlorination of these compounds as well. In the majority of the bottles, there was a consistently long lag observed prior to the initiation of *cis*-DCE dechlorination. This lag was generally even lengthier than the one observed prior to transformation of TCE. In certain bottles, *cis*-DCE was never dechlorinated. In addition to the possibility that there were few dechlorinating organisms present in the Fort Lewis sediment material, there is a concern that overall biomass was low as well. Even over the course of nearly 300 days, there was little degradation of propionate, benzoate, and acetate in reactors supplemented with these growth substrates. Given the wide number of organisms capable of utilizing these substrates, the lack of observed degradation was surprising. A slow establishment of these populations may have contributed to the low dechlorinating activity, a process that may have been stimulated by more extensive fermentation of the added substrates.

The two amendments that did result in complete conversion to ethene in two of the three replicates were butyrate and high concentrations of YE. Because the observed degradation of butyrate is slow, it appears to provide a relatively steady, long-term supply of electron equivalents for use. Therefore, butyrate was selected for use in the subsequent field study. To facilitate later comparison with results from the field study, the results of a microcosm that was fed butyrate + 20 mg/L YE + 0.05 mg/L B_{12} are presented in Figure 3-36.

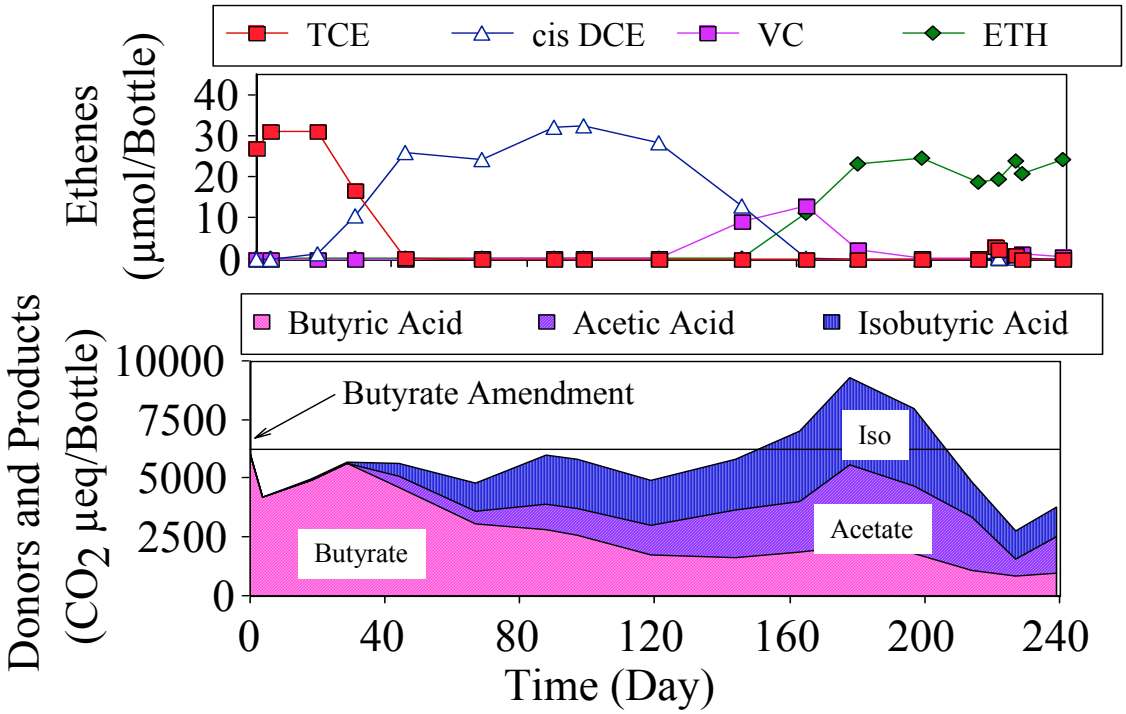


Figure 3-36. Results from Fort Lewis Microcosm (6-I) Fed 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12}

3.4.4 Field Testing – East Gate Disposal Yard

3.4.4.1 System Design/Installation. The design of the RABITT demonstration system at the EGDY was complicated by an existing site groundwater model that indicated a groundwater velocity of approximately 3 ft/day. It was desired to install the standard RABITT demonstration system described in the protocol, but the system would need to be 90 feet long in order to achieve the suggested 30-day hydraulic retention time (HRT). Before installing the system at such an unusual scale it was decided to install a series of six dual-level piezometers to verify the groundwater model predictions and ensure that fluid could be tracked through the heterogeneous formation over such a long distance. The piezometers were installed on July 28, 1999.

Groundwater samples collected from the piezometers and analyzed for VOCs revealed that TCE levels were much lower than expected and were inappropriate for a RABITT demonstration. As a result, 10 multilevel Strataprobe™ points were installed on October 19-22, 1999 in an effort to find a more contaminated zone within the plume. Groundwater samples from several Strataprobe™ sampling points did show high levels of localized contamination.

Once an area with sufficient TCE contamination had been identified, a preliminary bromide tracer test was conducted to determine the speed and direction of groundwater flow in the contaminated area. Results from this test, which are presented briefly in a subsequent section, were used to locate and size the RABITT demonstration system.

Installation of the RABITT demonstration system at the EGDY began on May 10, 2000. A total of 13 wells were installed with screened intervals ranging from 26 to 29 ft bgs. In addition, an existing well, designated A-15, that exhibited consistently high levels of TCE, was used to supply contaminated groundwater for the demonstration. Table 3-20 outlines well specifications and Figure 3-37 shows the relative locations of system wells.

All installed subsurface components were decommissioned in accordance with applicable state regulations the week of February 25, 2001.

Table 3-20. RABITT System Well Specifications at the EGDY, Fort Lewis, Washington

Parameter	Injection Wells	Monitoring Wells
Number of wells	3	10
Diameter (in.)	½	½
Screened Interval (ft bgs)	26 to 29	26.75 to 28.25
Slot Size (in.)	0.01	0.01
Material	CPVC	CPVC

CPVC- Chlorinated polyvinyl chloride.

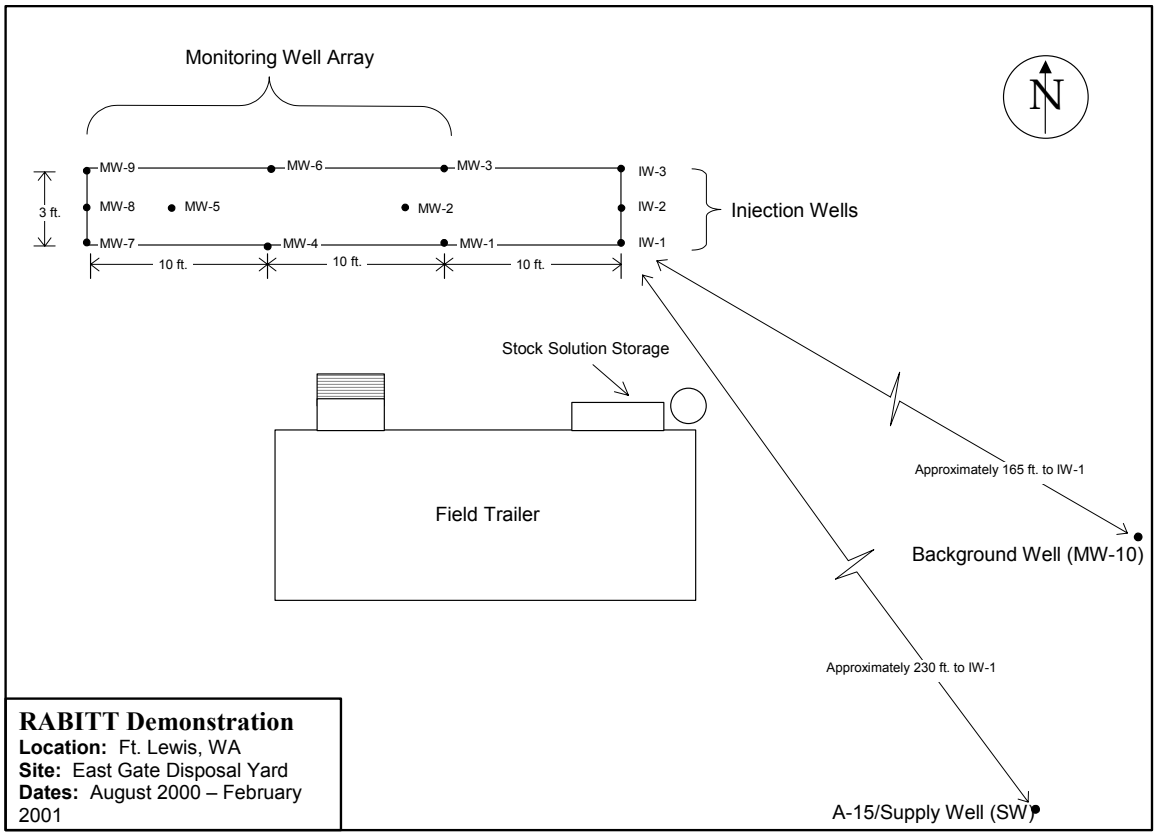


Figure 3-37. Plan View of RABITT Demonstration Site at the EGDY, Fort Lewis, Washington

3.4.4.2 Tracer Testing. Two bromide tracer tests were conducted at the Fort Lewis RABITT demonstration site. The first test began on November 15, 1999 and was designed to verify the groundwater velocity predicted by an existing site model. A 1,000-gal slug of 1,000-ppm sodium bromide solution was injected into piezometer PZ-1 over approximately 4 hours. Results showed groundwater moving to the northwest at approximately 0.75 feet per day (fpd), considerably more slowly than expected (data not shown).

The second tracer test was initiated on August 4, 2000. The newly installed RABITT demonstration system was used to continuously inject a 150-ppm sodium bromide solution down wells IW-1, IW-2, and IW-3. The total flowrate averaged about 1.5 L/min. Figure 3-38 shows a time series of contour plots, which illustrate the movement of bromide through the testing zone. Concentrations are given in mg/L. Plots were generated using data collected in the field using a bromide-specific electrode.

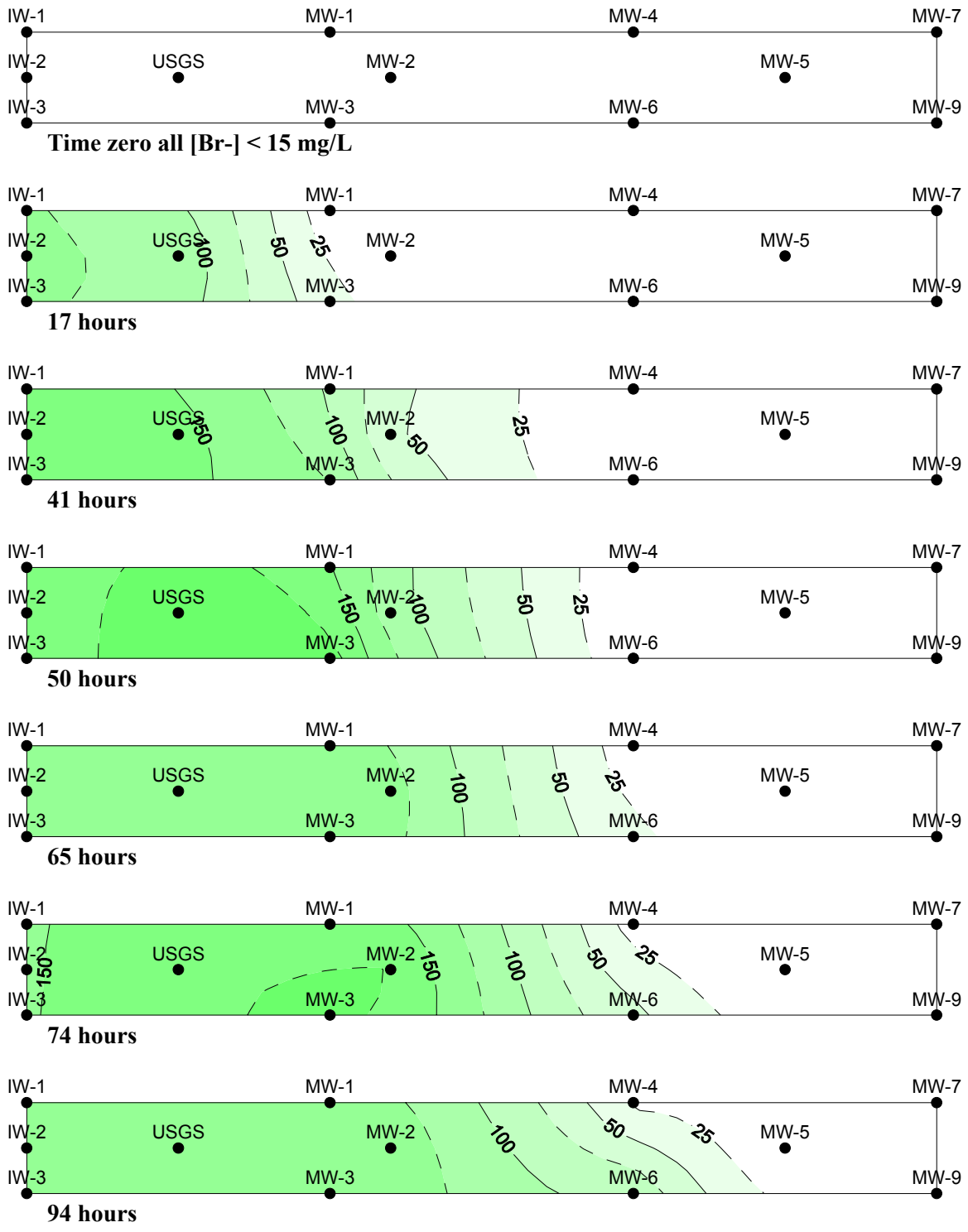


Figure 3-38. Bromide Tracer Testing Results from the EGDY, Fort Lewis, Washington

The data show that bromide tracer moved along the axis of the testing zone, but the slope of the leading contours suggests that the background groundwater flow was not from left to right as was expected, but rather appears to have been moving more perpendicular to the axis of the testing zone. Figure 3-39 illustrates the suspected alignment of the testing zone with respect to the movement of tracer in the groundwater.

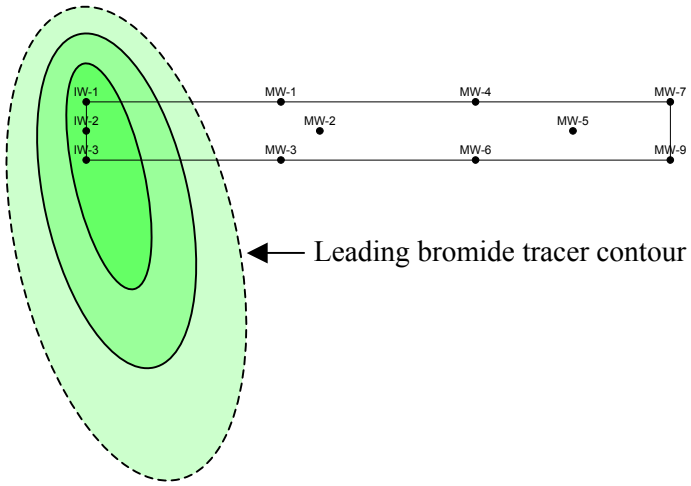


Figure 3-39. Suspected Alignment of Testing Zone with Respect to Background Groundwater Movement Illustrated by Bromide Tracer Concentration Contours

Although the injection flowrate appeared to have been sufficient to overwhelm the local background groundwater gradient and push injected fluid through the testing zone, results observed later during the treatability testing suggest that background groundwater did enter the far end of the testing zone, especially monitoring wells MW-7 and MW-9.

3.4.4.3 Treatability Testing

System Operation

Treatability testing at the EGDY involved the continuous extraction, amendment, and injection of TCE-contaminated groundwater for about 6.5 months. A submersible Grundfos™ pump was used to extract groundwater from an existing well, designated A-15, which supplied groundwater with a consistently high concentration of TCE.

The extracted groundwater was pumped into a field trailer where two dedicated metering pumps added amendments. The first metering pump fed a solution containing butyric acid (110g/L), YE (8.3 g/L), and sodium bromide (53.5 g/L) at about 2-3 mL/min. The second metering pump fed a sodium bicarbonate solution (30 g/L) at approximately 9 mL/min.

After the groundwater had been amended with nutrients in the field trailer, it was evenly split into the three injection wells. The total injection flowrate was approximately 1.5 L/min, resulting in approximately 500 mL/min down each injection well. Injection of the nutrient amended groundwater began on August 31, 2000, and ended on February 26, 2001.

The butyric acid-YE sodium bromide stock solution was prepared in two covered 15-gallon HDPE tanks using concentrated butyric acid, YE, sodium bromide, and tap water. Similarly, the sodium bicarbonate solution was prepared in a covered 55-gallon HDPE tank using sodium bicarbonate and tap water.

Sampling

The RABITT demonstration at the EGDY required the frequent sampling and analysis of a variety of groundwater parameters. Groundwater samples were collected every two weeks from each of 12 individual monitoring locations. Table 3-21 shows the specific sampling dates and sample types collected at the EGDY, and Table 3-22 lists the specific analytes for each sample type. Additional information regarding analytical methods, container types, sample preservatives, and holding times can be found in the Technology Demonstration Plan for Fort Lewis (Battelle et al., 2000).

A peristaltic pump was used to pump groundwater from monitoring wells and into a flowthrough cell. The flowthrough cell was instrumented with probes, which measured pH, temperature, redox potential, and DO. Groundwater was allowed to flow through the cell and into a waste container until redox potential and DO measurements stabilized. Once these measurements stabilized, all field measurements were recorded and groundwater samples were collected and prepared for shipment to the appropriate analytical laboratory. Additional groundwater samples were collected and used to measure the bromide ion and ferrous iron concentrations in the field.

Table 3-21. Sampling Schedule at the EGDY, Fort Lewis, Washington

Date	Elapsed Time (Weeks)	Field Data	Laboratory Analytes					
			VOCs	Dissolved Gases	Organic Acids	Inorganic Data	DOC	H_2
03-Aug-00	0 (preinjection)	X	X	X	X	X	X	
31-Aug-00	4 (injection begins)	X	X	X	X	X	X	X
13-Sept-00	6	X	X					
04-Oct-00	9	X	X	X	X	X	X	
12-Oct-00	10	X	X					
25-Oct-00	12	X	X	X	X	X	X	
08-Nov-00	14	X	X					
29-Nov-00	17	X	X	X	X	X	X	X
20-Dec-00	20	X	X					
16-Jan-01	24	X	X	X	X	X	X	
31-Jan-01	26	X	X					
14-Feb-01	28	X	X	X	X	X	X	
26-Feb-01	30	X	X	X	X	X	X	X

Table 3-22. Laboratory Analytes at the EGDY, Fort Lewis, Washington

Field Data	Laboratory Analytes					
	VOCs	Dissolved Gases	VFA Data	Inorganic Data	DOC	H_2
Water Level Redox potential pH Temperature Bromide DO Fe(II)	PCE TCE *cis*-DCE VC	Ethene Ethane Methane	Lactic acid Acetic acid Propionic acid Benzoic acid Butyric acid	pH Conductivity Alkalinity Nitrate Nitrite Ammonia Chloride Sulfate Bromide	Dissolved organic carbon	Dissolved hydrogen

3.4.4.4 Results. Results from the RABITT demonstration at the EGDY are presented in the following subsections. Concentrations of TCE and its primary dechlorination products, *cis*-DCE and VC, are presented in a series of contour plots showing the distribution of contaminant in both space and time. The remaining analytical parameters are presented in graphs that show their average concentration within the testing zone as a function of time. Average concentrations were calculated using data from monitoring wells MW-1 to MW-7 and MW-9. Monitoring well MW-8 did not produce enough water to permit the collection of samples. Data from the supply, injection, gradient, and background wells were not included unless otherwise specified. Average data were used to allow the assessment of the overall system performance while reducing the number of individual figures to a manageable limit. Results for individual monitoring locations and for other analytes (e.g., *trans*-DCE) are available in the Fort Lewis Database, which can be found on the CD-ROM supplied with this report.

Chloroethene Concentration Profiles

The results from selected TCE, *cis*-DCE, and VC sampling events are presented. Contour plot concentration units are in µM to allow for direct comparison between the three compounds on an equivalent basis. Results for the other chloroethenes (PCE, *trans*-DCE, 1,1-DCE) were unremarkable and are therefore not presented. In general, concentrations of each of these contaminants remained relatively low throughout the demonstration. In fact, the sum of all three usually contributed less than 1% of total chloroethenes on a molar basis.

Trichloroethene

Initial preinjection TCE concentrations ranged across the test plot from 11.0 to 47.9 µM (1,450 to 6,300 ppb). Injected groundwater initially contained moderately higher levels that tended to increase over the first 13 weeks of the demonstration from a low of 39.6 µM (5,200 ppb) at system startup to 148 µM (19,400 ppb) at Week 13. TCE concentrations remained within this range until Week 24 when concentrations spiked dramatically to 1,286 µM (169,000 ppb) (see Figure 3-40). It appears likely that this sudden increase in TCE concentration resulted from drum excavations performed near the supply well in early February 2001. Concerns that TCE levels of this magnitude would prove toxic to the microorganisms catalyzing the dechlorination reaction proved unwarranted as the conversion of TCE to *cis*-DCE continued unabated.

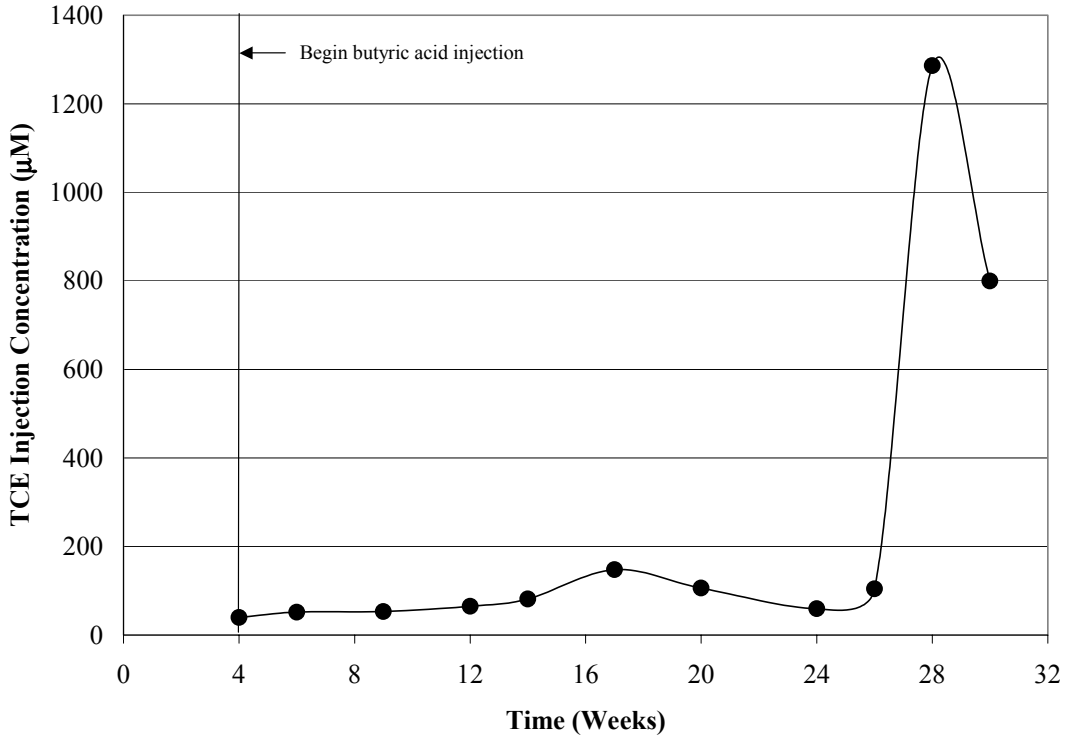


Figure 3-40. TCE Injection Concentration at the EGDY, Fort Lewis, Washington

Figure 3-41 shows a time series of TCE concentration contours. Butyric acid-amended groundwater was injected into the injection wells IW-1, IW-2, and IW-3 at the left end of the plot and moved generally to the right. The elevated levels of TCE observed at the right end of the test plot suggest that background groundwater was continuously entering that end of the testing zone. This observation is consistent with the results of the bromide tracer test, which suggested that the background groundwater was moving perpendicular to the test plot.

After eight weeks of electron donor injection, the influent concentration of TCE was reduced 99.94% from 65 µM (8,500 ppb) to an average concentration of 0.04 µM (5 ppb) by the time it reached the first row of monitoring wells approximately 50 hours later. Assuming pseudo-first-order kinetics, this rate of TCE removal translates into a half-life of 4.7 hrs ($k = -0.1488$ hrs^{-1}). This rate of removal remained constant when the influent concentration of TCE increased to 1,286 µM (169,000 ppb) during Week 28. The concentration in the injected water, once it reached MW-3, was only 0.53 µM (69.4 ppb), which translates into a half-life of 4.4 hrs ($k = -0.155$ hrs^{-1}).

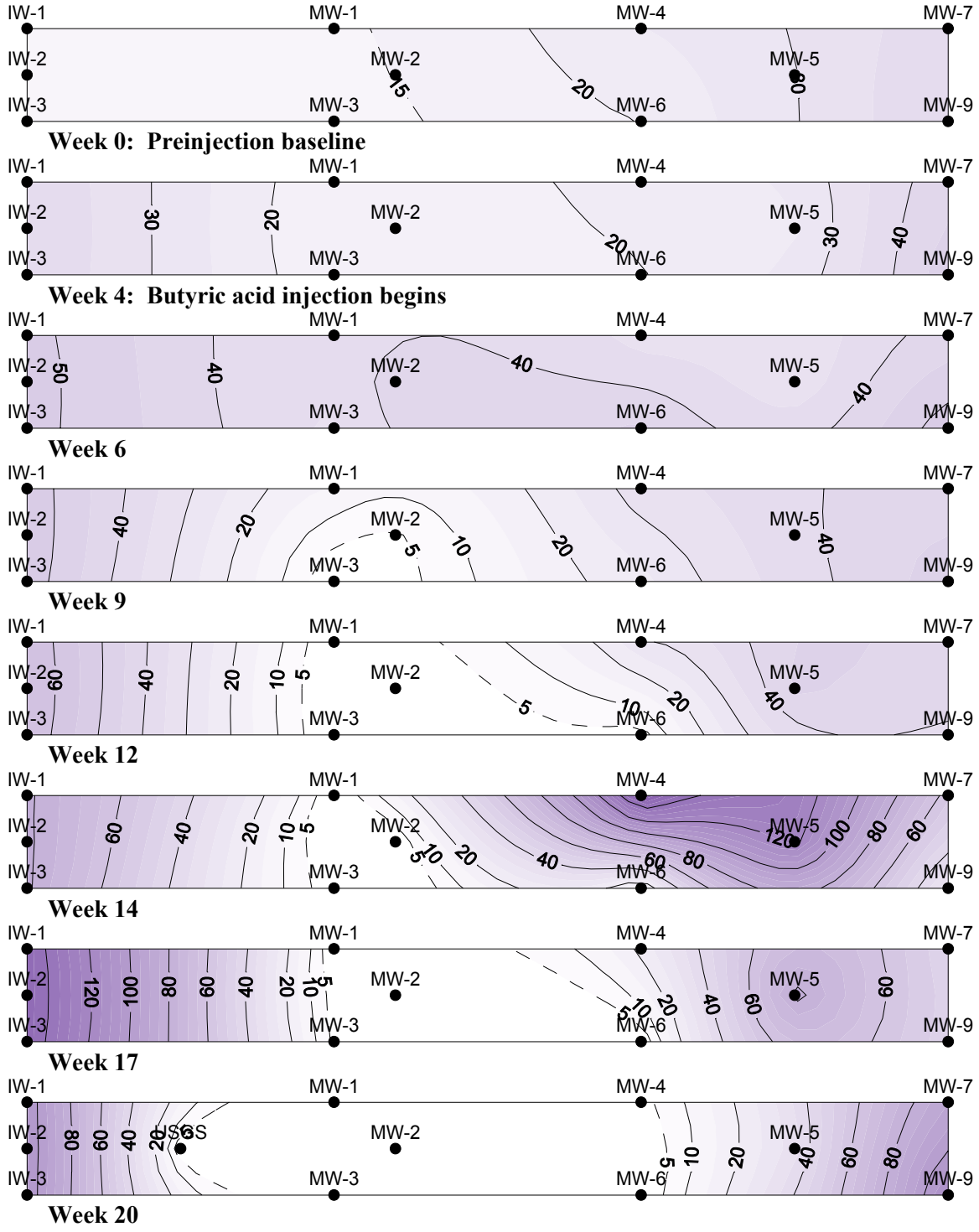


Figure 3-41. TCE Concentration Contours at the EGDY, Fort Lewis, Washington

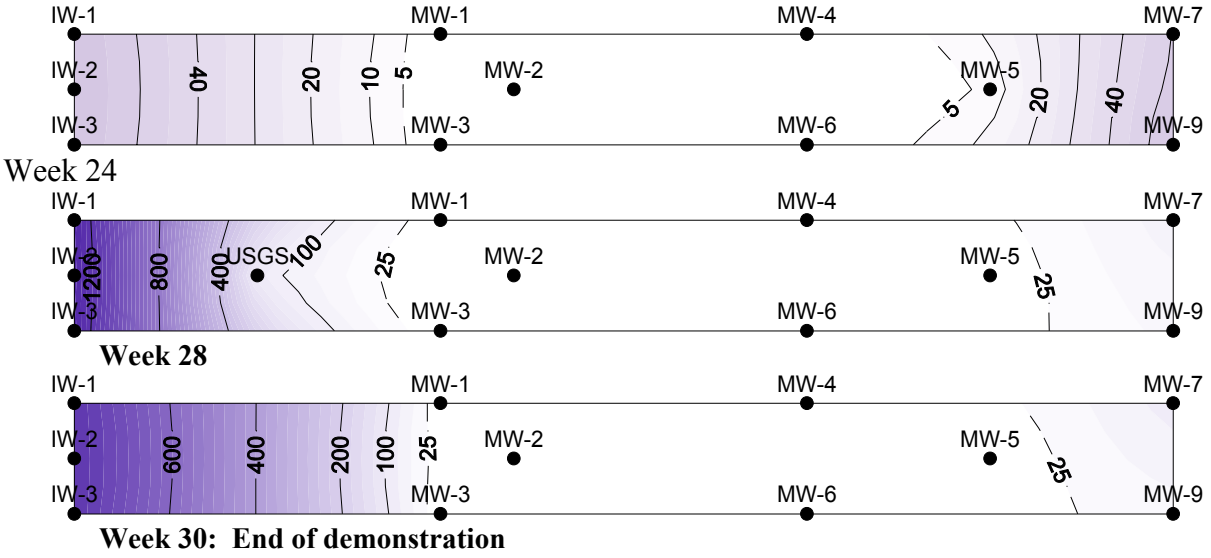


Figure 3-41. TCE Concentration Contours at the EGDY, Fort Lewis, Washington (Continued)

cis-*Dichloroethene*

Initial preinjection *cis*-DCE concentrations ranged across the plot from 0.47 µM (45.9 ppb) to 1.29 µM (125 ppb). The initial increase in *cis*-DCE seen at Week 4 in Figure 3-42 was due to the higher levels of *cis*-DCE present in the injected groundwater. After about nine weeks, *cis*-DCE levels at the first row of monitoring wells exceeded injection levels, indicating that reductive dechlorination of TCE had begun. This observation correlates well with the disappearance of TCE seen in Figure 3-41 at Week 9, which shows TCE concentrations beginning to drop near the first row of monitoring wells. cis-DCE levels continued to climb until they peaked during Week 28, when influent TCE concentrations were at their highest.

Vinyl Chloride

Prior to groundwater injection, VC was not detected in groundwater samples collected from the test plot. Figure 3-43 shows that as the demonstration proceeded, VC levels slowly increased from nondetect levels to a high of about 3.5 µM (217 ppb). VC levels within the plot did eventually exceed injected concentrations, suggesting that *cis*-DCE was being dechlorinated; however, the concentrations of VC observed were orders of magnitude lower.

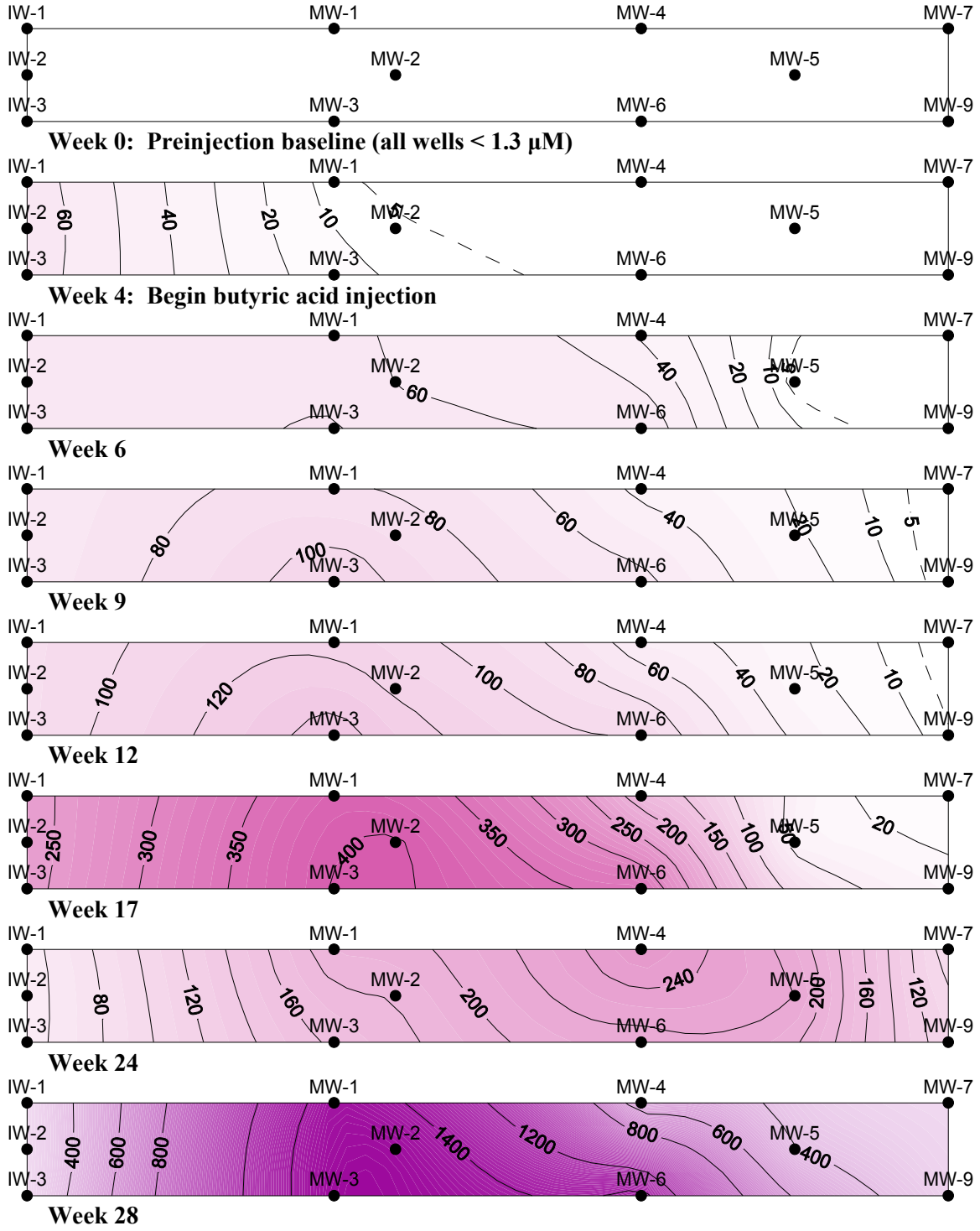


Figure 3-42. *cis*-DCE Concentration Contours at the EGDY, Fort Lewis, Washington

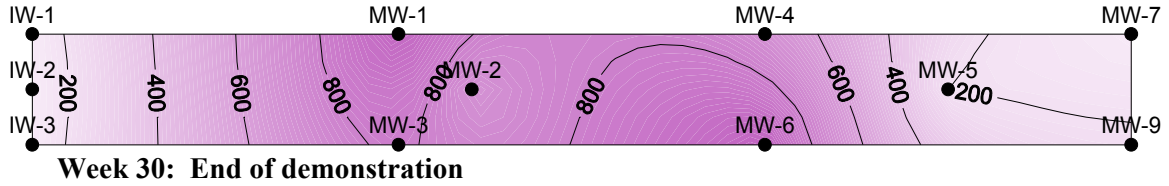


Figure 3-42. *cis*-DCE Concentration Contours at the EGDY, Fort Lewis, Washington (Continued)

It is unclear why the dechlorination of *cis*-DCE proceeded at such a slow rate. One possible explanation is that the majority of treatment occurred near the injection wells where there was a constant supply of TCE, which would serve as a preferential competitive electron acceptor. VC production did not begin in microcosms until TCE had been depleted for about 100 days. This is consistent with previously published research that found that VC dechlorination did not begin until all other parent chloroethenes had been reduced (Tandoi et al., 1994). In addition, it has been pointed out that microcosms did not exhibit significant VC production until about Day 150, which would be nearly the entire period of the field demonstration. And finally, the redox potential in situ may never have been depressed enough to achieve significant levels of *cis*-DCE dechlorination. The relatively high levels of iron at the site may have buffered it against attempts to drive down the redox potential to less than –200 mV.

Dissolved Gases

The dissolved gases ethene, ethane, oxygen, methane and hydrogen were monitored during the field demonstration to determine the extent of chloroethene degradation and assess microbiological conditions within the testing zone. Results from ethene, ethane, methane and hydrogen samples are shown in this section. DO results are presented with other electron accepting species in a following subsection.

Figure 3-44 shows that ethene and ethane concentration remained at or below detection limits throughout most of the demonstration, indicating that no significant portion of TCE was being converted to these two innocuous gases.

Methane concentrations remained very low (< 0.25 mg/L) throughout the demonstration despite a 10-fold spike in methane levels during Week 17. The reason for the spike is unknown, but it may be related to a pumping irregularity that occurred during Week 15. The supply-well pump shut down while the butyric acid metering pump continued to meter down concentrated butyric acid stock solution. This resulted in a concentrated slug of butyric acid being slowly fed into the injection wells. It appears that the excess dose of electron donor may have contributed to the onset of localized methanogenesis near the injection wells and that this impacted the average plot concentration.

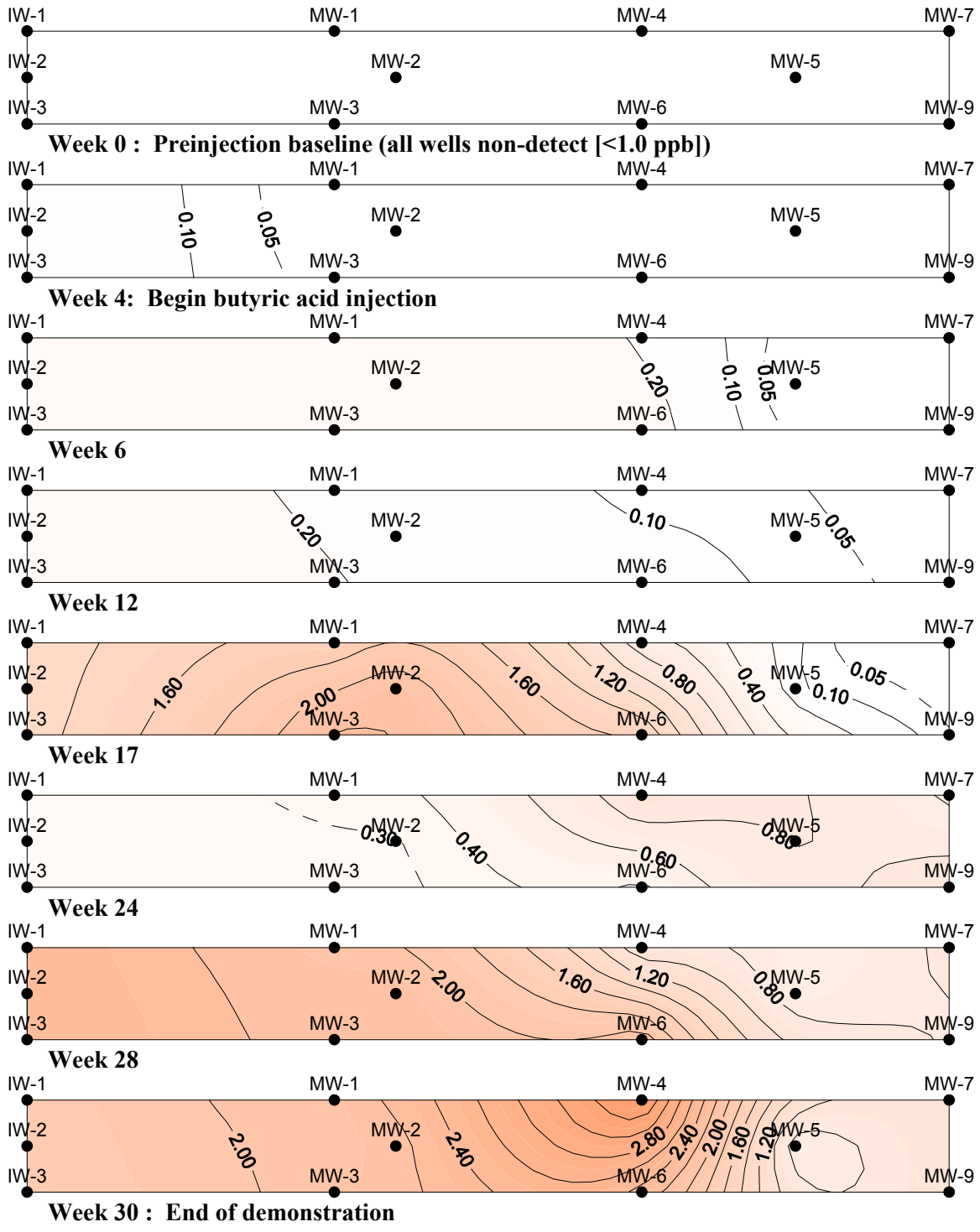


Figure 3-43. VC Concentration Contours at the EGDY, Fort Lewis, Washington

A new analytical laboratory was used to analyze samples collected from the Week 24 and Week 30 sampling events, and the reported detection limit was considerably higher (97 µg/L). The data from these sampling events is not included on Figure 3-44 because in both cases the results were reported as below detection limits. As a consequence, it is only possible to say that methane levels dropped to at least half of their peak level.

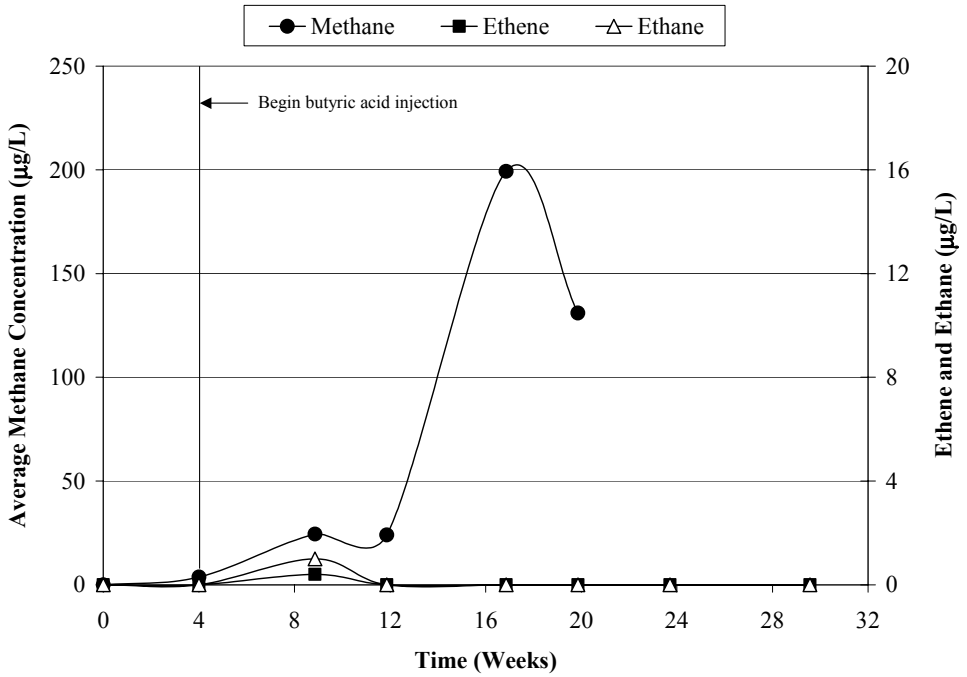


Figure 3-44. Average Methene, Ethane, and Ethene Concentrations at the EGDY, Fort Lewis, Washington

Table 3-23 outlines the baseline, mid-demonstration and final dissolved hydrogen results, and Table 3-24 provides a correlation between dissolved hydrogen concentration and predominant terminal electron accepting process.

Baseline dissolved hydrogen results appear to suggest that nitrate and iron reduction may have been the predominant terminal electron accepting process at the site; however, field testing at that time indicated that DO levels were higher than 5 mg/L. The presence of DO supersedes the dissolved hydrogen measurements, because DO is the preferred electron acceptor and can cause unreliable dissolved hydrogen results.

Mid-demonstration and final measurements of dissolved hydrogen show that the addition of electron donor significantly increased dissolved hydrogen levels within the plot. The peak levels of hydrogen observed during Week 17 correlate well with peak methane levels. DO levels dropped to less than 0.5 mg/L within two weeks after the addition of electron donor (data not shown).

Table 3-23. Dissolved Hydrogen Concentrations at the EGDY, Fort Lewis, Washington

Monitoring Location	Hydrogen Concentration (nM)		
	Baseline Measurement Week 4	Mid-demonstration Measurement - Week 17	Final Measurement Week 30
MW-1	32	80	32
MW-2	28	74	32
MW-3	0.14	57	40
MW-4	0.53	13	48
MW-5	0.18	4.3	46
MW-6	0.16	54	23
MW-7	0.64	0.08	0.66
MW-9	2.3	0.23	4.2
Background	0.17	0.64	< 0.1

Table 3-24. Correlation of Dissolved Hydrogen Concentrations with Terminal Electron-Accepting Process

Terminal Electron-Accepting Process	Hydrogen Concentration (nM)
Methanogenesis	> 5
Sulfate Reduction	1 to 4
Ferric Iron Reduction	0.2 to 0.8
Denitrification	< 0.1

Source: U.S. EPA, 1998

Organic Acids

The concentrations of butyric, acetic, lactic, and propionic acids were tracked during the field demonstration to ensure sufficient butyric acid was being administered and to examine the fate of added reducing equivalents. Figure 3-45 shows the average concentration of each of these acids within the testing zone. At this site, injection well data were included in the calculation of the average concentrations shown in the figure.

The data show that the butyric acid injection concentration of 3,000 μM maintained a significant level of electron donor over a large portion of the testing zone. Not surprisingly, butyric acid and its fermentation products were detected at their highest concentrations in monitoring wells nearest the injection wells. Organic acid concentrations in distant wells (e.g., MW-7 and MW-9) were commonly below detection limits. Lactic acid was detected at low levels in only five samples throughout the demonstration, which resulted in a very low average concentration. As a result, the average lactic acid data is not shown in Figure 3-45.

Data points from the Week 24 and Week 30 sampling events are not shown for either acetic or propionic acid. A change in the analytical laboratory resulted in higher detection limits for acetic acid (1,670 μM) and propionic acid (1,350 μM). Consequently, the results were reported as below detection, but may have been within the same range as previous data.

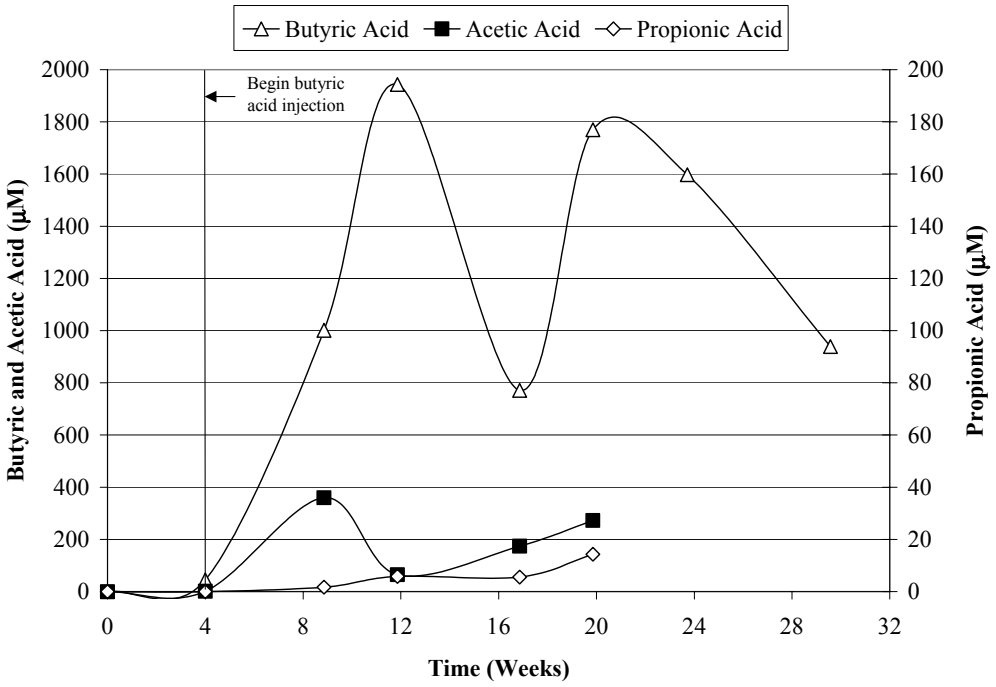


Figure 3-45. Average Organic Acid Concentrations at the EGDY, Fort Lewis, Washington

Inorganics

Several inorganic species were tracked throughout the field demonstration, including ph, alkalinity, nitrate, nitrite, ammonia, sulfate, and chloride. Data for each of these species is described in the following subsections and is presented in Figures 3-46 through 3-50.

pH and Alkalinity

Despite the addition of sodium bicarbonate to buffer the aquifer against pH changes caused by the addition of butyric acid, the average groundwater pH within the testing location slowly decreased. Figure 3-46 shows that the average pH across the test plot decreased from a baseline value of 6.88 to a final value of 6.36, despite the increase in measured alkalinity.

Dissolved Oxygen and Ferrous Iron

Previous site characterization data from the EGDY indicated that the aquifer contained low levels of DO and might be under iron-reducing conditions; however, the initial characterization data we collected told a different story. The groundwater in the testing zone contained a relatively high level of DO (~5 mg/L) and essentially no ferrous iron (see Figure 3-47). The average DO concentration within the testing zone was quickly reduced following butyric acid injection, but DO levels in water obtained from the supply remained high throughout the demonstration. This constant influx of oxygen must have been quickly scavenged and did not appear to inhibit dechlorination activity in the testing zone.

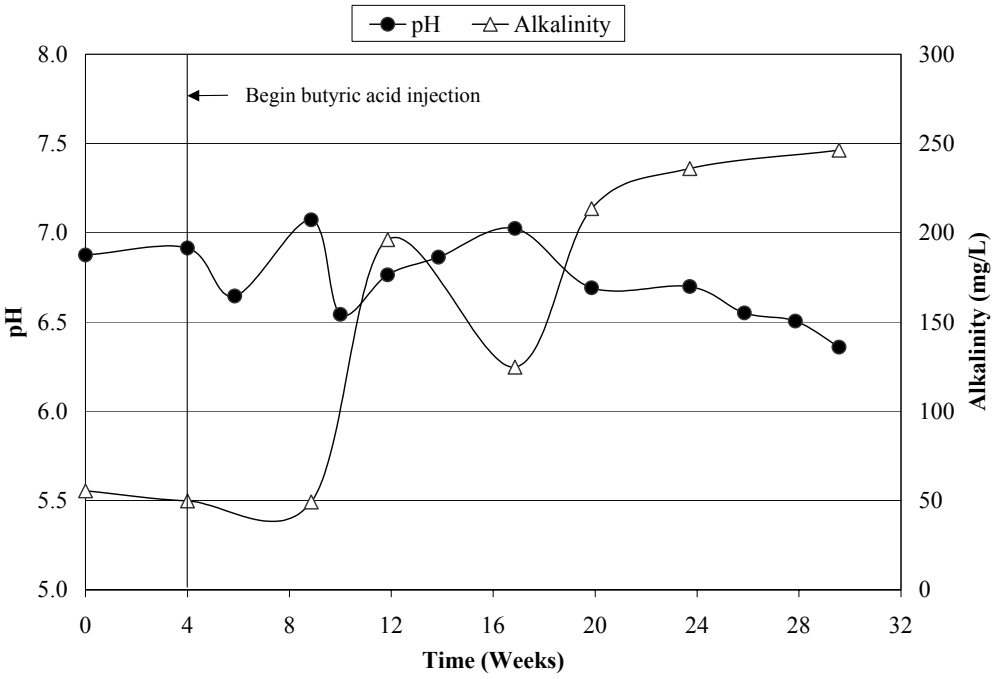


Figure 3-46. Average pH and Alkalinity Concentrations at the EGDY, Fort Lewis, Washington

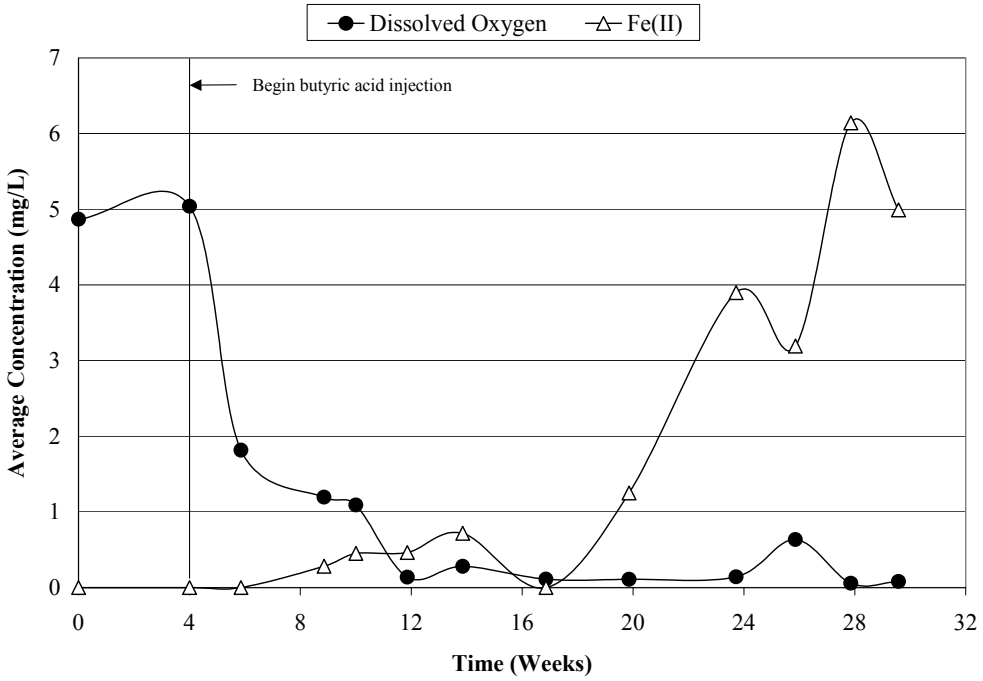


Figure 3-47. Average Dissolved Oxygen and Ferrous Iron Concentrations at the EGDY, Fort Lewis, Washington

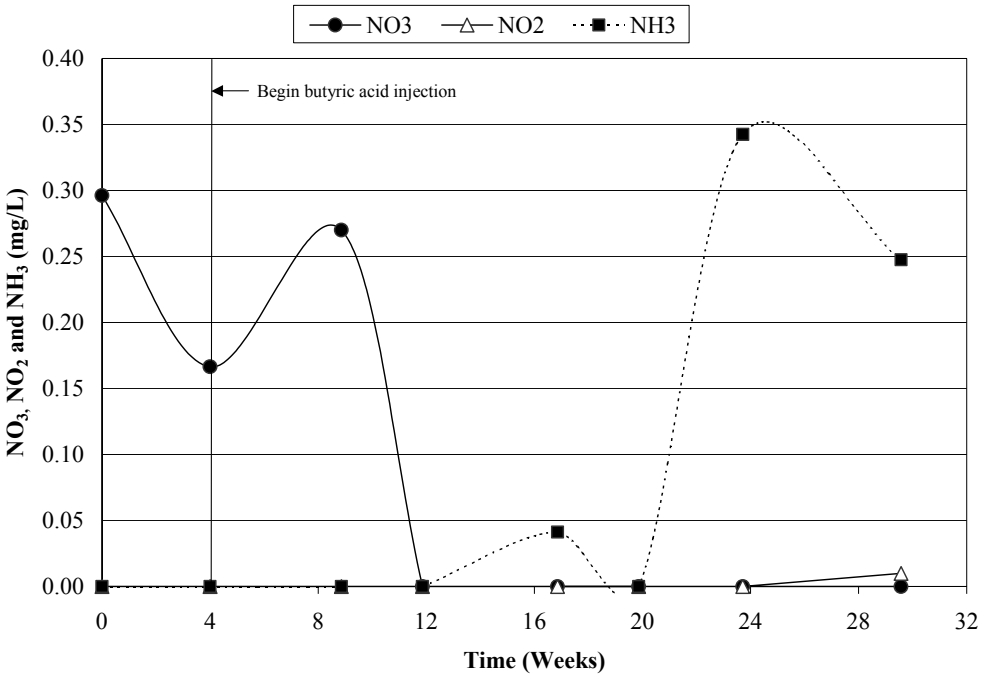


Figure 3-48. Average Nitrate, Nitrite, and Ammonia Concentrations at the EGDY, Fort Lewis, Washington

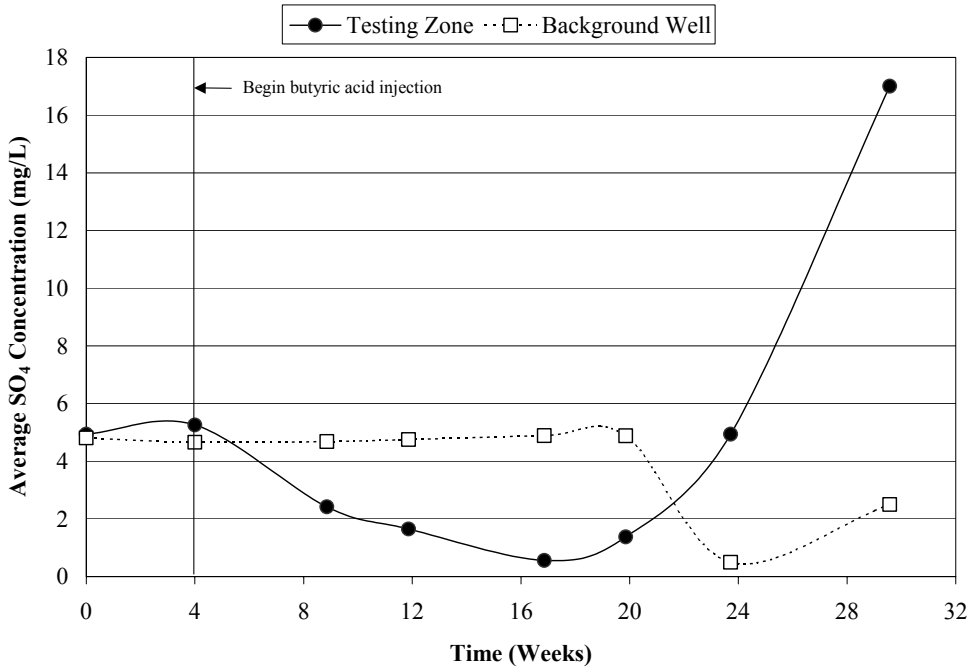


Figure 3-49. Average Sulfate Concentrations at the EGDY, Fort Lewis, Washington

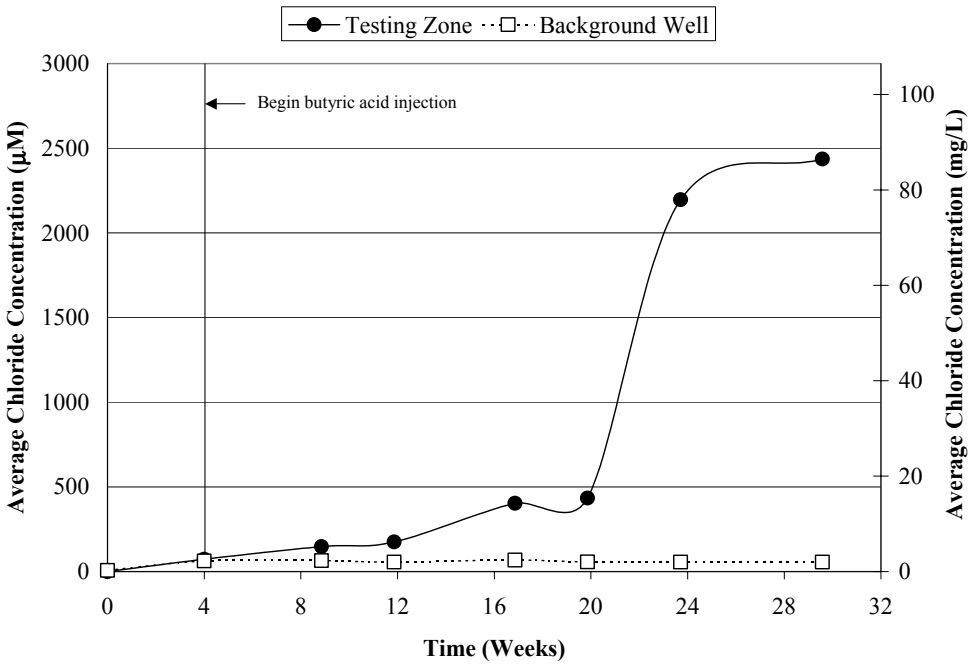


Figure 3-50. Average Chloride Concentrations at the EGDY, Fort Lewis, Washington

The elevated oxygen concentrations may be the result of an air-stripping tower installed at the northwest edge of the EGDY. Extracted groundwater is treated in the tower and then pumped to the south end of the EGDY where it is released into an infiltration gallery. DO levels in the background well, which was located somewhat closer to the infiltration gallery, were exceptionally high, averaging 8.2 mg/L.

The depletion of oxygen at monitoring wells near the injection wells was soon followed by the production of ferrous iron, indicating that iron reduction had become a significant terminal electron accepting process at the site. The average ferrous iron concentration continued to rise throughout most of the demonstration as the zone impacted by the butyric acid grew.

Nitrate, Nitrite, and Ammonia

The groundwater at the EGDY contained a remarkably low level of dissolved solids. Nitrate levels were initially low at only 0.3 mg/L and nitrite concentrations were below detection. As redox conditions in the testing zone became more reduced by the addition of butyric acid, the concentration of nitrate quickly dropped off. Figure 3-48 illustrates the conversion of nitrogen species from nitrate to ammonia.

Sulfate

Figure 3-49 shows that average sulfate concentrations within the testing zone remained relatively low (< 5 mg/L) throughout most of the demonstration. The average sulfate level in the testing zone began to decline once electron donor injection was initiated, but levels in the background

well remained stable, suggesting that sulfate reduction was occurring in the testing zone. The reason for the rebound in the testing zone sulfate concentration is not entirely clear, but a spike in the influent sulfate concentration observed during Week 30 certainly contributed to the jump at the end of the demonstration. Over the first 24 weeks of the demonstration, sulfate levels in the supply well ranged between 4 and 6.3 mg/L, but levels jumped to 17 mg/L during Week 30. Drum removal activities conducted near the supply well in early February may have impacted the local sulfate levels.

Chloride

Groundwater at the EGDY had very low initial concentrations of chloride which made it possible to observe increases in the average concentration resulting from dechlorination. Initially, all monitoring wells within the testing zone were below the 0.5 mg/L detection limit, but as the demonstration progressed, levels steadily increased until Week 20, when levels spiked (see Figure 3-50). The reason for the spike is not clear. A spike in the influent TCE concentration did occur during Week 28 (see Figure 3-40), but that certainly could not have contributed to the jump in chloride levels observed between Weeks 20 and 24.

Chloride concentrations in both the background and supply wells remained below concentrations observed within the test plot. Background concentrations were relatively stable at about 2 mg/L. Supply well concentrations were typically less than 15 mg/L but did fluctuate slightly and peaked at the end of the demonstration at 22 mg/L.

Dissolved Organic Carbon

Dissolved organic carbon measurements were made at the EGDY to determine their value as a surrogate parameter for the more costly organic acid analysis. Figure 3-51 shows measured DOC values versus the total organic acid concentration represented as DOC equivalents. Injection well data were included in the calculation of the average DOC and organic acid concentrations. The figure shows that measured DOC values accurately reflected the total concentration of organic acids over the first 20 weeks of the demonstration. The very low levels of background DOC in the groundwater at the EGDY certainly contributed to the close correlation.

The data also indicate that organic carbon concentrations in the aquifer were significantly increased and sustained by the addition of butyric acid.

The total average organic acid concentration from the Week 24 and Week 30 sampling event are not shown in Figure 3-51 because a change in analytical laboratories resulted in considerably higher detection limits for acetic acid (40 mg/L as DOC equivalents) and propionic acid (49 mg/L as DOC equivalents). These new detection limits were higher than previously observed concentrations and caused the laboratory to report the results as below detection. Because no numerical value could be assigned, the total average organic acid concentration could not be calculated. The sum of butyric and lactic acid was significantly lower than DOC measurements for those weeks.

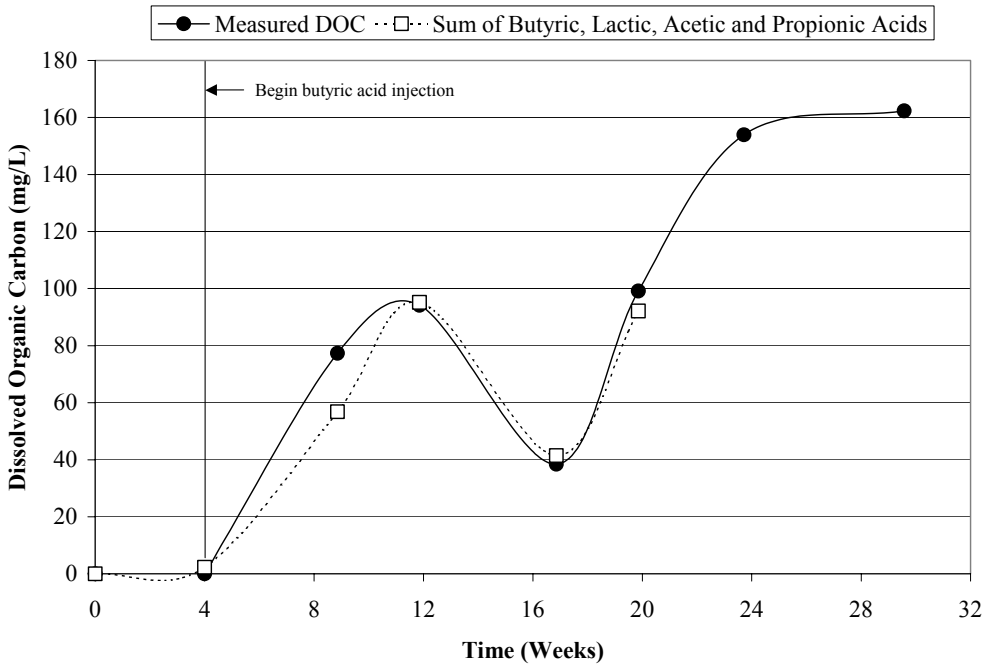


Figure 3-51. Average Dissolved Organic Carbon Concentration at the EGDY, Fort Lewis, Washington

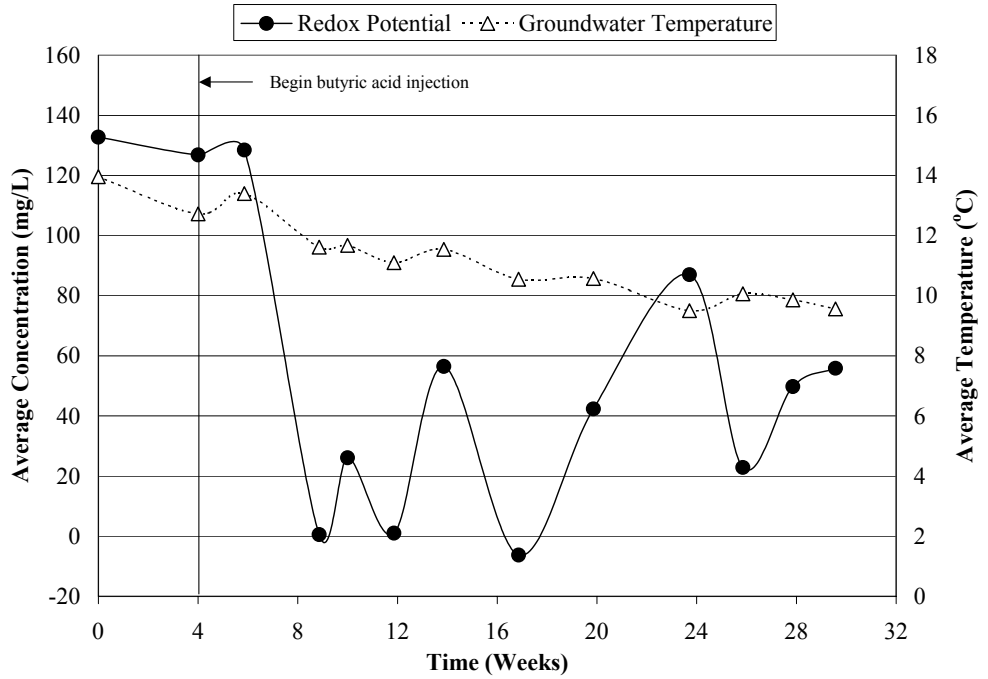


Figure 3-52. Average Redox Potential and Temperature at the EGDY, Fort Lewis, Washington

Redox Potential and Temperature
The RABITT demonstration at the EGDY maintained the highest average redox potential of the four RABITT demonstration sites. In fact, the average redox potential dropped below +0 mV only once during the demonstration despite the continuous injection of butyric acid (see Figure 3-52). Surprisingly, even monitoring wells only 10 ft from the injection wells never fell below -100 mV. Redox potential measurements in the background well fluctuated between +94 mV and +181 mV with no apparent trend.

The groundwater temperature at the EGDY showed a consistent decline that reflected the change in seasons from August 2000 (Week 0) to February 2001 (Week 30). Over the course of the demonstration the average groundwater temperature ranged from 14°C to 9.5°C.

3.4.4.5 Conclusions. Results from the RABITT field demonstration at the EGDY show that biologically catalyzed reductive dechlorination of TCE can be stimulated at the site, but that the process may not achieve complete dechlorination to ethene. This is in contrast to microcosm results, which did eventually show complete stoichiometric conversion of TCE to ethene. In the field, *cis*-DCE accumulated, VC was produced at low levels, and ethene was not observed in significant quantities. It is not clear what caused the discrepancy between field and microcosm results, but several key differences could be responsible.

Microcosm results suggest that daughter products are not readily dechlorinated until the parent compound has been depleted. For example, VC production, which is the best indicator of *cis*-DCE dechlorination, did not occur in microcosms until Day 144, long after all TCE had been degraded. Similarly, ethene production, which is the best indicator of VC dechlorination, coincided with the depletion of *cis*-DCE, about 163 days into the incubation.

Unlike microcosm testing, the field demonstration had a constant influx of TCE into the testing zone. This resulted in a continuous presence of *cis*-DCE. It seems plausible that the presence of TCE inhibited the dechlorination of *cis*-DCE and that *cis*-DCE inhibited the dechlorination of VC. The presence of VC in the testing zone does not invalidate this hypothesis, because TCE had been depleted at some locations in the testing zone.

Testing this hypothesis might have been easily accomplished. The site maintained a relatively high level of residual butyric acid (700-2000 μM), so groundwater injection could have been temporarily suspended to give the microbial community time to degrade the *cis*-DCE without interference from fresh inputs of TCE. Of course, in the field it is difficult to know whether one is simply observing an extended lag period or actual inhibition. Nonetheless, the revised RABITT protocol will suggest using a pulsed feeding strategy at sites that accumulate daughter product in areas containing residual electron donor.

Another key difference between the microcosm and field studies was duration. Production of ethene in one butyric-acid-fed microcosm bottle did not begin until Day 163 and was not complete until Day 178. The field demonstration ran for 179 days and only two sampling events occurred after Day 163. The onset of VC dechlorination likely had not yet occurred in the field.

Biologically catalyzed reductive dechlorination appears to be a fairly robust process, which was not adversely affected by TCE concentrations up to 169,000 ppb. In addition, dechlorination was stimulated in an aquifer that had recently been aerobic and was fed water containing fairly high concentrations of dissolved oxygen.

Dissolved hydrogen measurements were not useful for determining the terminal electron accepting process in the testing zone. The injection of electron donor caused dissolved hydrogen concentrations in situ to greatly exceed those seen in natural attenuation settings; as a result, previously published diagnostic relationships are not applicable.

Based on data collected at the EGDY, DOC measurements could be used as a surrogate parameter for estimating the in situ electron donor concentration; however, this could present problems if fermentation products (e.g., acetic acid) are not used by dechlorinating organisms. This appeared to be the case at the EGDY, where acetic acid (a fermentation product of butyric acid) did not produce significant dechlorination in microcosms.

The low levels of background chloride at the EGDY made it possible to observe the accumulation of chloride caused by the dechlorination of TCE at the EGDY. This provided a useful secondary confirmation that reductive dechlorination was occurring.

3.5 Camp Lejeune – Site 88

3.5.1 Site Description – Site 88. Camp Lejeune is situated on the Atlantic coastline just southeast of Jacksonville, North Carolina. Site 88 is located within the Hadnot Point area of Camp Lejeune, which falls just east of the New River. Hadnot Point consists of suburban-style development. It contains paved roads, parking lots, and low-rise troop housing, recreation, and administrative and service buildings surrounded by grassy yards and trees. Underground infrastructure, such as sewer and electrical conduits, also are present. Site 88 consists of the dry-cleaning facility known as "Building 25, Morale, Welfare, and Recreation (MWR) Dry Cleaners" and its immediate surroundings.

The MWR dry cleaner has been operating as a dry-cleaning facility since the 1940s. An underground storage tank (UST) area, consisting of five tanks, was formerly located on the north side of Building 25. These tanks, installed in the 1940s, were used to store Varsol™, a petroleum distillate dry-cleaning fluid. The USTs were used in conjunction with the dry-cleaning operation until the early 1970s. Varsol's flammability prompted its replacement by PCE in the 1970s. PCE was stored in 150-gallon aboveground storage tanks (ASTs) outside of Building 25. It has been reported that dry-cleaning personnel disposed of spent PCE in floor sewer drains (Baker Environmental, Inc., 1998).

3.5.2 Site Assessment/Selection – Site 88. The contaminant profile at Camp Lejeune's Site 88 featured high levels of PCE as the predominant contaminant. Groundwater samples collected from the site during 1996 and 1997 revealed that PCE, TCE, and *cis*-DCE were the most commonly detected contaminants, and that each greatly exceeded North Carolina Water

Quality Standards (NCWQS) (Baker Environmental Inc., 1998). This contaminant profile made Site 88 an attractive RABITT demonstration site for several reasons: First, it would be the first site tested that had PCE as the parent compound. Second, PCE levels were high enough to provide a consistently high influent concentration at the injection wells. As a result, decreases in the PCE concentration could be followed over three or four orders of magnitude, and the relatively high initial PCE concentrations also could provide insight into microbial tolerance to PCE. Third, this profile suggested that the reductive dechlorination of PCE to *cis*-DCE might already have been occurring, thereby increasing the likelihood of stimulating dechlorination.

Slug tests conducted at Site 88 provided estimates of the subsurface hydraulic conductivity as a function of depth (Baker Environmental Inc., 1998). Hydraulic conductivity increased with depth. Upper surficial aquifer (8 to 23 ft bgs) values ranged from 1.41×10^{-4} cm/sec to 1.05×10^{-2} cm/sec (0.4 ft/day to 29.7 ft/day). Values in the lower surficial aquifer (45-50 ft bgs) were significantly higher, ranging from 1.99×10^{-2} cm/sec to 3.02×10^{-2} cm/sec (56.4 ft/day to 85.5 ft/day). Running a RABITT demonstration in the upper surficial aquifer was expected to be challenging because of its lower average hydraulic conductivity and greater degree of heterogeneity, so only the lower surficial aquifer was considered for the demonstration.

The geochemistry at Site 88 covered a fairly wide range of conditions, which varied with geographic location and depth. However, the geochemistry did not present any obvious problems that could not be overcome with a proper system design.

A site rating system developed in the draft RABITT protocol was used to assess the potential for enhancing biologically catalyzed reductive dechlorination at Camp Lejeune's Site 88 and to allow the rating system to be evaluated after demonstration completion. Average conditions found within the lower surficial aquifer were obtained from previously conducted site characterization work and compared against criteria in the rating system. The results from this comparison are listed in Table 3-25 along with the corresponding rating score.

The Lower Surficial Aquifer at Site 88 scored a total point value of 36 out of 75 total possible points, which fell into the range considered "Satisfactory" in the RABITT protocol.

3.5.3 Microcosm Testing – Site 88

3.5.3.1 Microcosm Setup. Field activity was initiated at Camp Lejeune on October 25, 2000 with the collection of aquifer cores and groundwater for use in a laboratory microcosm study. Mud-rotary drilling was used to advance three boreholes (PZ1, PZ2, and PZ3) in the vicinity of existing monitoring well 88-MW05IW. A 2-inch-diameter core barrel lined with acetate sleeves was used to collect aquifer material from two depths (18.5-22.5 bgs and 45-49 ft bgs, respectively) from each of the three boreholes. In addition, 6 liters of groundwater was collected from each of two monitoring wells, 88-MW05 (8-23 ft bgs) and 88-MW05IW (45-49 ft bgs).

Table 3-25. RABITT Rating System Score Summary for Site 88, Camp Lejeune, North Carolina

Rating Parameter	Lower Surficial Aquifer Conditions at Site 88	Score
Contaminant Profile	*cis*-DCE present	5
Hydraulic Profile	~2.5×10^{-2} cm/sec	25
Geochemical Profile		
Dissolved Oxygen	≤ 1.0 mg/L	1
Nitrate	< 1 mg/L	3
Hydrogen Sulfide	Not detected	0
Sulfate	~ 27 mg/L	0
Redox potential	Variable, -200 mV to +100 mV	0
Temperature	18 to 22 °C	3
Dissolved Organic Carbon	≤ 4.0 mg/L	0
Bicarbonate Alkalinity	~ 28 mg/L	-1
pH	5.4 to 7.5	0
Methane	85 μg/L	0
Total Point Value		36

PZ1, PZ2, and PZ3 are located on a roughly straight line westward from the existing intermediate Monitoring Well 5 (MW05IW). PZ1 lies 25 ft west of MW05IW, PZ2 lies 35 ft west of PZ2, and PZ3 is another 40 ft beyond PZ2. The line of coring locations is paralleled by a paved road to the north and an extended fence to the south (consistently 12 to 14 ft from PZ1, PZ2, and PZ3). Cores and groundwater were shipped via ice-packed coolers to the laboratory following the second day of collection and were stored at 4°C following arrival.

The decision to collect soil and groundwater from two different depths was made in order to investigate the distinctly different, vertically stratified contaminant and geochemical zones observed in previous monitoring at Site 88. Separate microcosms were constructed using material from each of the two ("upper" and "intermediate") depths.

Because two distinct microcosm sets were to be created, sediment from all cores taken at the upper depth was blended (to create a composite sample) separately from sediment taken at the intermediate depth. For blending within each type, cores and sterile mixing utensils were transferred to a separate, new disposable glovebag that had been purged for several hours to ensure anaerobic conditions. Microcosms from each depth were prepared with their corresponding groundwaters, in the usual ratio of 50 grams (dry weight) soil + 100 grams groundwater. Upon setup, all the microcosms were purple-tinted, indicating that the conditions were not fully reducing; however, after delivery of electron donor, reducing conditions were rapidly attained.

As expected, pH measurements indicated that the upper groundwater was decidedly acidic (5.76), although higher values were observed in mixed, sediment/groundwater microcosms (6.33). Alkalinity analysis (Table 3-26) confirmed that the buffer capacities of both groundwater and sediment/groundwater microcosms were lower than the desired level of 0.05 eq/L. Based on these measurements and previous results with buffering microcosms, it was decided to provide alkalinity to the upper-aquifer groundwater through the addition of sterile $NaHCO_3$ in the amount of 398 mg/L. This addition was performed under the anaerobic conditions of a disposable glovebag prior to any substrate supplementation.

Table 3-26. Initial Characterization of Camp Lejeune Soil and Groundwater

Parameter	Upper Aquifer (18.5 to 22.5 ft bgs)	Intermediate Aquifer (45 to 49 ft bgs)
Mixed Core Moisture Content (% moisture)	16.2	14.5
Groundwater pH	5.76	7.10
Groundwater Total Alkalinity, eq/L (mg/L as $CaCO_3$)	0.00026 (13 mg $CaCO_3$/L)	0.00375 (188 mg $CaCO_3$/L)
Soil/Groundwater Mixture[(a)] pH	6.33	7.55
Soil/Groundwater Mixture[(a)] Total Alkalinity, eq/L	0.0026 (130 mg $CaCO_3$/L)	0.535 (26,750 mg $CaCO_3$/L)

1. At ratio used in microcosms.

Although the measured alkalinity in the groundwater from the intermediate aquifer was not particularly high, there was an abundance of alkalinity in the constructed microcosms from this depth due to the presence of large amounts of carbonate-rich shell material. For this reason, it was decided that the intermediate-aquifer microcosms contained sufficient long-term capacity to buffer any acids produced during substrate utilization and that no $NaHCO_3$ supplementation was necessary.

The bottles were incubated quiescently at 22°C (the approximate prevailing in situ groundwater temperature at Camp Lejeune) until December 4, 2000 while the autoclaving of the controls was conducted. The following day, several bottles were analyzed to determine background pollutant concentrations. The estimated background levels of volatiles in the upper-aquifer microcosms were: PCE, 15 µM; TCE, 0.5 µM; *cis+trans* DCE, 2.6 µM; 1,1-DCE, 1.9 µM; VC, ND; ethene, ND; methane, 0.33 µM; and hydrogen, $10^{-5.5}$ atm. In intermediate-level microcosms, the levels were: PCE, 4.6 µM; TCE, 4.0 µM; *cis+trans* DCE, 18.6 µM; 1,1-DCE, ND; VC, ND; ethene, ND; methane,1.7 µM; and hydrogen, $10^{-5.2}$ atm. The background levels were low enough to require supplementation with PCE to reach desired initial concentration of that compound (roughly 30 µmol/bottle or 300 µM nominal concentration). Over the course of the next day, microcosms were purged with N_2/CO_2 (at compositions calculated to prevent excessive shifts in pH) and resulted in near nondetectable levels of all volatile analytes. Filter-sterilized PCE was

added on December 6, 2000, and bottles were placed on a rotary shaker set at 120 rpm for the next three days. After headspace sampling of a number of bottles confirmed that dissolution and gas/liquid partitioning of the volatile pollutant was complete, the appropriate amendments were added to each bottle as per Table 3-26 (but with propionate at 3 mM and with the inclusion of a nine set of bottles with 3 mM acetate + YE + B_{12}). Following supplementation, bottles were incubated quiescently at 22°C for between 200 and 226 days, with periodic monitoring.

3.5.3.2 Microcosm Results

Intermediate Aquifer Microcosms

Intermediate-aquifer microcosms were run for 226 days. Within the first two weeks of monitoring, all bottles were reduced as indicated by the change in color from pink to clear. The exceptions were the unamended and low-YE-amended biotic controls, neither of which attained a clear color. No significant dechlorination was observed in any of the controls throughout the period of monitoring. The highest dechlorination activity was observed in the butyrate- and propionate-amended bottles (Table 3-27), with butyrate-amended bottles evidencing activity earlier than propionate-amended bottles. Thus, butyrate was selected as donor for the subsequent field-test, which was planned for installation in the intermediate aquifer zone.

Table 3-27. Dechlorination Products in Camp Lejeune Microcosms Seeded with Material from 45 to 49 ft bgs (226 Days After Addition Of Donor and Nutrients)

Bottle Set/Donor	Triplicate I	Triplicate II	Triplicate III
4 (200 mg/L YE)	TCE (37%) *cis*-DCE (34%)	TCE (30%) *cis*-DCE (52%)	TCE (39%) *cis*-DCE (28%)
5A (Lactate only)	*cis*-DCE (100%)	TCE (39%) *cis*-DCE (24%)	TCE (21%) *cis*-DCE (<1%)
5B (Lactate + 20 mg/L YE)	TCE (7%) *cis*-DCE (89%)	*cis*-DCE (100%)	TCE (40%) *cis*-DCE (22%)
5C (Lactate + B_{12})	*cis*-DCE (98%)	TCE (18%) *cis*-DCE (1%)	*cis*-DCE (100%)
5D (Lactate + 20 mg/L YE + B_{12})	*cis*-DCE (99%)	*cis*-DCE (100%)	TCE (25%) *cis*-DCE (7%)
6 (Butyric Acid + 20 mg/L YE + B_{12})	*cis*-DCE (100%)	*cis*-DCE (100%)	*cis*-DCE (100%)
7 (Lactate/Benzoate + 20 mg/L YE + B_{12})	TCE (26%) *cis*-DCE (8%)	TCE (27%) *cis*-DCE (12%)	TCE (2%) *cis*-DCE (6%)
8 (Propionic Acid + 20 mg/L YE + B_{12})	*cis*-DCE (100%)	*cis*-DCE (100%)	*cis*-DCE (100%)
9 (Acetic Acid + 20 mg/L YE + B_{12})	TCE (4%) *cis*-DCE (4%)	TCE (17%) *cis*-DCE (9%)	TCE (11%) *cis*-DCE (0%)

Note: No dechlorination was observed in any of the control sets (autoclaved groundwater, autoclaved sediment + groundwater, unamended sediment + groundwater, low-YE-amended sediment + groundwater).

An exemplary butyrate-fed microcosm (6-III) is depicted in Figure 3-53). This dechlorination activity was accompanied by significant butyrate degradation (primarily to acetate) (Figure 3-54), and eventually significant methane production (presumably from acetate). Although conversion to *cis*-DCE was relatively rapid in these bottles, only trace dechlorination beyond *cis*-DCE was observed. In fact, there was no significant (i.e., < 1%) VC or ethene formation in any treatment set.

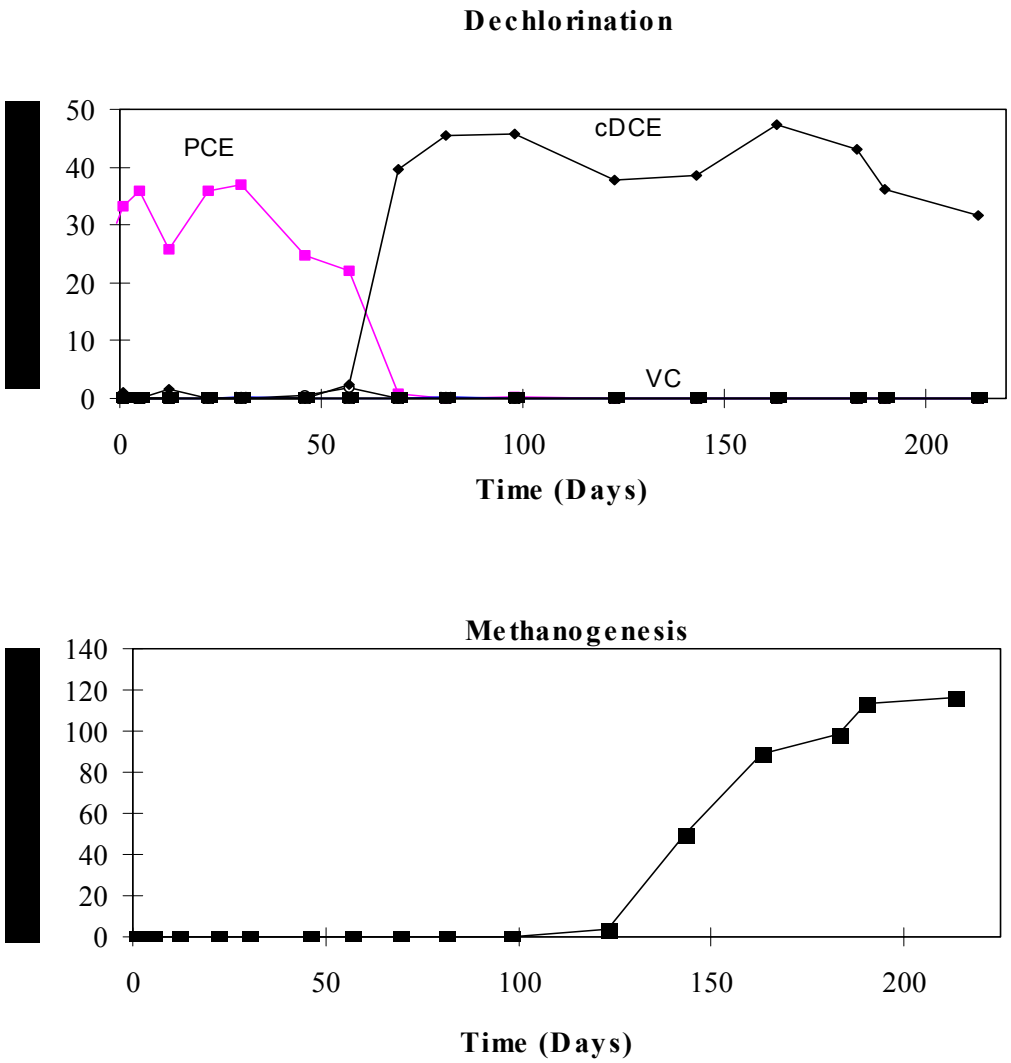


Figure 3-53. Dechlorination and Methanogenesis in a Camp Lejeune Microcosm (6-III) Amended with 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} (Intermediate Aquifer Material, 45-49 ft bgs)

Upper Aquifer Microcosms
Upper-aquifer microcosms were run for 204 days. Like the microcosms seeded with intermediate aquifer material, reduced conditions were established in all bottles in this treatment set within the first two weeks of monitoring. Again, the exceptions were the unamended and low-YE-amended biotic controls, and no dechlorination was observed in any of the controls.

In general, dechlorination activity in the entire treatment set was markedly lower than with the intermediate-aquifer microcosms. Little happened within the first 100-150 days; beyond that, a few microcosms demonstrated conversion to TCE and/or *cis*-DCE. Examples (with onset-time of PCE dechlorination, and TCE%/*cis*-DCE% of total remaining ethenes) include: high-YE-fed

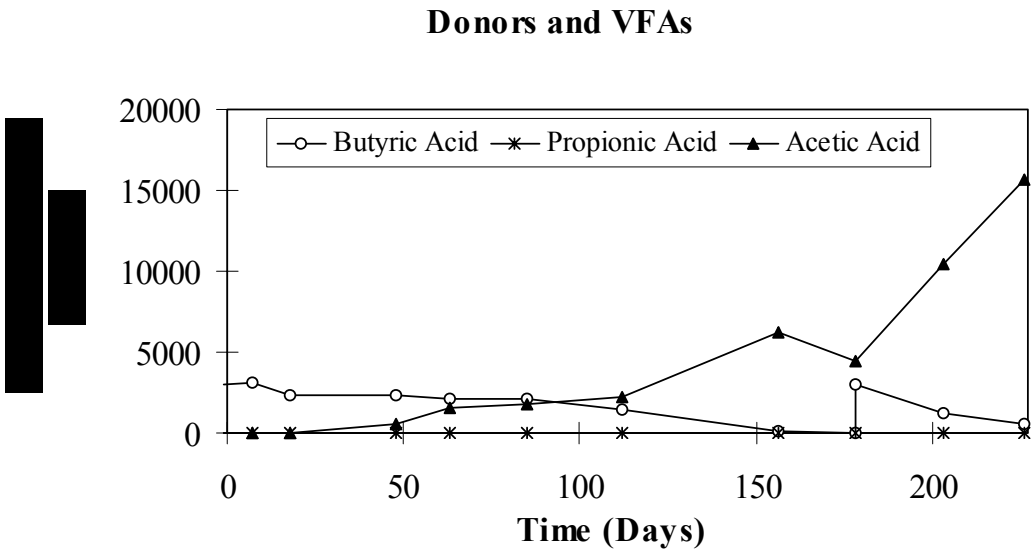


Figure 3-54. Fate of Added Donor and Appearance of VFAs in a Camp Lejeune Microcosm (6-III) Amended with 3mM Butyrate + 20 mg/L YE + 0.05 mg/L B_{12} (Intermediate aquifer material, 45-49 ft bgs)

bottles (100-150 d, 25%/25%); lactate-fed bottles, with no consistent distinction among nutrient-conditions (150 d, 25%/25% - 0%/100%); and butyrate-fed bottles (150 d, 25%/0%). No practically significant dechlorination occurred in microcosms amended with lactate/benzoate, propionate, or acetate. It should be noted that, even in microcosms not evidencing significant dechlorination, donor was fermented (albeit slowly in some cases) and detectable methanogenesis ensued 100-150 days into the run.

The low pH of the original source material (before the addition of alkalinity via $NaHCO_3$) suggests that initial activity in the sediment and groundwater was likely very low. Establishment of viable populations of both specific dechlorinators and other anaerobes took longer than in the intermediate-aquifer microcosms.

3.5.4 Field Testing – Site 88

3.5.4.1 System Design/Installation. The installation of the RABITT demonstration system at Camp Lejeune began on April 17, 2001. A conventional RABITT test system was installed at Site 88, with the exception that the gradient well, which was deemed unnecessary, was removed from the design. The three injection wells were spaced approximately 2 ft apart; the distances between the injection wells and each row of monitoring wells was 10 ft, which resulted in plot dimensions of approximately 4 ft by 30 ft. Installation of all wells was completed on April 22, 2001.

A total of 12 wells were installed with screened intervals ranging from 45 to 48 ft bgs. Three wells, designated MW-1, MW-3, and MW-4, were installed using a 3.25-inch-I.D. hollow stem auger. The remaining nine wells were installed using mud rotary drilling. A polymeric drilling fluid additive, Insta-Vis™ Plus, was used to prevent the collapse of the borehole during installation of these wells. This material, which had the consistency of syrup, was present in purge water for several weeks following well installation despite assurances from the driller that it would biodegrade within 48 hours.

Two existing wells were used during the demonstration. The first, designated 88-MW05IW, exhibited consistently high levels of PCE and was used to supply contaminated groundwater for the demonstration. The second, designated 88-MW03IW, was used to collect background samples. Table 3-28 outlines well specifications and Figure 3-55 shows the relative locations of system wells.

Table 3-28. Well Construction Details at Site 88, Camp Lejeune, North Carolina

Parameter	Injection Wells	Monitoring Wells	88-MW05IW	88-MW03IW
Number of wells	3	9	1	1
Diameter (inches)	0.75	1	2	2
Screened Interval (ft bgs)	45-48	45.75-47.25	45-50	45-50
Slot Size (inches)	0.01	0.01	0.01	0.01
Material	Sch. 80 PVC	Sch. 80 PVC	Sch. 40 PVC	Sch. 40 PVC

3.5.4.2 Tracer Testing. Following the installation of system wells, a bromide tracer test was initiated on May 18, 2001 to determine the direction of groundwater flow through the monitoring well array. A review of existing groundwater potentiometric contour maps seemingly indicated that the general movement of groundwater in this area would be to the northwest, but tracer-testing results would contradict that assumption.

Groundwater was continuously pumped from monitoring well 88-MW05IW and amended with a concentrated sodium bromide solution in the on-site field trailer. A calibrated metering pump

was used to add a consistent amount of bromide stock solution to the groundwater flow. After amendment with bromide stock solution, the flow was evenly split and injected into injection wells IW-1, IW-2, and IW-3. The target bromide concentration for injected water was 100 mg/L. The bromide stock solution was prepared by adding 3.038 kg of NaBr to 15 gallons of tap water. Flowrates and concentrations are presented in Table 3-29.

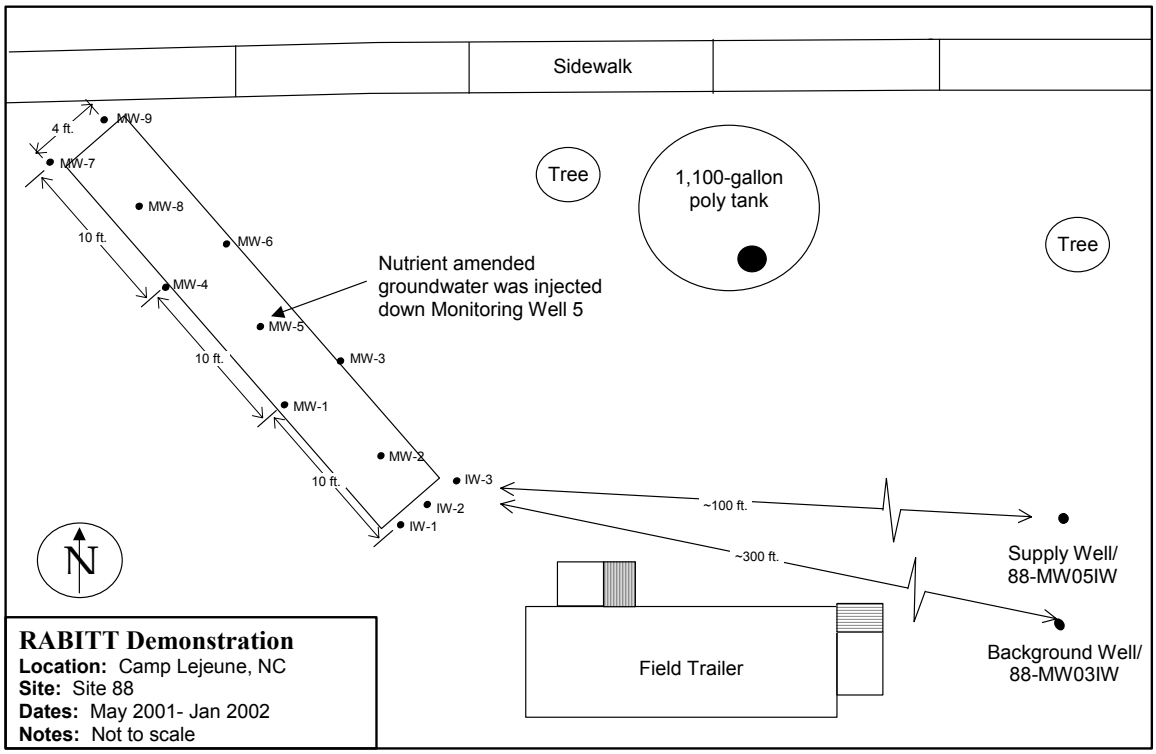


Figure 3-55. Plan View of RABITT Demonstration at Site 88, Camp Lejeune, North Carolina

Table 3-29. Tracer Testing Flow Rates and Concentrations at Site 88, Camp Lejeune, North Carolina

Operational Parameter	Initial Design (May 2001)	Modified Design (June 2001)
Total pumping rate from 88-MW05IW	1.8 L/min	0.6 L/min
Bromide stock solution feed rate	4.34 mL/min	1.44 mL/min
Bromide stock solution concentration	41,550 mg/L as [Br^-]	41,550 mg/L as [Br^-]
Bromide concentration of injected water	100 mg/L	100 mg/L
Wells used for injection	IW-1, IW-2, IW-3	MW-5

After four days the bromide concentration in the monitoring wells closest to the injection wells had increased far less than expected. In addition, there was evidence that bromide levels might be increasing in the supply well (88-MW05IW). This prompted a shutdown of the tracer test and a reexamination of water levels within the monitoring well array. Because the monitoring wells are located so near each other, it was difficult to measure significant differences in water elevation; nonetheless, water level measurements did suggest that the primary direction of groundwater flow might be to the northeast. DOC measurements suggested that residual drilling fluid was present on the northwestern side of the plot. It is possible that this residual drilling fluid may have decreased hydraulic conductivity within the monitoring well array and impacted local groundwater movement.

Tracer testing was restarted on June 22, 2001, but with a modified design. For this second phase of testing the bromide amended groundwater was injected into MW-5, in the center of the monitoring well array. This strategy was used to ensure the movement of tracer could be observed regardless of the direction of groundwater flow. Because the number of injection wells had been reduced from three to one, the injection flowrate was reduced from 1.8 L/min to 0.6 L/min, and the bromide stock solution feed rate was reduced from 4.3 mL/min to 1.4 mL/min. Figure 3-56 shows a time series of contour plots, which illustrate the movement of bromide through the testing zone. Plots were generated using data collected in the field with an Orion™ 290A field meter and a bromide-specific electrode.

The first contour map in Figure 3-56 shows data collected three days prior to initiation of the June 22 tracer test. These data show that bromide from the May 18 tracer test was still present in the injection wells IW-1, IW-2, and IW-3, and that bromide had begun to impact monitoring wells MW-2, MW-3, and MW-5. Subsequent contour maps show the radial movement of bromide from MW-5, which served as the point of injection for the tracer test initiated on June 22.

Despite the fact that bromide was being injected at only 100 mg/L, the concentration of bromide measured in the plot using the bromide-specific electrode was considerably higher. Because laboratory measurements did not corroborate these elevated concentrations, and because the bromide concentration in the supply well remained consistently low (<3.3 mg/L) throughout the demonstration, it is suspected that the bromide-specific electrode provided artificially high bromide values due to the presence of interfering ions. The manufacturer lists seven ions capable of interfering with the bromide-specific probe, but only ammonia (NH_3) and sulfide (S^{-2}) are likely to have been present at concentrations high enough to cause interference. In addition, the suspiciously high bromide concentrations were only observed after the injection of electron donor, and only in areas with very low redox potentials, which is exactly where one would expect to see the formation of ammonia and sulfide. Although the specific bromide concentration data in these areas appear to have been compromised, the data do provide an indication that these areas were highly reduced and were probably impacted by the addition of electron donor.

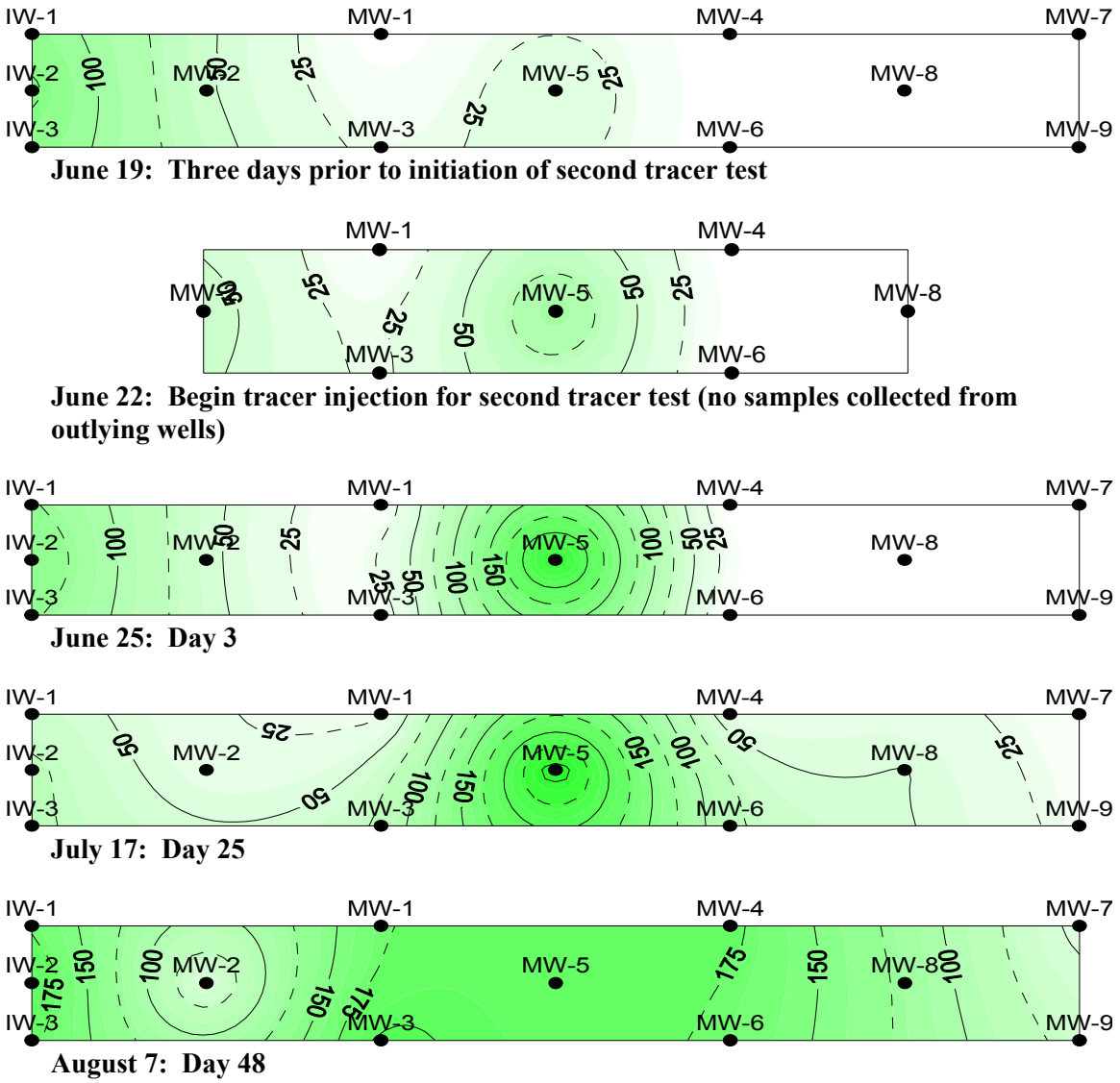


Figure 3-56. Bromide Tracer Testing Contours from Site 88, Camp Lejeune, North Carolina

Assuming an in situ bromide concentration of 100 mg/L, the maximum allowable NH_3 and S^{-2} concentrations are 4.3×10^{-2} mg/L and 4×10^{-6} mg/L, respectively. Ammonia concentrations ranging up to 1 mg/L were observed within the boundaries of the test plot. Sulfide ion measurements were not made.

3.5.4.3 Treatability Testing

System Operation

Treatability testing at Site 88 involved the continuous extraction, amendment and injection of PCE-contaminated groundwater for 6.5 months. A submersible Grundfos™ pump was used to extract groundwater from an existing well, designated 88-MW05IW, which supplied groundwater with a consistently high concentration of PCE. The extracted groundwater was pumped into a field trailer where a dedicated metering pump added a solution containing butyric acid (110 g/L), YE (8.3 g/L), and sodium bromide (53.5 g/L) at ~ 1 mL/min. After the groundwater had been amended with nutrients in the field trailer it was injected into monitoring well MW-5. Injection wells IW-1, IW-2 and IW-3 were not used to inject electron donor solution (see Section 3.5.4.2). The total injection flowrate was approximately 600 mL/min. Injection of the nutrient-amended groundwater began on June 25, 2001 and ended on January 7, 2002.

The butyric acid-YE-sodium bromide stock solution was prepared in two covered 15-gallon HDPE tanks using concentrated butyric acid, YE, sodium bromide, and tap water.

Sampling

The RABITT demonstration at Site 88 required the frequent sampling and analysis of a variety of groundwater parameters. Groundwater samples were collected every three weeks from each of 12 individual monitoring locations. Table 3-30 shows the specific sampling dates and sample types collected at Site 88, and Table 3-31 lists the specific analytes for each sample type. Additional information regarding analytical methods, container types, sample preservatives, and holding times can be found in the Technology Demonstration Plan for Camp Lejeune (Battelle et al., 2001).

A peristaltic pump was used to pump groundwater from monitoring wells and into a flowthrough cell without exposing it to the atmosphere. The flowthrough cell was instrumented with probes, which measured pH, temperature, redox potential, and DO. Groundwater was allowed to flow through the cell and into a waste container until redox potential and DO measurements

stabilized. Once these measurements stabilized, all field measurements were recorded and groundwater samples were collected and prepared for shipment to the appropriate analytical laboratory. Additional groundwater samples were collected and used to measure the bromide ion and ferrous iron concentrations in the field.

3.5.4.4 Results. Results from the RABBIT demonstration at Site 88 are presented in the following subsections. Chloroethene concentrations are presented in a series of contour plots showing the spatial distribution of contaminant in the test plot over time. The remaining analytical parameters are presented in graphs that show the average concentration in the test plot over time. The data presented in these graphs represent the average total concentration from monitoring wells MW-1 to MW-9 and injection well IW-2 (used as a monitoring well). Data from the supply and background wells were not included. Results for individual monitoring

Table 3-30. Sampling Schedule at Site 88, Camp Lejeune, North Carolina

Date	Elapsed Time (Weeks)	Field Data	Laboratory Analytes					
			VOCs	Dissolved Gases	VFA Data	Inorganic Data	DOC	H_2
16-May-01	0 (preinjection)	19-Jun	X	X	X	X	X	
25-Jun-01	5 (injection begins)	X	X	X	X	X	X	21-Jun
17-Jul-01	8	X	X					
07-Aug-01	11	X	X	X	X	X	X	
28-Aug-01	14	X	X					
02-Oct-01	19	X	X	Not Analyzed	X	X	X	X
23-Oct-01	22	X	X					
13-Nov-01	25	X	X	X	X	X	X	
04-Dec-01	28	X	X	X				
18-Dec-01	30	X	X	X				
07-Jan-02	33	X	X	X	X	X	X	X

Table 3-31. Field and Laboratory Analytes at Site 88, Camp Lejeune, North Carolina

Field Data	Laboratory Analytes					
	VOCs	Dissolved Gases	VFA Data	Inorganic Data	DOC	H_2
Water Level Redox potential pH Temperature Bromide DO Fe(II)	PCE TCE *cis*-DCE VC	Ethene Ethane Methane	Lactic acid Acetic acid Propionic acid Butyric acid	pH Conductivity Alkalinity Nitrate Nitrite Ammonia Chloride Sulfate Bromide	Dissolved organic carbon	Dissolved hydrogen

locations and for other analytes (e.g., *trans*-DCE) are available in the Camp Lejeune Database, which can be found on the CD-ROM supplied with this report.

Chloroethene Concentration Profiles

Results from selected PCE, TCE, *cis*-DCE, and VC are presented. Contour plot concentration units are in μM to allow for direct comparison between the four compounds on an equivalent basis.

Tetrachloroethene

PCE-contaminated groundwater was being continuously pumped from the supply well, amended with electron donor solution and then injected into MW-5. This injection strategy ensured that contaminated groundwater within the plot was not simply displaced with uncontaminated injection solution. During each sampling event, injection was stopped briefly so a groundwater sample from MW-5 could be obtained. Approximately one well volume was purged before the groundwater sample was collected. A comparison of PCE concentrations in the supply well and MW-5 groundwater samples indicates that PCE dechlorination occurs very rapidly after injection, with PCE concentrations in MW-5 typically less than 30% of those observed in the supply well (see Figure 3-57).

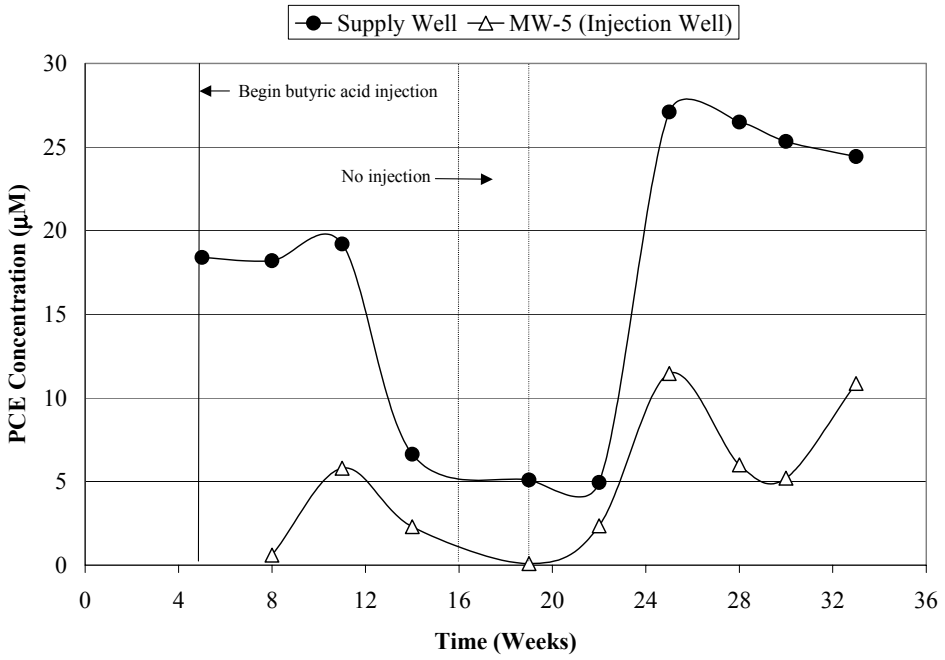


Figure 3-57. PCE Concentration in Injected Groundwater at Site 88, Camp Lejeune, North Carolina

The disappearance of PCE within the test plot is illustrated in Figure 3-58, which shows a time series of PCE concentration contours. The figure shows that preinjection PCE concentrations (time zero) ranged across the test plot from 18.1 µM (3,000 ppb) to 53.8 µM (8,920 ppb), and that the degradation of PCE proceeded relatively quickly following the initiation of electron donor injection. Injection was interrupted from Weeks 16-19 due to a pump malfunction, so for the Week 19 samples no groundwater had been injected for the previous three weeks. The PCE observed around MW-5 in the latter weeks of the demonstration illustrate the constant influx of PCE-contaminated groundwater into MW-5.

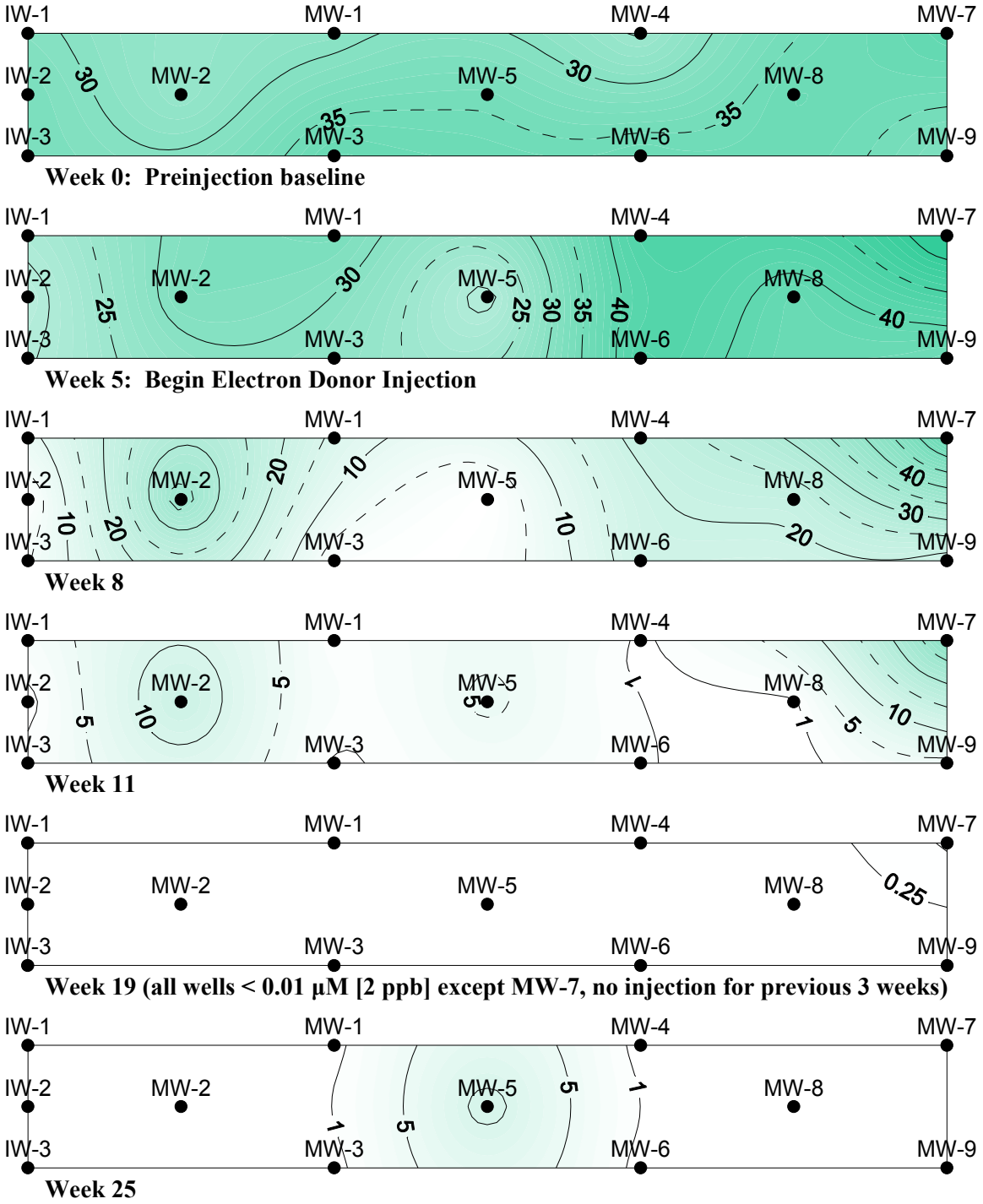


Figure 3-58. PCE Concentration (µM) Contour Plots at Site 88, Camp Lejeune, North Carolina

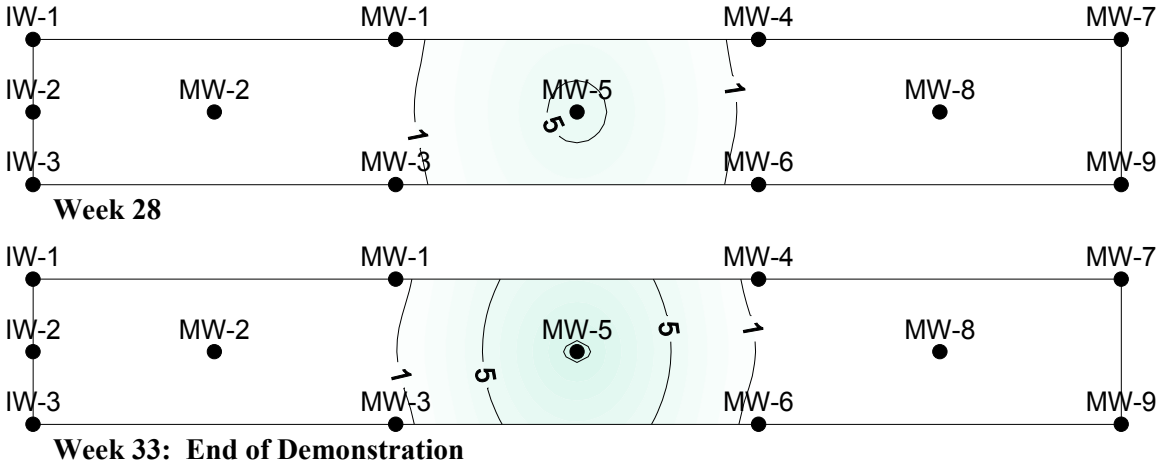


Figure 3-58. PCE Concentration (µM) Contour Plots at Site 88, Camp Lejeune, North Carolina (Continued)

Trichloroethene

TCE was present within the test plot prior to the injection of the nutrient-amended groundwater solution, but at lower levels than PCE. Preinjection TCE concentrations ranged from 1.63 µM (201 ppb) to 5.19 µM (682 ppb). Figure 3-59 shows that as the demonstration progressed, TCE concentrations were significantly reduced throughout most of the test plot. Increases in the TCE concentration observed around MW-5 were caused by two factors. First, the injected nutrient-amended groundwater consistently contained higher TCE concentrations than those observed initially in the test plot; injection concentrations ranged from 8.37 µM (1,100 ppm) to 21.31 µM (2,800 ppb), except during Weeks 16-19 when no injection occurred. The second factor was the continuous degradation of PCE to TCE that occurred around MW-5. The Week 19 contour plot shows that reductive dechlorination continues temporarily in the absence of nutrient injection.

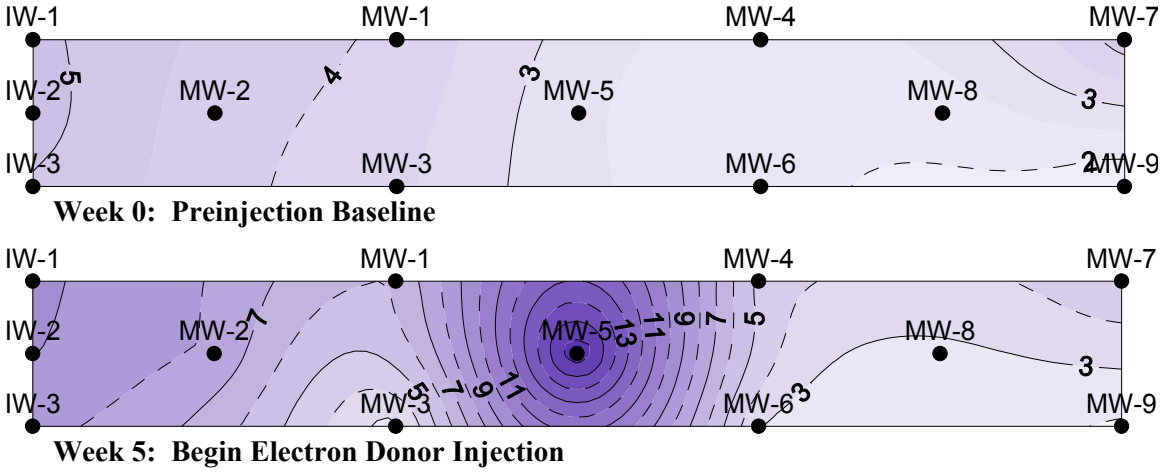


Figure 3-59. TCE Concentration (µM) Contour Plots at Site 88, Camp Lejeune, North Carolina

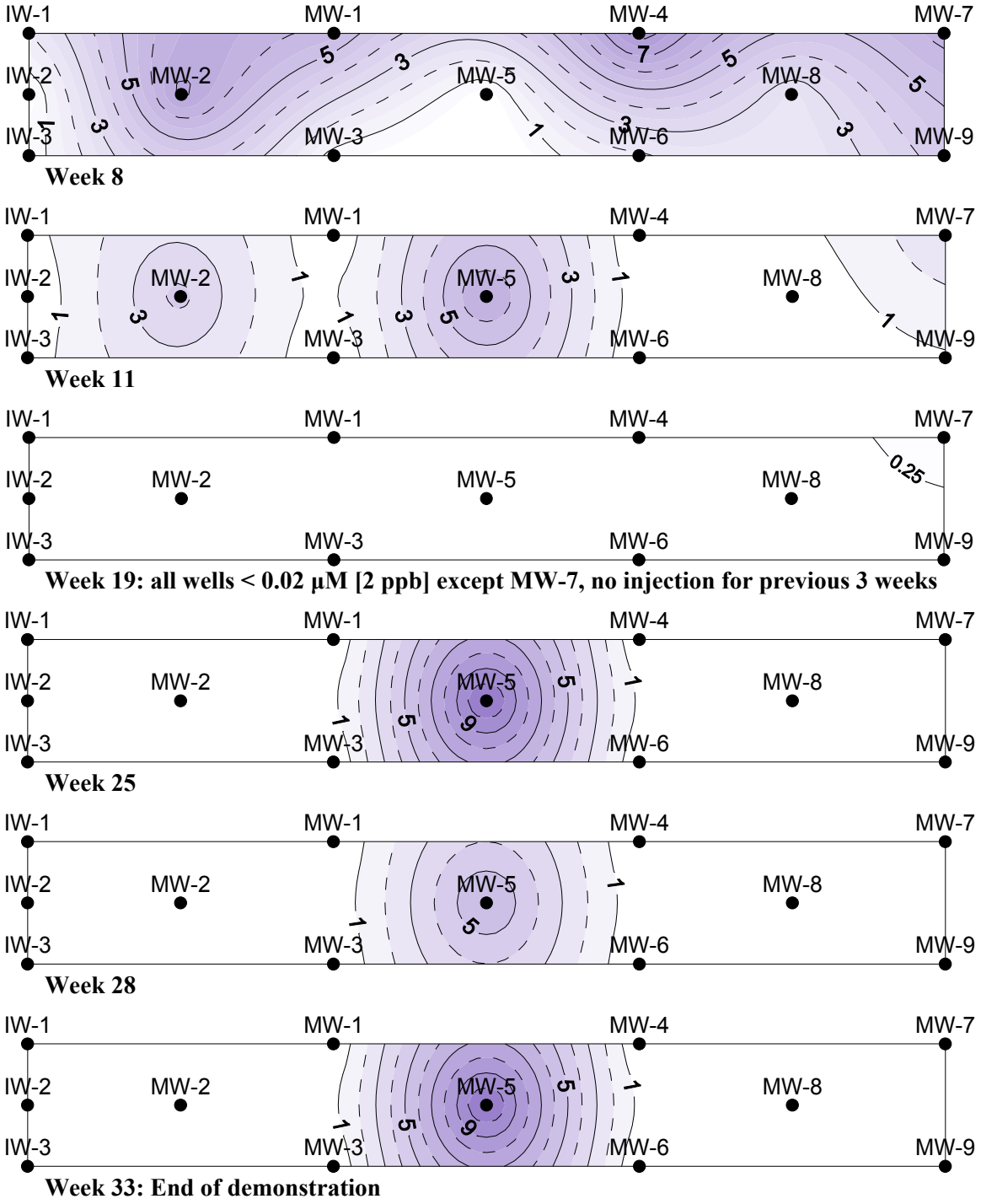


Figure 3-59. TCE Concentration (µM) Contour Plots at Site 88, Camp Lejeune, North Carolina

***cis*-Dichloroethene**

Initial preinjection *cis*-DCE concentrations were fairly low; they ranged across the test plot from 1.22 µM (42 ppb) to 0.43 µM (118 ppb). The initial increase in *cis*-DCE shown during Week 5 in Figure 3-60 resulted from higher levels of *cis*-DCE present in injected groundwater during tracer testing. Notice that the highest *cis*-DCE concentrations are found around wells that had been used for the injection of tracer (i.e., IW-1, IW-2, IW-3 and MW-5).

Three weeks after beginning butyric acid injection, *cis*-DCE levels had risen dramatically to greater than 80 µM in some locations. This provides compelling evidence that reductive dechlorination of PCE and TCE was occurring because the *cis*-DCE concentrations in injected groundwater never exceeded 22 µM (2,133 ppb). It also suggests that the reductive dechlorination of *cis*-DCE was occurring considerably slower than the dechlorination of its parent compounds, resulting in its accumulation. By the end of the demonstration, *cis*-DCE levels had begun to taper off, suggesting that *cis*-DCE dechlorination had begun.

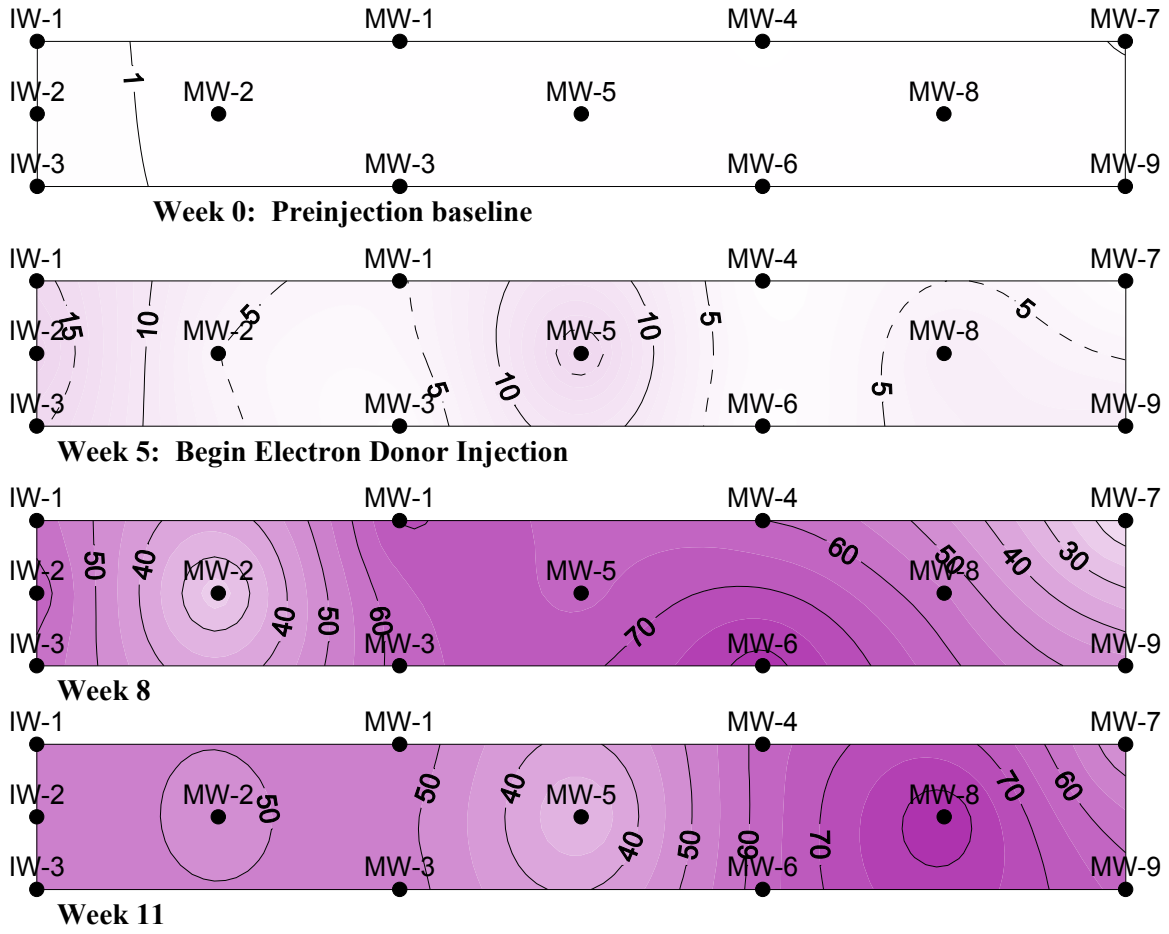


Figure 3-60. *cis*-DCE Concentration (µM) Contours at Site 88, Camp Lejeune, North Carolina

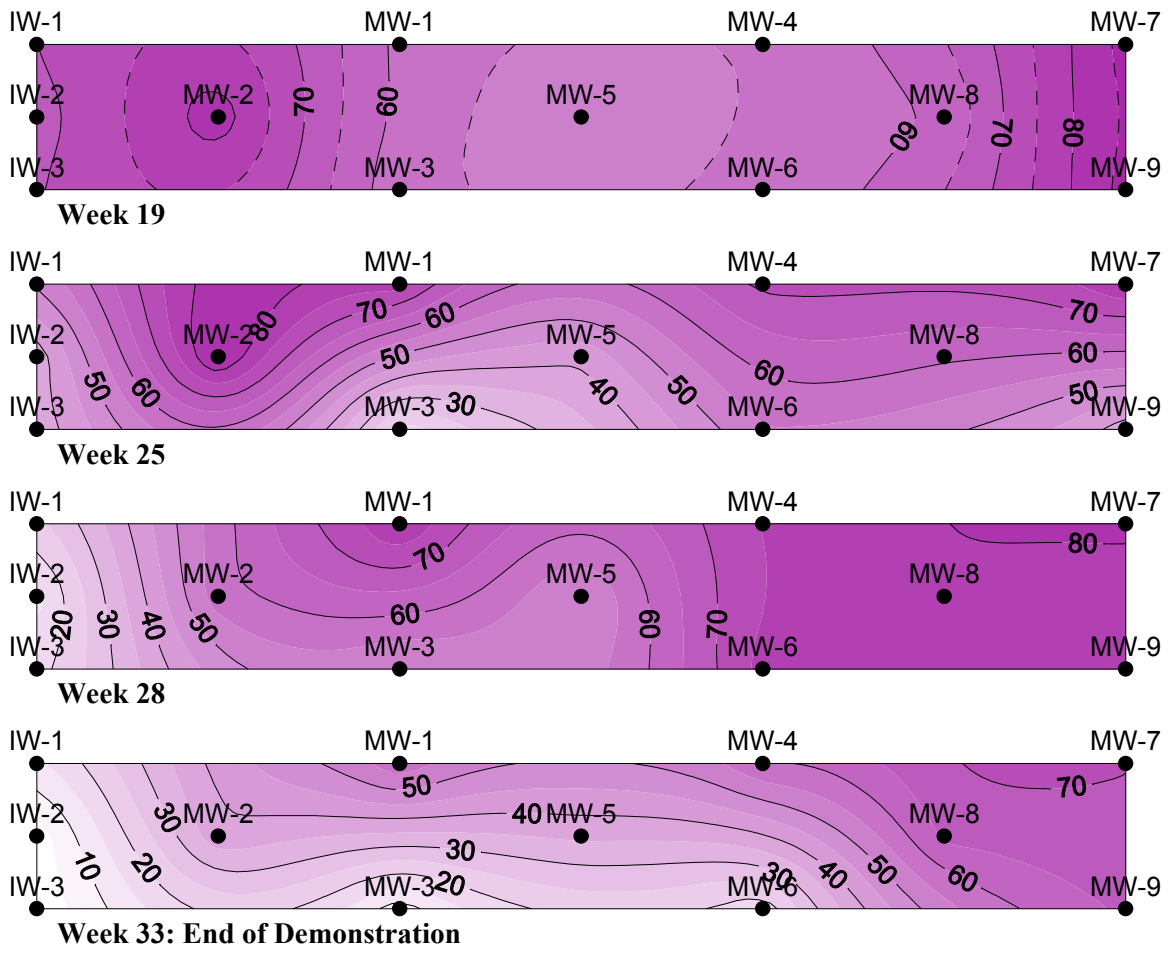


Figure 3-60. *cis*-DCE Concentration (µM) Contours at Site 88, Camp Lejeune, North Carolina (Continued)

Vinyl Chloride

VC was not initially present within the test plot (see Figure 3-61), nor was it present in the injected groundwater. The absence of VC in the test plot for the first 19 weeks of the demonstration shows that a considerable lag occurred before the dechlorination of *cis*-DCE began. An examination of the *cis*-DCE and VC contour plots from Weeks 25, 30, and 33 reveals a strong spatial correlation between decreases in *cis*-DCE concentrations and increases in VC concentrations. The production of VC and its correlation with decreasing *cis*-DCE concentrations demonstrate that reductive dechlorination of *cis*-DCE was occurring within the test plot. Interestingly, microcosms constructed from sediments in this area did not demonstrate dechlorination of *cis*-DCE. The reason for this discrepancy is unknown.

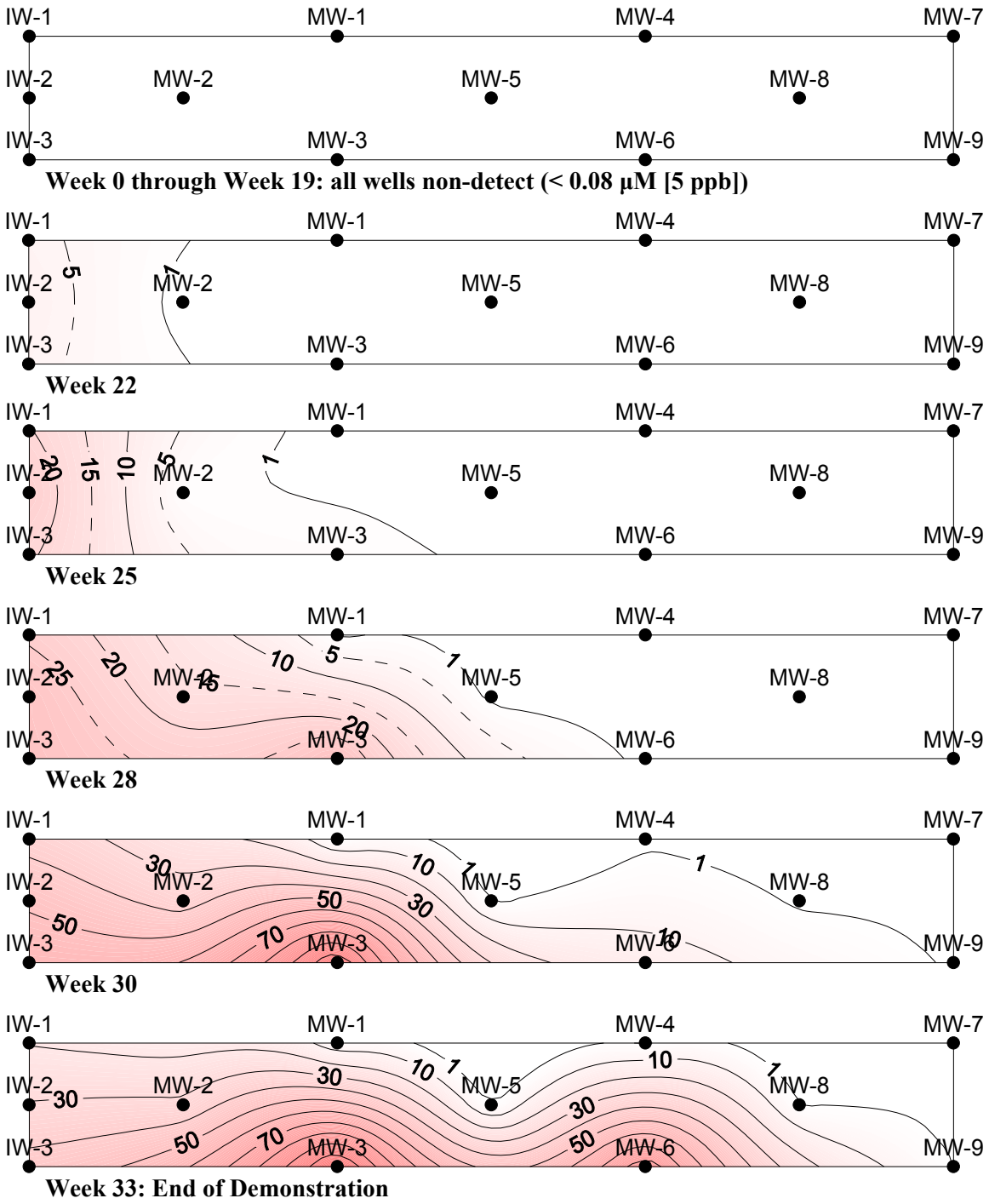


Figure 3-61. Vinyl Chloride Concentration (µM) Contours at Site 88, Camp Lejeune, North Carolina

Dissolved Gases
The dissolved gases ethene, ethane, and methane were monitored during the field demonstration to determine the extent of chloroethene degradation and assess the microbiological conditions within the testing zone. Dissolved gas samples were collected only once every 6-8 weeks, and unfortunately, the samples collected during Week 19 were not analyzed due to a laboratory error.

Ethene
Ethene was not detected in groundwater samples collected through the first 11 weeks of the demonstration (see Figure 3-62). By Week 25, ethene had begun to appear in IW-2, which is the same location VC was first observed. The correlation between VC and ethene would become evident over the next eight weeks as the concentration and distribution of ethene continued to increase in locations that showed the presence of VC. This observation supports the conclusion that chloroethenes can be completely dechlorinated to a nonhazardous endpoint by native microbial flora.

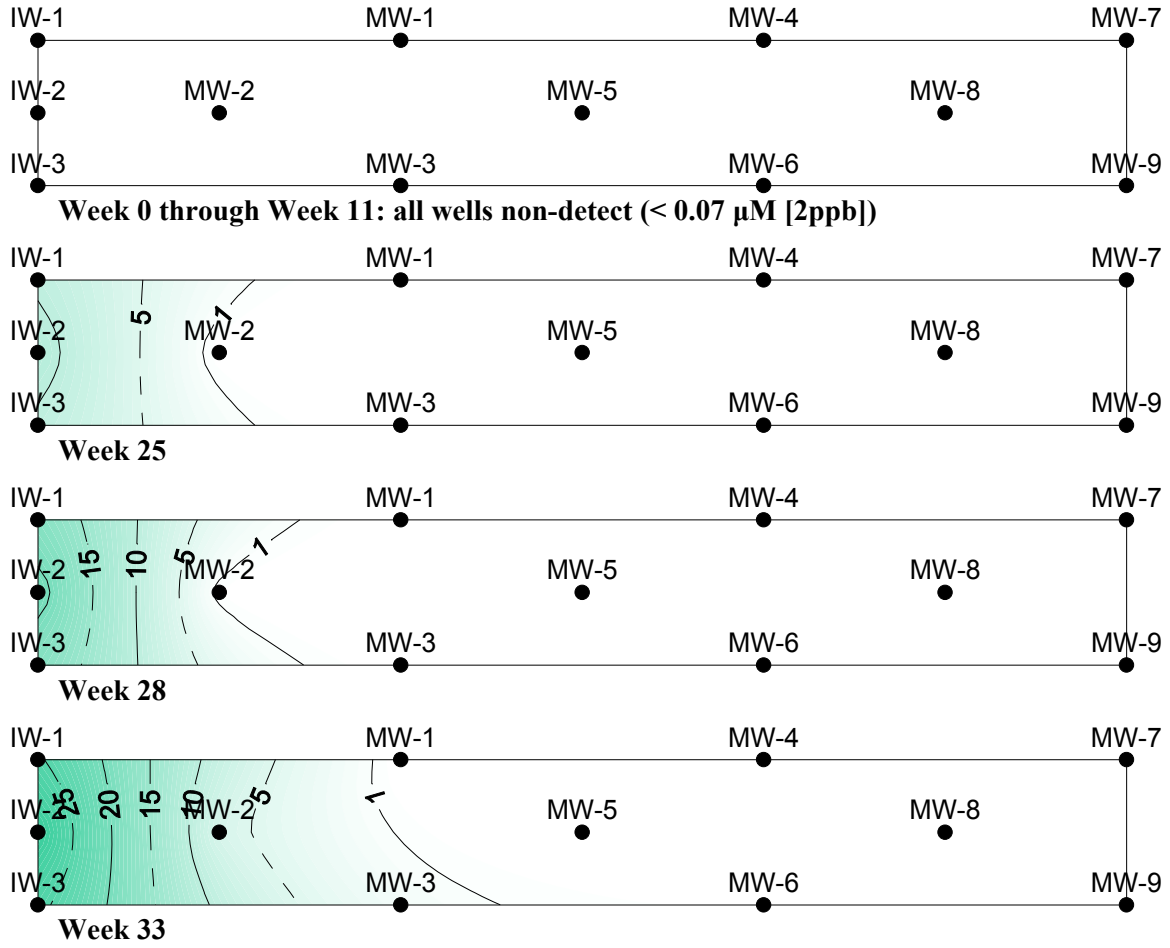


Figure 3-62. Ethene Concentration (µM) Contours at Site 88, Camp Lejeune, North Carolina

Figure 3-63 shows the average ethene, ethane, and methane concentrations across the test plot. Ethane remained below the detection limit throughout the demonstration. Methane results show that concentrations increased fairly rapidly and remained high through the end of the demonstration. Field notes report the formation of bubbles in groundwater samples collected after Week 22. This observation suggests that degassing was occurring and would tend to corroborate the high levels of dissolved methane observed in the latter few weeks of the demonstration.

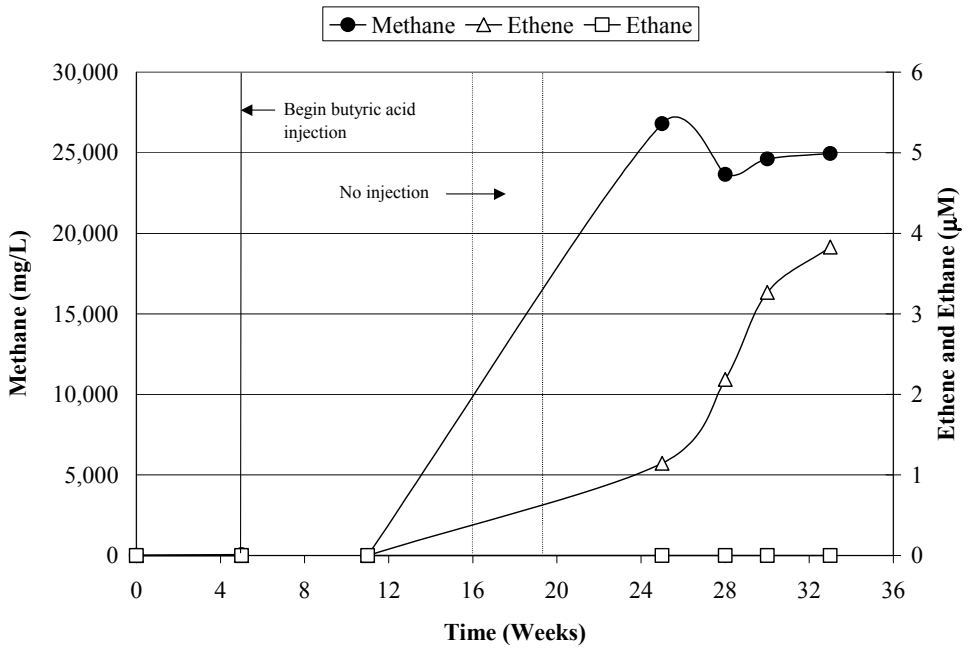


Figure 3-63. Average Dissolved Ethene, Ethane, and Methane Concentrations at Site 88, Camp Lejeune, North Carolina

Hydrogen

Dissolved hydrogen samples were collected three times during the demonstration using the bubble-strip method. Samples were collected four days prior to injection, at mid-demonstration (Week 19), and at the end of the demonstration (Week 33). Table 3-32 outlines the results. A previously published correlation between dissolved hydrogen concentration and predominant terminal electron accepting process is shown in Table 3-24. Although results did suggest that the subsurface environment was highly reduced, they did not provide any diagnostic value. The unusually high dissolved hydrogen concentrations observed prior to electron donor injection could not be explained, but may have been linked to the residual polymeric drilling fluid that remained in the testing zone for several weeks following well installation. Despite these high hydrogen levels, methanogenesis did not appear to be the predominant electron accepting process early in the demonstration (see Figure 3-63).

Table 3-32. Dissolved Hydrogen Concentrations at Site 88, Camp Lejeune, North Carolina

Monitoring Location	Hydrogen Concentration (nM)		
	Preinjection Week 5	Mid-demonstration Week 19	Final Week 33
IW-2	Not Sampled	6	2.3
MW-1	4	7	5.2
MW-2	2	41	3.7
MW-3	830	10	5
MW-4	21	8	5.3
MW-5	120	19	10
MW-6	410	10	7
MW-7	230	59	6.3
MW-8	130	29	4.9
MW-9	34	75	7.2

Organic Acids

The concentrations of acetic, butyric, lactic, and propionic acids were tracked during the field demonstration to ensure that sufficient butyric acid was being injected and to examine the fate of added reducing equivalents. Figure 3-64 shows the average concentration of each of these acids within the test plot. The injection concentration of butyric acid was 3,000 µM throughout the demonstration, except from Week 16 to Week 19 when electron-donor injection was interrupted. The data show that a residual concentration of butyric acid was maintained in the test plot and that acetic acid was the predominant fermentation product.

Inorganics

Several inorganic species were tracked throughout the field demonstration, including: pH, alkalinity, nitrate, nitrite, ammonia, sulfate, and chloride. Data for each of these species is described in the following subsections and is presented in Figures 3-65 through 3-69.

pH and Alkalinity

The average groundwater pH within the testing zone dropped quickly following butyric acid injection, but appeared to stabilize between 6.5 and 7.0 after 11 weeks (see Figure 3-65). The stabilization of pH measurements coincides with a three-fold increase in the average alkalinity concentration. Alkalinity jumped from 150 mg/L to 456 mg/L in the 14 weeks following the injection of butyric acid. Unlike previous demonstrations at Alameda Point and Fort Lewis, no sodium bicarbonate was added to the injected groundwater. Increases in the alkalinity at Site 88 were the result of natural processes.

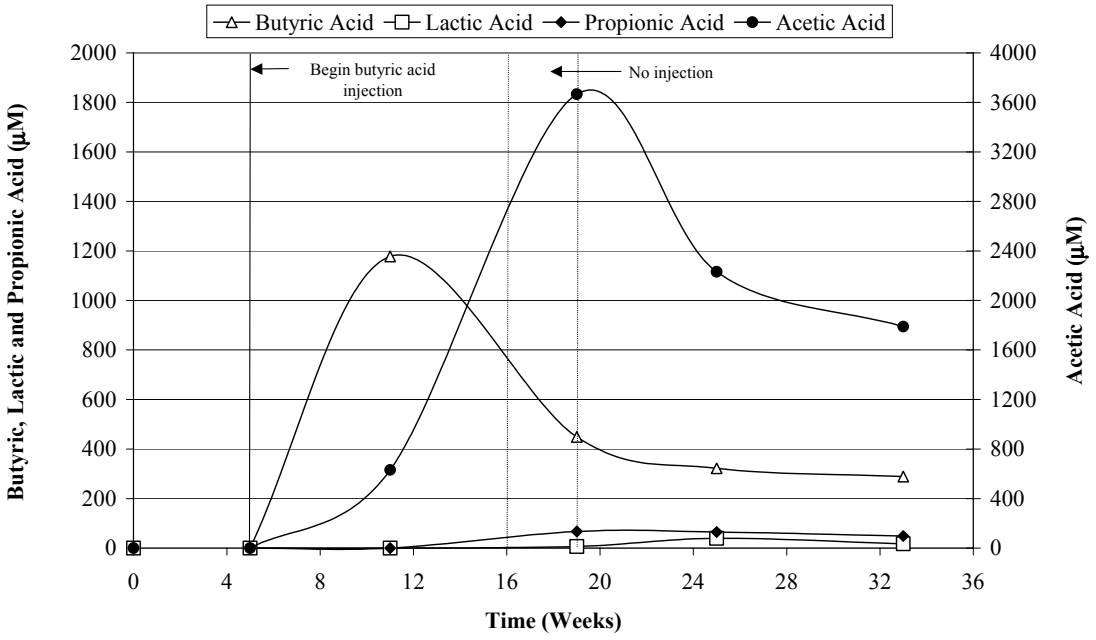


Figure 3-64. Average Organic Acid Concentrations at Site 88, Camp Lejeune, North Carolina

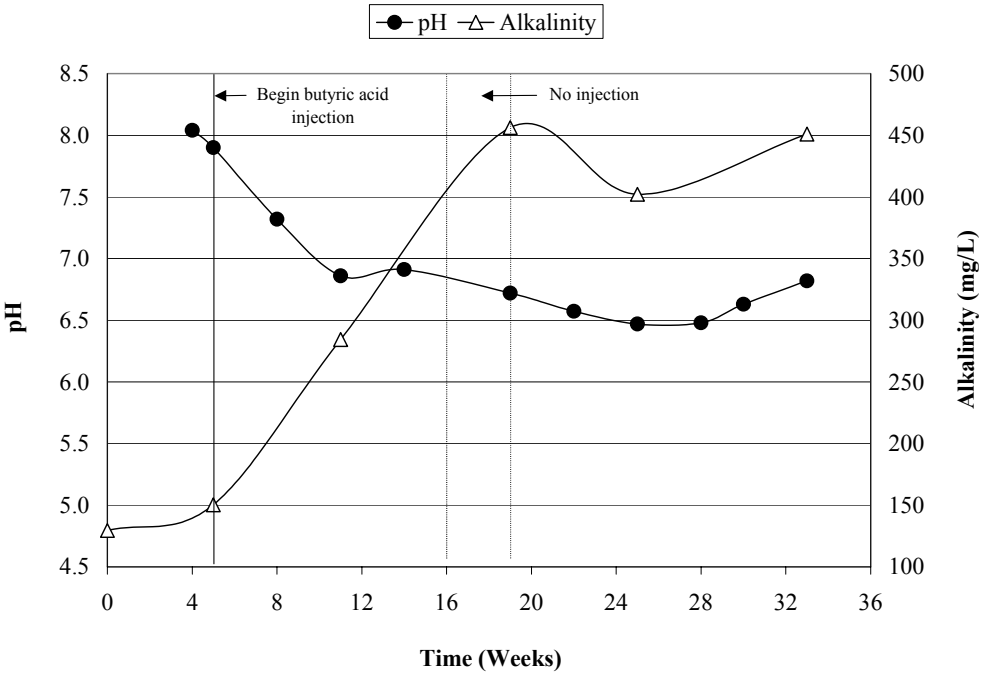


Figure 3-65. Average Field pH and Alkalinity Concentrations at Site 88, Camp Lejeune, North Carolina

Dissolved Oxygen and Ferrous Iron

DO measurements taken at Site 88 showed that anoxic conditions prevailed in the testing zone at Site 88 even before butyric acid injection began. In fact, the average DO concentration in the groundwater exceeded 0.5 mg/L only twice during the 33 week demonstration (see Figure 3-66). These results indicate that aerobic microbial activity in the testing zone was minimal and therefore did not consume a significant portion of the injected butyric acid.

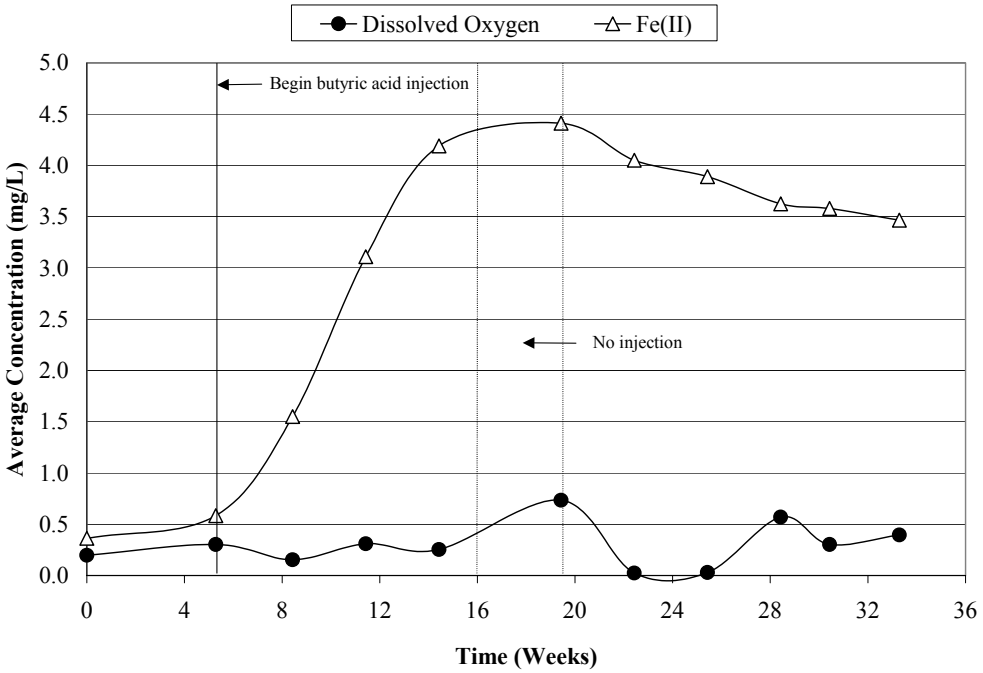


Figure 3-66. Average Dissolved Oxygen and Ferrous Iron Concentrations at Site 88, Camp Lejeune, North Carolina

In contrast to DO measurements, which were relatively stable, the average ferrous iron concentration jumped from an initial concentration of 0.36 mg/L to a peak concentration of 4.41 mg/L. The dramatic increase in the average ferrous iron concentration observed in the nine weeks following butyric acid injection indicates that iron reduction was a significant terminal-electron accepting process during that period. The supply of bioavailable ferric iron in the testing zone must have been exhausted by Week 19; as a result, ferrous iron concentrations begin to slowly taper off.

Ferrous iron ranged between 0 and 2.8 mg/L in the background well and between 0.8 and 1.9 mg/L in the supply well, with no trend evident in either well.

Nitrate, Nitrite, and Ammonia

Nitrate and nitrite concentrations at Site 88 were initially very low in the test plot and remained low throughout the demonstration despite some minor fluctuations (see Figure 3-67). Ammonia levels were fairly stable during the demonstration after an initial 80% drop that occurred during tracer testing. Ammonia was found at concentrations an order of magnitude greater than either nitrate or nitrite. These observations coupled with field measurements showing the depletion of oxygen suggest that the plot had exhausted the electron acceptors oxygen, nitrate, and nitrite even before the demonstration began.

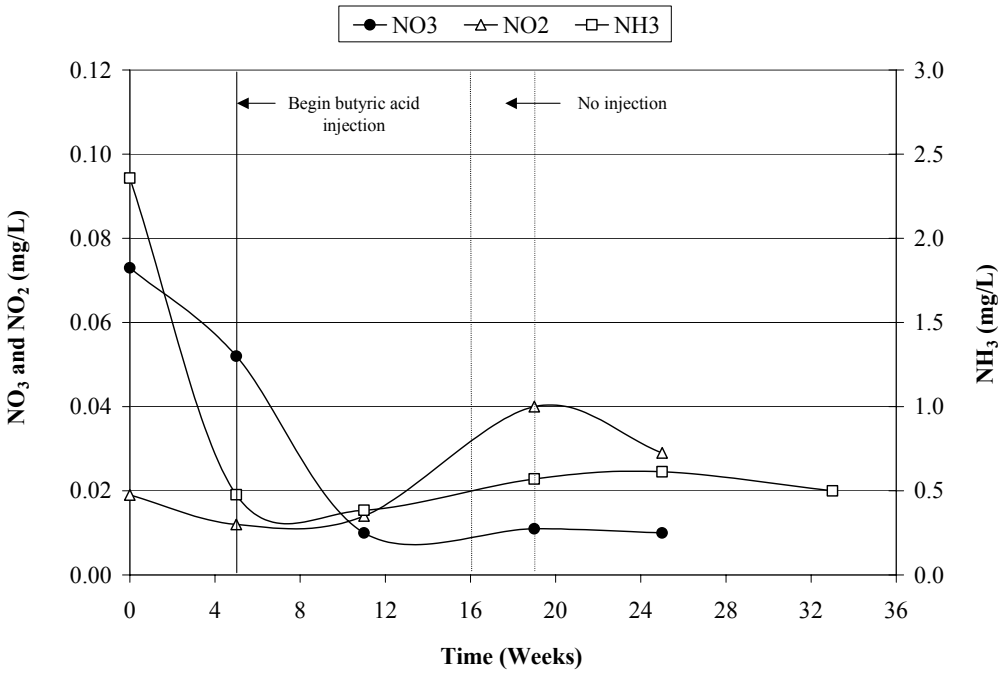


Figure 3-67. Average Nitrate, Nitrite and Ammonia Concentrations at Site 88, Camp Lejeune, North Carolina

Sulfate

The initial average sulfate concentration (71 mg/L) in the testing zone at Site 88 was considerably higher than that pumped from the supply well (24 mg/L). The continuous injection of supply well water into the testing zone during tracer testing significantly impacted the average testing zone sulfate concentration. Figure 3-68 shows that the initial sulfate concentration had dropped 38% by Week 5, the end of tracer testing, and then dropped an additional 38% over the next six weeks before stabilizing at about 17 mg/L. This initial consistent decrease in sulfate is attributed primarily to dilution, however, the drop in concentration observed over the last eight weeks of the demonstration probably resulted from microbially catalyzed sulfate reduction. During this period, ferrous iron levels were stable and methane production had begun, indicating that conditions were sufficiently reduced to promote sulfate reduction.

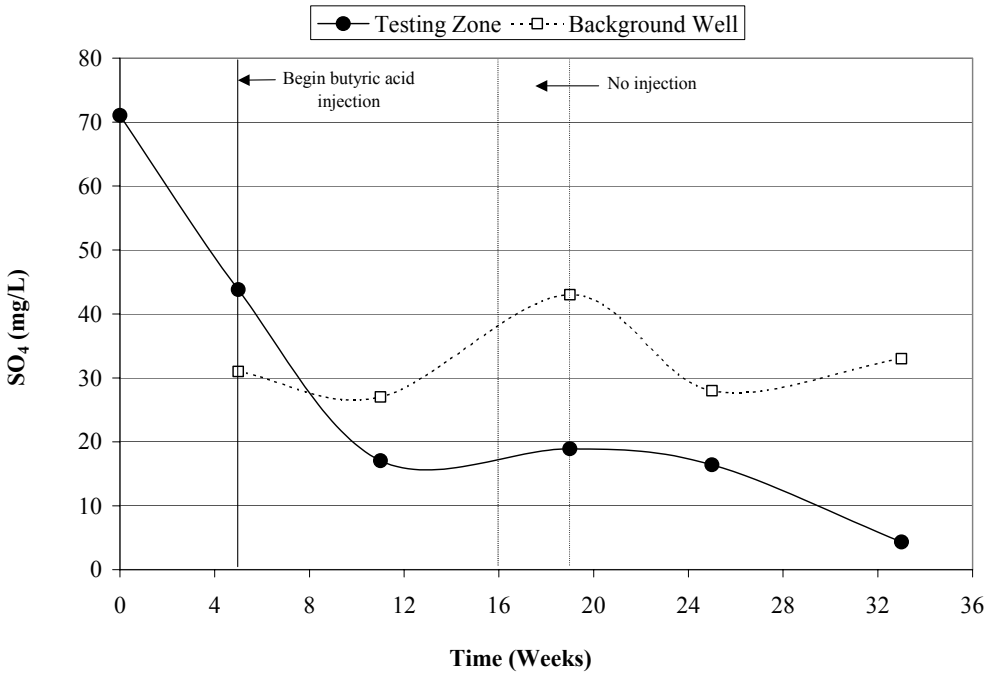


Figure 3-68. Average Sulfate Concentrations at Site 88, Camp Lejeune, North Carolina

Influent concentrations of sulfate from the supply well ranged from 24 to 35 mg/L.

Chloride

The reductive dechlorination process causes increases in local chloride levels as chlorine atoms are sequentially removed from parent chloroethene compounds. Measurements of chloride at the Camp Lejeune demonstration site showed an initial increase in chloride levels immediately following the injection of electron donor (see Figure 3-69). The increase in chloride concentration during the first six weeks of the demonstration was about six times higher than expectations based on the average concentration of chloroethenes injected into MW-5. This discrepancy could have resulted from the dechlorination of chloroethenes sorbed to soils within the test plot and/or by the accumulation of injected chloroethenes within the testing zone.

Midway through the demonstration, chloride levels stabilized and then dropped off dramatically. The pump failure that stopped injection of the nutrient-amended groundwater from Week 16 to Week 19 contributed to the lower rate of chlorine production that occurred between Week 11 and Week 19, but cannot explain the subsequent declines in chloride levels. The reason for the dramatic decline in chloride was never determined.

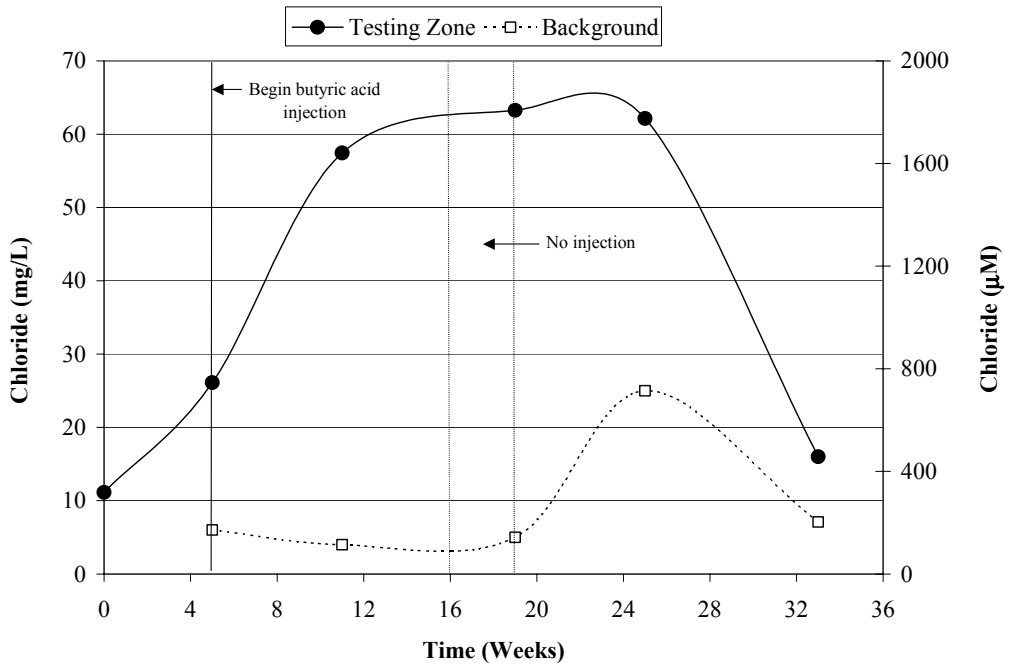


Figure 3-69. Average Chloride Concentrations at Site 88, Camp Lejeune, North Carolina

Chloride concentrations in both the background and supply wells remained relatively low. Background concentrations remained between 4 and 25 mg/L and supply well concentrations ranged from 11 to 13 mg/L.

Dissolved Organic Carbon

DOC measurements made at Site 88 demonstrate that initial DOC concentrations were dramatically increased by the addition of butyric acid. Figure 3-70 shows the DOC concentration data and compares it to the sum of butyric, lactic, acetic and propionic acids shown in units of DOC equivalents. Although the curves generated have a similar shape, the numerical result of the analyses differed by up to 34%. Anyone considering using DOC as a surrogate measurement for the analysis of individual organic acids should be aware of the rough correspondence between the measurements. In addition, organic acid analyses at Site 88 showed that acetic acid was by far the most prevalent source of DOC in the testing zone, which would not have been evident from the exclusive use of the DOC measurement. Unfortunately, acetate did not promote significant levels of dechlorination in microcosms.

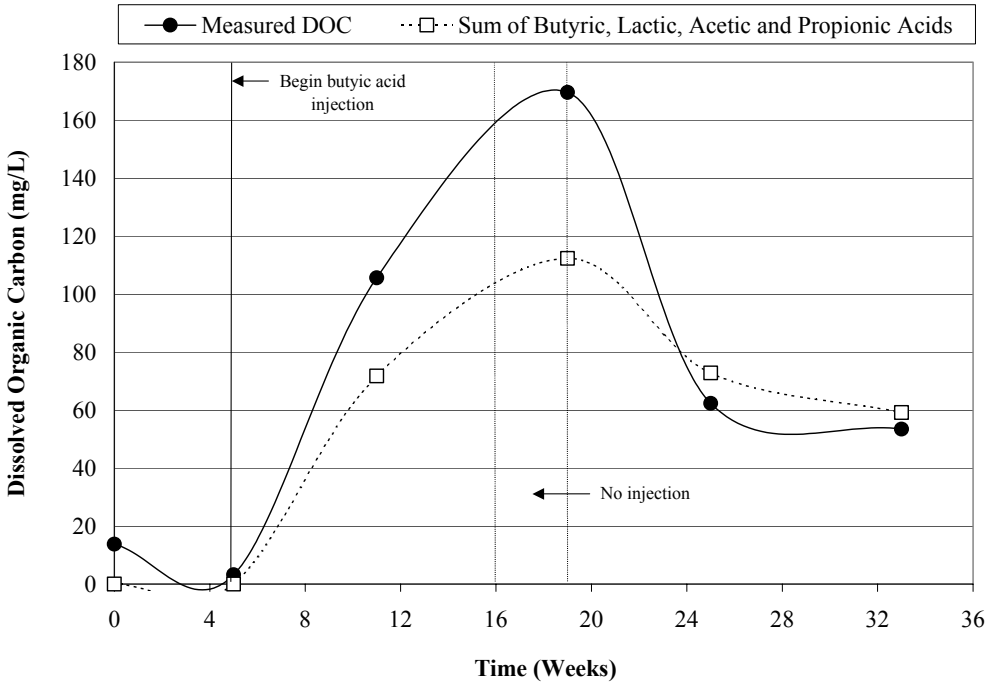


Figure 3-70. Average Dissolved Organic Carbon Concentrations at Site 88, Camp Lejeune, North Carolina

Redox Potential and Temperature

Site 88 exhibited the lowest average redox potential values of any of the RABITT demonstration sites. Average redox potential measurements were below -270 mV (see Figure 3-71); measurements in individual wells fell below -313 mV.

The average groundwater temperature at Site 88 ranged from 18.3°C to 23.6°C. The demonstration began in May (Week 0) and ended in January (Week 33), but the seasonal variation in temperature was very subtle, which is not surprising considering the mild climate on the North Carolina coastline.

3.5.4.5 Conclusions. Results from the RABITT field demonstration at Camp Lejeune show that native subsurface microbial populations are capable of sequentially reducing PCE to ethene. PCE and TCE concentrations were reduced to below detectable levels in almost all wells after 14 weeks and remained depressed throughout the remainder of the demonstration. The degradation of PCE and TCE was so rapid that injected PCE-contaminated groundwater was free of both PCE and TCE by the time it reached the first monitoring well only 5.4 ft away. As a result, kinetic parameters could not be estimated.

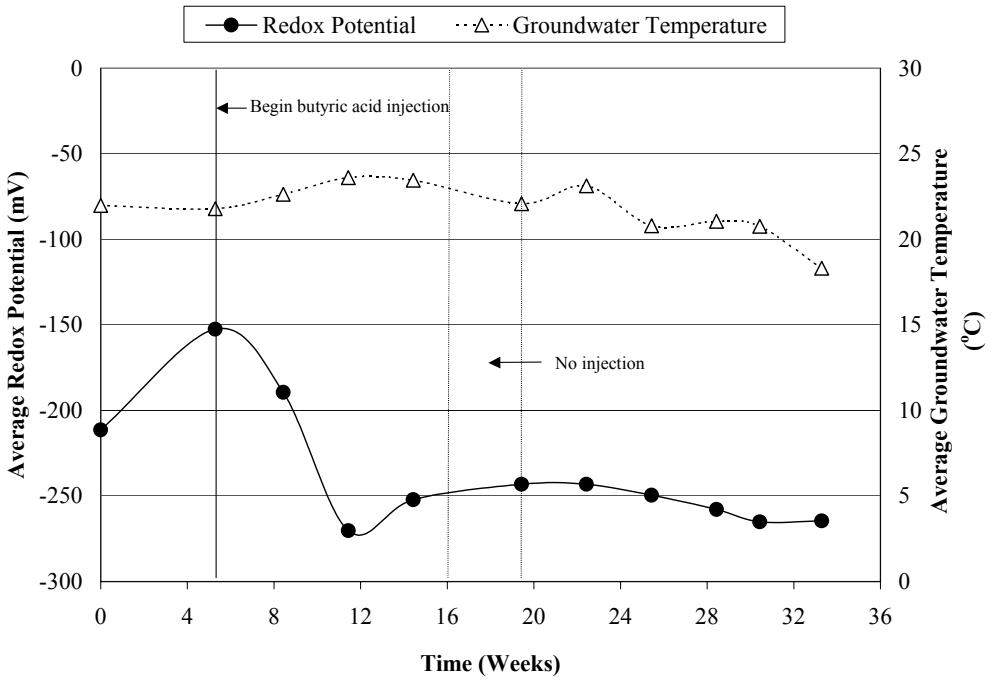


Figure 3-71. Average Redox Potential and Groundwater Temperature at Site 88, Camp Lejeune, North Carolina

As one would expect, the dechlorination of *cis*-DCE was considerably slower than that of PCE and TCE. As a result, *cis*-DCE temporarily accumulated in the testing area. After approximately 20 weeks, a proportional conversion of *cis*-DCE to VC and finally to ethene was observed at the eastern edges of the testing location. Neither VC nor ethene had been detected previously, strongly supporting the premise that reductive dechlorination was occurring.

The overall impact of the demonstration on the subsurface included subtle changes in several geochemical parameters. The addition of the butyric acid solution raised the level of dissolved organic carbon in the aquifer and contributed to a slight drop in the average site pH from an initial value of 7.9 to a final value of 6.8. Most electron accepting species were depleted in the testing area prior to the demonstration and were therefore unaffected. The relatively low levels of sulfate present at system startup were reduced by about an order of magnitude.

The most significant geochemical change that occurred within the testing location was the production of methane towards the end of the demonstration. The accumulation of methane shows that a large portion of added reducing equivalents was being used by methanogens, possibly reducing the efficiency of the process. An alternative feeding strategy (e.g., pulsed feeding) may help alleviate methane production and increase treatment efficiency.

The RABITT demonstration system installed at Site 88 provided convincing evidence that native microorganisms can be stimulated in situ to catalyze the complete reductive dechlorination of chlorinated ethenes. Based on testing results, this technology appears to be a viable candidate for achieving reductions in chloroethene contamination at Site 88. Any application of this technology would require a thorough understanding of the local subsurface hydrogeology and an engineered approach to electron donor dosing and distribution.

4.0 Performance Assessment

4.1 Overview of Field Results

During the development of the draft RABITT protocol, authors and reviewers attempted to outline quantitative criteria for a successful treatability test, but uncertainty regarding the overall performance of the EBRD process prevented such criteria from being included. Protocol developers were reluctant to predict lag periods or assume the extent or rate of biodegradation. The draft RABITT protocol eventually just suggested that success would be defined by site-specific goals.

Shortly after completing the draft protocol, work began on the site-specific work plan for Facility 1381 and the issue of quantitative criteria for success was raised again. The same uncertainties that plagued the development of the draft protocol caused the assignment of modest performance objectives. The quantitative performance objective for the six-month demonstration at Facility 1381 included a 20% reduction in the mass of TCE with a concurrent equimolar increase in *cis*-DCE, VC, ethene, or ethane. The rationale behind the objective was that such a finding would indicate that reductive dechlorination had been stimulated within the six-month testing window. However, it soon became clear that the performance objectives were too modest.

Results from the field demonstrations showed relatively short lag periods, rapid parent compound degradation and, with the exception of the Fort Lewis site, substantial conversion of parent compound to ethene. Table 4-1 provides an overview of the field results. It shows that reductive dechlorination began only 3-5 weeks after starting electron donor injection. Parent compounds were degraded quickly, with half-lives measured in hours. The system design at the Cape Canaveral site made calculating an accurate TCE half-life impossible, but the average TCE concentration within the treatment cell had dropped by approximately 50% after only two weeks of system operation. Because it took several days to distribute electron donor throughout the test cell, it is reasonable to conclude that the TCE half-life was less than 2 weeks, which is similar to half-lives observed at the other demonstration sites. In addition to being rapidly degraded, a large portion of the parent compound was converted to ethene at three of the four demonstration sites. The rate, extent, and consistency of EBRD at the sites were somewhat surprising and very encouraging.

Table 4-1. Overview of Field Results

Observation	Cape Canaveral	Alameda Point	Fort Lewis	Camp Lejeune
Parent Compound	TCE	TCE	TCE	PCE
Onset of Dechlorination	4 weeks	4 weeks	5 weeks	3 weeks
Parent Compound Half-life	Not determined	~ 20 hours	≤ 4.7 hours	≤ 164 hours
Reaction Endpoint	Ethene	Ethene	VC	Ethene
Molar Conversion to Endpoint (Plot Average)	66%	49%	<1%	5%
Molar Conversion to Endpoint (Active Monitoring Well)	MP 3-15 99+% ethene	MW-1 99+% ethene	MW-4 <1% VC	IW-2 28% ethene

The Fort Lewis demonstration provided an interesting contrast to the other three sites. It was the only site that was initially aerobic, but it showed the most rapid dechlorination of TCE. It also demonstrated how robust an EBRD system could be. Groundwater injected into the Fort Lewis test plot consistently contained high levels of dissolved oxygen (~6 mg/L), which was no doubt quickly scavenged in the highly reducing zone immediately around the injection wells. In addition to the high dissolved oxygen levels, the plot was subjected to extraordinarily high TCE concentrations when TCE levels in the injected groundwater spiked late in the demonstration. At their peak, levels reached 169,000 ppb. Despite the nearly constant influx of oxygen and the extreme TCE concentrations, the rate of TCE dechlorination remained rapid and stable. These observations indicate that EBRD is a robust process and suggest that it may be applicable to a wide variety of sites, including source zones.

Although the Fort Lewis demonstration site exhibited the most rapid dechlorination of TCE, it did not achieve the desired ethene endpoint. This was surprising because two of the three butyrate-amended Fort Lewis microcosms showed complete conversion of TCE to ethene within six months. Assuming the microcosms did not constitute a false positive result, the reason for the discrepancy was explored and a plausible explanation was determined. A review of microcosm data showed that the presence of parent compounds might have inhibited the dechlorination of daughter species. In microcosms, vinyl chloride was never produced in the presence of TCE. In fact, a considerable lag period (75-100 days) occurred between the time TCE was depleted and VC was produced. Similarly, ethene was never produced in the presence of *cis*-DCE, although no significant lag period was observed once *cis*-DCE had been exhausted. In the field, TCE was being injected constantly into the most highly active area of the test plot and may have inhibited the conversion of *cis*-DCE to VC. The continuous injection of TCE into the testing zone created a large build-up of *cis*-DCE, which may have precluded the dechlorination of VC. Inhibition could be avoided in future demonstrations by using a pulsed-feeding strategy that allows the depletion of parent compounds in the presence of residual electron donor. In fact, this strategy will be incorporated into the revised protocol.

Despite the somewhat disappointing results at Fort Lewis, the four RABITT field demonstrations showed that EBRD quickly and effectively degrades parent chloroethenes under a variety of site conditions. The system was not susceptible to upset by changes in parent compound concentration nor was it adversely affected by unplanned interruptions in electron donor dosing. At three of the four sites, the parent compound was converted to the non-hazardous ethene endpoint within the six-month testing window, and there is reason to believe that the fourth site may have reached that endpoint had a pulsed injection strategy been used. The overall performance of EBRD at the four sites exceeded expectations.

4.2 Overview of Microcosm Results

The draft RABITT protocol included both microcosm and field testing so electron donors could be screened in the laboratory before being taken to the field. This approach assumed that the selection of electron donor would significantly impact dechlorination performance. Results indicated that electron donor selection typically did not affect the reaction endpoint, but that it did impact the duration of the lag period and rate of dechlorination.

Table 4-2 outlines the performance of electron donors at each of the four demonstration sites by indicating the most reduced daughter product detected after six months of incubation and specifying the molar conversion to that product in parentheses. The table shows that the selection of the electron donor typically did not change the most reduced daughter product detected, but it did influence the rate and therefore the extent of dechlorination.

Consistent reaction endpoints were observed at Cape Canaveral, Alameda Point and Camp Lejeune. At Cape Canaveral and Alameda Point, ethene was detected in at least one replicate of each electron donor tested, and at Camp Lejeune all microcosms produced at least some *cis*-DCE but no VC or ethene. This suggests that all of the electron donors tested would eventually lead to the same endpoint and that electron donor screening may not be absolutely necessary to achieve the same level of treatment.

Inconsistent results from replicate Fort Lewis microcosms made assessing electron donor performance more challenging than at the other three sites. Each of the electron donors tested did produce *cis*-DCE within the six-month testing window, and most electron donors exhibited dechlorination to VC and ethene in at least one of the three replicate bottles. Microcosms were allowed to continue incubating beyond the six-month testing window to see if lagging bottles would eventually reach the same endpoint as more active replicates. The bottles were incubated a total of 292 days. By the end of the incubation some of the lagging replicates had begun dechlorinating long-standing accumulations of *cis*-DCE or VC; however, it was common for at least one replicate to remain stuck at *cis*-DCE. Only in bottles amended with propionic acid did all replicates fail to exhibit *cis*-DCE dechlorination, even after the extended incubation.

Although the endpoint of the dechlorination reaction typically was not affected by the choice of electron donor, the time until the onset of dechlorination and the rate of dechlorination were. For example, Camp Lejeune microcosms amended with butyrate showed a rapid and nearly complete conversion of PCE to *cis*-DCE between Day 57 and Day 69 (see Figure 4-1). In contrast, acetic acid-amended bottles from Camp Lejeune did not begin to produce *cis*-DCE until Day 192, if at all. Not only did some electron donors exhibit longer lag periods, but they also showed slower dechlorination rates. Figure 4-2 illustrates the dechlorination observed in a yeast extract-amended microcosm from Camp Lejeune. The figure shows that the dechlorination of TCE and *cis*-DCE was considerably slower than that observed in butyrate-amended bottles. The differences in lag period and dechlorination rate between donors are reflected in extent of dechlorination reported in Table 4-2. Donors with shorter lags and/or faster dechlorination rates achieved higher molar conversions after six months. Overall, butyrate provided the most complete dechlorination within six months and was therefore selected for use at three of the four field sites, but lactate did not usually lag too far behind.

Table 4-2. Overview of Microcosm Results – Dechlorination Endpoints and Molar Conversions after 6 Months

Donor	Cape Canaveral			Alameda			Fort Lewis			Camp Lejeune		
	Replicate			Replicate			Replicate			Replicate		
	I	II	III	I	II	III	I	II	III	I	II	III
Yeast Extract (200 mg/L)	VC (98%)	VC (98%)	E (5%)	E (100%)	E (100%)	E (62%)	E (87%)	VC (22%)	cis (100%)	cis (33%)	cis (46%)	cis (8%)
Lactate (3mM)	E (2%)	E (1%)	E (99%)	E (41%)	E (47%)	E (26%)	cis (99%)	cis (99%)	cis (99%)	cis (75%)	cis (17%)	cis (4%)
Lactate, YE, B_{12} (3mM, 20 mg/L, 0.05 mg/L)	E (4%)	E (2%)	E (2%)	E (100%)	E (67%)	E [a] (100%)	cis (100%)	E (73%)	cis (99%)	cis (99%)	cis (8%)	cis (9%)
Butyrate, YE, B_{12} (3mM, 20 mg/L, 0.05 mg/L)	E (8%)	E (1%)	E (21%)	E (100%)	E [a] (100%)	E (100%)	E (99%)	E (100%)	cis (100%)	cis (100%)	cis (100%)	cis (100%)
Lactate/Benzoate, YE, B_{12} (1.5/1.5mM, 20 mg/L, 0.05 mg/L)	E (5%)	E (15%)	E (2%)	E (3%)	E (3%)	E [a] (99%)	cis (100%)	cis (99%)	VC (30%)	cis (4%)	cis (3%)	cis (4%)
Propionic Acid, YE, B_{12} (3mM, 20 mg/L, 0.05 mg/L)	E (1%)	E (3%)	E (2%)	E [a] (99%)	E (100%)	E (100%)	cis (99%)	cis (99%)	cis (99%)	cis (100%)	cis (100%)	cis (100%)
Acetic Acid, YE, B_{12} (3mM, 20 mg/L, 0.05 mg/L)	NA	NA	NA	NA	NA	NA	cis (99%)	cis (99%)	cis (99%)	cis (3%)	cis (4%)	cis (4%)

a) Percentage reached prior to respiking (approx. 142 days into test)
E = ethene
cis = *cis*-DCE
NA = test condition not performed for this site

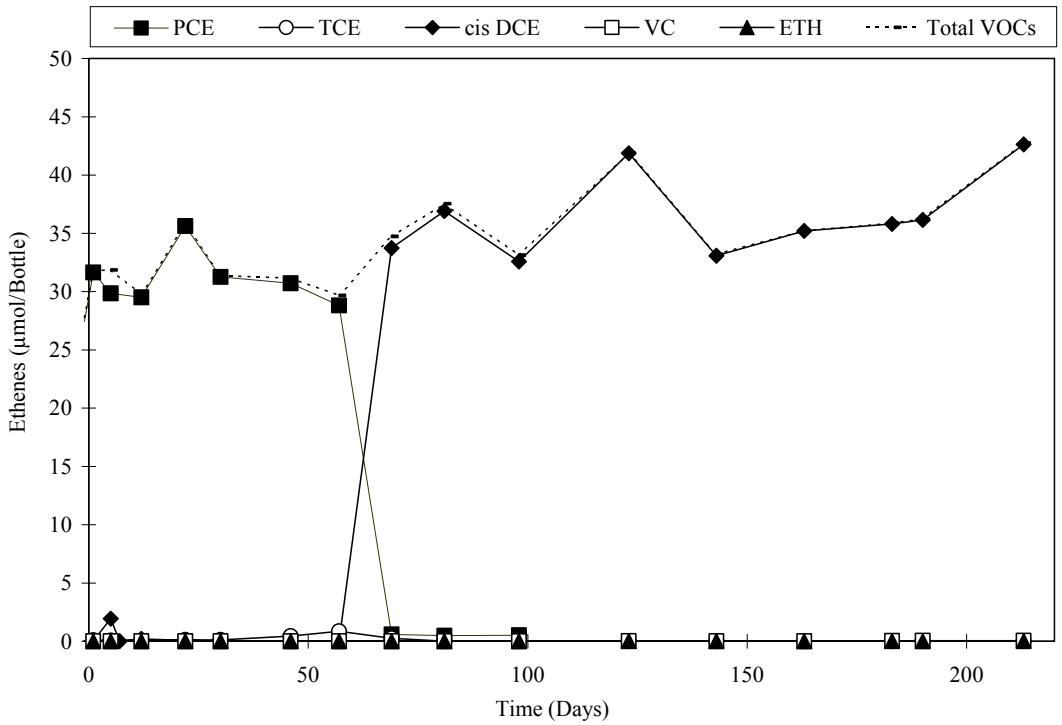


Figure 4-1. Results from Butyrate-Amended Camp Lejeune Microcosm (6-I)

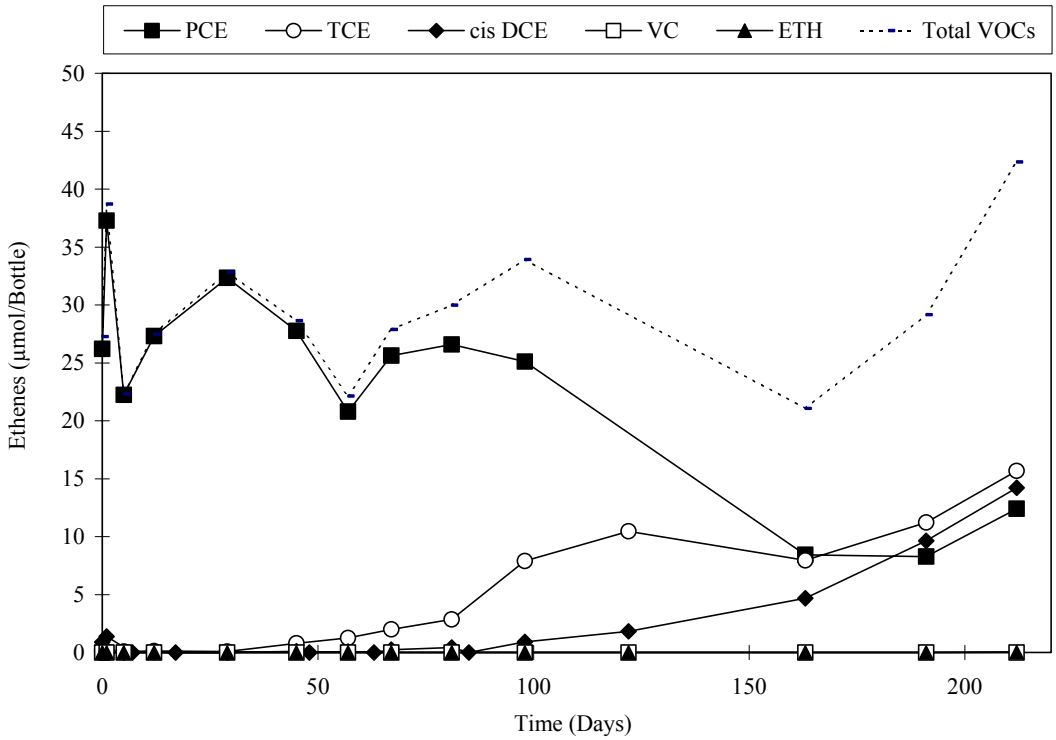


Figure 4-2. Results from Yeast Extract-Amended Camp Lejeune Microcosm (4-I)

In addition to differences in dechlorination rate, a carefully designed and monitored microcosm test can reveal information about the fate of electron donors and how efficiently they are used in the dechlorination process. For example, microcosm results from Alameda Point suggested that sulfate-reducers did not use butyrate as readily as lactate. This was an important finding, since the groundwater at Alameda Point had initial sulfate concentrations exceeding 600 mg/L. By selecting butyric acid over lactic acid for the field demonstration, it was possible to avoid substantial competition for the reducing equivalents supplied by the electron donor.

Microcosm testing provides an opportunity to examine the performance of a variety of electron donors, thereby producing useful information regarding lag periods and dechlorination rates, but that information can be corrupted by inconsistency between replicate microcosms. The unusually inconsistent results from the Fort Lewis microcosms raised some concerns that using composited core material to construct microcosms may not always overcome the heterogeneous distribution of dechlorinating activity found at a specific site. Furthermore, it may not be possible to identify a false positive microcosm result, particularly when it is assumed that if one replicate shows more complete dechlorination, then it is sufficient evidence that the pathway exists at the site. Despite these concerns, microcosm testing is a useful tool that prompted the selection of an effective electron donor at each of the field demonstration sites.

4.3 Microcosm Testing versus Field Testing

Because the draft RABITT protocol included both microcosm and field testing, it provided an opportunity to compare the results of the two testing methodologies for consistency and perhaps determine which provides the most cost effective approach to assessing a sites dechlorination potential. Surprisingly, results from field demonstrations corroborated microcosm results only half the time. Table 4-3 outlines the results.

The Cape Canaveral and Alameda Point demonstrations showed a good correlation between field and microcosm results. Both achieved the desired ethene endpoint relatively quickly. It is interesting to note that ethene was detected in Alameda Point microcosms before it was detected in the field. It is generally expected that microcosms will suffer longer lag periods due to the disruption caused to the aquifer material during aquifer sampling and microcosm construction, and the results from the Cape Canaveral demonstration would seem to support that expectation.

As it turns out, the difference between the two sites may have resulted from the differing field system designs. At Cape Canaveral, a circulation system was used so there was no continuous input of parent compound at the point of electron donor injection. This resulted in a relatively rapid progression through the daughter products to achieve ethene. In contrast, the Alameda Point system received a continuous dose of parent compound at the head of the testing zone. The continuous supply of parent compound probably caused a delay in ethene production. As the zone of dechlorinating activity expanded, parent compounds were more likely to be depleted before reaching its edges and therefore more complete dechlorination was possible.

Table 4-3. Comparison of Microcosm and Field Results at the Four Demonstration Sites

Demonstration Site/ Electron Donor	Parameter	Microcosm Results	Field Results
Cape Canaveral/ Lactic Acid (3 mM)	Most Reduced Daughter Product	Ethene	Ethene
	Time to Appear (days)	113 – 163[(a)]	63
	Molar Conversion (%)	1 – 99	66
Alameda Point/ Butyric Acid (3 mM), Yeast Extract (20 mg/L), Vitamin B_{12} (0.05 mg/L)	Most Reduced Daughter Product	Ethene	Ethene
	Time to Appear (days)	56[(a)]	119
	Molar Conversion (%)	100	49
Fort Lewis/ Butyric Acid (3 mM), Yeast Extract (20 mg/L), Vitamin B_{12} (0.05 mg/L)	Most Reduced Daughter Product	Ethene[(b)]	VC
	Time to Appear (days)	144 – 163[(a)] (*cis*-DCE – 4)	90
	Molar Conversion (%)	100 (*cis*-DCE – 100)	<1
Camp Lejeune/ Butyric Acid (3 mM), Yeast Extract (20 mg/L), Vitamin B_{12} (0.05 mg/L)	Most Reduced Daughter Product	*cis*-DCE	Ethene
	Time to Appear (days)	1 – 5[(a)]	141
	Molar Conversion (%)	100	5

(a) Approximate time to appear based on 1% molar conversion
(b) Ethene in two of three bottles and *cis*-DCE in one bottle

Microcosms more closely reflected the Cape Canaveral design, in which depletion of parent compounds occurred, thus prompting the dechlorination of daughter products. This observation suggests that microcosms may in fact suffer from slightly longer lag periods resulting from the disruption of aquifer material.

Unlike the results from the Cape Canaveral and Alameda Point demonstrations, results from the Fort Lewis and Camp Lejeune demonstrations showed a relatively poor correlation between field and microcosm studies.

At Fort Lewis, two of three butyrate-amended microcosms showed complete conversion of TCE to ethene, but the field demonstration showed only sparing production of VC. Although this appears to be a false positive result, it needs to be recognized that microcosms did not duplicate field conditions. As noted previously, it is suspected that the continuous influx of TCE into the Fort Lewis testing zone and the subsequent accumulation of *cis*-DCE may have caused the discrepancy between field and microcosm results. In this case, the data produced by the microcosms, namely that daughter products were not degraded in the presence of parents, suggested a cause for the lack of dechlorination in the field and allowed the development of a possible solution.

At Camp Lejeune, the microcosms failed to achieve full dechlorination whereas the field test saw the production of ethene. This false negative may have resulted from the drilling method used to retrieve the cores used for microcosm construction. The aquifer at Camp Lejeune consisted of heaving sands and required the use of mud-rotary drilling to maintain an open borehole. As a result, core material retrieved from the borehole may have been impacted by its contact with drilling fluid.

The comparison of microcosm and field data from the four RABITT demonstration sites revealed that each testing methodology had strengths and weakness, but that neither was clearly superior in every case.

The strength of microcosm testing is its ability to screen the performance of a variety of electron donors under controlled conditions. Results from the RABITT demonstration sites clearly show that the selection of the electron donor can significantly alter the rate of dechlorination, which in turn could dramatically impact the duration of a cleanup operation. The electron donor performance data gained from microcosm testing may ultimately provide a cost savings for those designing large or expensive full-scale EBRD treatments systems by allowing the selection of an electron donor that minimizes the required treatment time.

The weakness of microcosm testing stems primarily from the fact that they may not always accurately reflect the existing subsurface conditions. Inadvertent contamination in the laboratory or the field may cause erroneous results, and incomplete homogenization may cause discrepancies between replicate bottles. In addition, microcosm testing must overcome the heterogeneous distribution of dechlorinating activity to avoid the reporting of false negative results. Each of these obstacles can be overcome with a well-developed sampling plan and careful sampling and microcosm construction techniques.

The strength of field testing lies in its fidelity to in situ conditions and the fact that it impacts a much larger mass of subsurface material, thereby reducing potential problems caused by the heterogeneous distribution of dechlorinating activity. In addition, field testing will presumably result in some level of cleanup at the site, which could be prove to be a compelling factor at relatively small sites.

The weaknesses of field testing include its susceptibility to heterogeneous or unpredictable hydrogeology, and the difficulty involved with testing multiple electron donors. Although recommended field testing designs will dictate closely spaced wells, there is always the possibility that a subsurface anomaly will hydraulically isolate the wells and prevent the collection of useful data. In addition, electron donors would have to be tested in series, which will require considerably more time.
Although the two testing methodologies have complementary strengths and weaknesses, the information they provide was determined to be too redundant to justify the cost of performing both. As a result, the revised RABITT protocol will recommend performing only one of the two procedures, the selection of which will depend upon site-specific conditions (e.g., small plume) and biases (e.g., desire to achieve some cleanup during testing).

5.0 Revising the Draft Protocol

The experiences and data generated at the four RABITT demonstration sites prompted considerable revision of the draft RABITT protocol. Every aspect of the draft protocol, from the effectiveness of the overall technical approach to the utility of individual analyses was revisited. Only components determined to provide cost-effective information have been retained.

5.1 Technical Approach

The most substantial revision to the draft protocol involved modifying the technical approach. The original approach, which is illustrated in Figure 3-1, consists of four main components: the site assessment (steps 1-4), test preparations (steps 5-7), microcosm testing (steps 8-9), and field-testing (steps 10-12). The approach requires that each of these components be performed in sequence; however, results from the four demonstration sites make it difficult to justify the time and expense required to conduct both microcosm testing and field-testing. In addition, neither microcosm testing or field-testing proved to be superior in all situations. As a result, the revised technical approach recommends using one of the two testing methods, but not both.

Figure 5-1 shows an overview of the revised technical approach. Of the four original components only three, the site assessment, microcosm testing and field-testing, are evident in the revised approach. The missing component, test preparations, has been combined with the specific testing methodology so preparations can be tailored to the actual on-site activity.

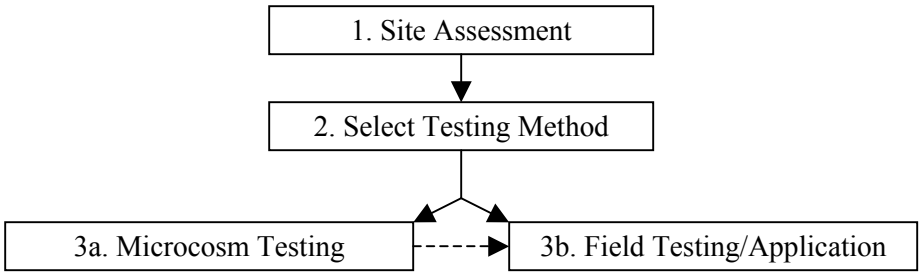


Figure 5-1. Revised Technical Approach

5.2 Individual Protocol Components

In addition to the overall change in the technical approach, each individual draft protocol component has been reviewed with respect to its performance at the four RABITT demonstration sites. The following sections will describe the layout of the revised protocol. Modifications of the draft protocol will be explained in terms of observations at the demonstration sites.

5.2.1 Preliminary Site Assessment. The site assessment described in the draft RABITT protocol suggests that users define their project goals, examine existing data, develop a conceptual model, and assess the site's overall potential using a site rating system that was specifically developed for the RABITT protocol. Each of these fundamental recommendations

was applied at the four RABITT demonstration sites and its value assessed to determine if it should be retained in the revised protocol.

5.2.1.1 Project Goals. The draft protocol recommends that users define three specific site cleanup goals before initiating any type of treatability testing: the target cleanup level, time to completion, and cost. Outlining these goals should help screen prospective technologies and may prevent the performance of an unnecessary treatability test. In most cases, regulatory and administrative constraints will dictate these goals.

The recommendation to define site cleanup goals is retained in the revised protocol; however, additional guidance has been included based on results from the four RABITT demonstration sites that should help a user determine if enhanced reductive dechlorination can achieve his/her goals. This guidance includes the degree of treatment that can be obtained and how long it may take to stimulate that treatment. For instance, it was determined that reductive dechlorination was stimulated at all four of the RABITT demonstration sites within 5 weeks, and >99% of the injected parent compound (i.e., PCE or TCE) concentration was degraded before reaching the first set of monitoring wells. A user of the protocol then could apply this information to set treatment goals that are based on empirical data.

5.2.1.2 Site History and Existing Data Review. A thorough understanding of a site's history and an evaluation of any relevant existing data is necessary to make informed decisions regarding remedial activities at any site. The information uncovered during the site history and existing data review at each demonstration site was essential to all subsequent activities. Consequently, this section remains unchanged in the revised protocol.

5.2.1.3 Development of Conceptual Model. This relatively small section in the draft protocol recommends compiling existing data into a conceptual model that provides a fundamental understanding of site characteristics. Hydrogeological, geochemical and contaminant data were compiled and viewed as a whole at the demonstration sites.

The conceptual models developed for the four RABITT demonstration sites were not always accurate. For example, existing data at the East Gate Disposal Yard suggested very high groundwater velocities that could not be corroborated later. Nonetheless, the development of a conceptual model is still recommended because it creates familiarity with measured site characteristics. As a result, this section remains unchanged in the revised protocol.

5.2.1.4 Site Potential. The draft protocol included a site-rating system designed to provide users with an a priori assessment of their site's potential for stimulating enhanced reductive dechlorination. That rating system has been removed because reductive dechlorination was stimulated at all four demonstration sites, and can probably be stimulated to some degree at most sites. As a result, the rating system has been replaced with a discussion of known problematic site characteristics (for example, the extreme sulfate concentrations found at Fallon, NV).

5.2.2 Component 2: Selecting a Testing Method – Microcosm versus Field Testing. The draft protocol did not require users to choose between microcosm and field testing since both were prescribed; however, the technical approach in the revised protocol does require users to make this decision. As a result, a new component has been added to the revised protocol that outlines the advantages and disadvantages of each approach and provides guidance for selecting the appropriate approach for specific site characteristics such as hydrogeologic complexities, remoteness and/or accessibility, and the availability of on-site infrastructure. Ultimately the user is required to make the final selection based on their site-specific conditions and balancing the risks with the costs of implementing the protocol.

5.2.3 Component 3a: Microcosm Testing. The draft RABITT protocol called for evaluating a number of electron-donor and nutrient conditions: (1) 200 mg/L yeast extract (YE); (2) lactate; (3) lactate + 20 mg/L YE; (4) lactate +0.05 mg/L B_{12}; (5) lactate + 20 mg/L YE + 0.05 mg/L B_{12}; (6) butyrate; and (7) a lactate/benzoate mixture. The project team added two additional conditions during protocol evaluation: (8) acetate; and (9) propionate.

Based on lessons learned in protocol evaluation, and mindful of the expense associated with microcosm studies, the revised protocol will recommend a more limited number of conditions for microcosm studies. Studies at the four RABITT evaluation sites did not demonstrate a sufficiently compelling reason to retain the various nutrient amendments (20 mg/L YE and/or 0.05 mg/L B_{12}) as part of the protocol. Also, acetate, propionate, or lactate/benzoate did not ever indicate sufficient promise as donors to warrant their inclusion. Consequently, the revised protocol will recommend the following electron-donor conditions for microcosm studies: (1) 200 mg/L YE; (2) 3mM lactate; (3) 3 mM butyrate. These, of course, would be in addition to abiotic (autoclaved-unfed) and biotic (unfed) controls. These changes reduce the number of microcosm bottle-types from 10 (in the draft protocol) to 5 (in the revised protocol).

YE represents a "complex donor," and thus is advisable to include. Lactate is a commonly used donor (e.g., it is the active ingredient of at least one commercially available slow-release donor preparation), and one that generates a relatively high H_2 level. Butyrate worked well in microcosm studies at all four of the RABITT test sites and represents a donor that generates a relatively low H_2 level. Also, butyrate is not as readily used by sulfate-reducers as is lactate.

The draft protocol recommended conducting microcosm studies at ambient laboratory temperature. The revised protocol will recommend employing an incubation temperature that matches in situ subsurface conditions. Also, the draft protocol advised monitoring of headspace H_2, but this is no longer considered worthwhile. Despite the importance of H_2 as a donor, its measurement is not trivial and the level measurements indicated only obvious conclusions (i.e., when donor was present, H_2 was high; when donor became depleted, H_2 was low). Hydrogen levels were not found to be useful in interpretation of microcosm results.

The revised protocol will recommend that initial levels of sulfate be measured in representative microcosms. If significant (i.e., greater than 100 mg/L) acid-volatile sulfide should be measured at the end of microcosm studies in representative microcosms of each type, to allow estimation

of the extent of sulfate-reduction in microcosms. Sulfide levels in donor-fed bottles can be compared to levels in abiotic and biotic controls. This will allow a determination of the degree to which donor equivalents were channeled to sulfate-reduction, versus dechlorination and methanogenesis. Procedures will be presented in the revised protocol.

5.2.4 Component 3b: Field Testing. Users of the revised protocol who pursue the field-testing option are provided guidance on selecting a testing location, making administrative preparations, designing a test system, selecting on electron donor, installing a test system, conducting tracer and treatability testing, and examining the results.

5.2.4.1 Selecting a Testing Location. The draft protocol presents four technical criteria to use when searching for a field-testing location within a plume. These criteria, which were used to select the testing locations for the demonstration sites, are listed as follows.

1. Contaminant concentrations will be at least two orders of magnitude greater than the contaminant's detection limit, but below levels indicative of DNAPL contamination (approximately 1% of the contaminant's solubility limit). The presence of DNAPL pockets likely would affect observable reductions in parent compound and produce misleading data.

2. The hydraulic conductivity in the proposed treatment zone will be $>10^{-4}$ cm/sec.

3. Groundwater velocities between 0.2 ft/day and 1.0 ft/day will be preferred, as will areas with relatively constant and predictable groundwater flow.

4. Relatively homogeneous areas or zones with well-defined stratigraphy will be preferred.

Experiences at the four RABITT demonstration sites show that the contaminant concentration and groundwater velocity ranges specified in the draft protocol may be unnecessarily restrictive, but that low hydraulic conductivity and heterogeneous zones do cause problems. Changes made to the site selection criteria in the revised protocol are discussed in the following sections.

Initial Contaminant Concentration. Although the initial contaminant concentration within the testing zone is very important for test systems that circulate groundwater (such as the one used at Cape Canaveral), it is not particularly important for the extract-inject type systems used at the other three demonstration sites. When an extract-inject system is installed, the concentration of parent compound in the supply well is considerably more important than the concentration in the testing zone, as the water in the testing zone will presumably be displaced by injected groundwater. In these cases, the extraction well would ideally supply a consistently high (>1 ppm) concentration of parent compound. Of course the concentration of contaminant in the testing zone is not irrelevant. Regulators will certainly be hesitant to allow the injection of highly contaminated groundwater into an area with little or no contamination. In addition, the

dechlorination process may occur more rapidly in an area that has been previously exposed to chloroethenes.

The upper concentration limit specified in the selection criteria also may be unnecessarily low. The demonstration at the EGDY showed that the injection of TCE concentrations as high as 169 ppm or ~17% of its estimated solubility did not adversely affect dechlorination. This observation suggests that enhanced biological reductive dechlorination could be used effectively in source zones.

Hydraulic Conductivity. Each of the four RABITT demonstration sites had existing data suggesting that the average hydraulic conductivity for each site was $>10^{-4}$ cm/sec. Heterogeneities at Site 4 and the EGDY resulted in the installation of wells in layers with a lower conductivity. These wells could not be used for the demonstration because they did not produce sufficient groundwater for required sampling activities. The specific conductivity of demonstration wells was not routinely determined; as a result, there is no basis to change the recommended hydraulic conductivity found in the draft protocol. Despite the difficulties encountered, field testing was completed successfully at each of the demonstration sites, indicating that the recommended average hydraulic conductivity is reasonable.

Groundwater Velocity. The draft protocol suggests installing a field testing system in a location with a background groundwater velocity between 0.2 ft/day and 1.0 ft/day. This range was selected to achieve a HRT of approximately 30 days in a testing zone of 30 feet or less; however; it assumes that natural groundwater movement will dictate the HRT. In fact, the natural groundwater velocity is very difficult to predict with much certainty over such short distances, and the gradient caused by the injected groundwater is generally strong enough to overwhelm background conditions. As a result, the revised protocol describes a preference for areas with weak natural gradients and low groundwater velocities.

Heterogeneity. Heterogeneities in the subsurface geology encountered at Site 4 and at the EGDY required the installation of several additional wells to find testing areas with appropriate contaminant concentrations and hydraulic conductivity.

At Site 4, the demonstration system was inadvertently installed into a silt-clay lens that was not evident in existing site characterization records. The hydraulic conductivity in the lens made it impossible to inject groundwater or collect groundwater samples, so an additional set of wells had to be installed in a deeper, more conductive interval.

Similar problems were encountered at the EGDY demonstration site, where the geology included high conductivity layers consisting of cobbles and sands, low conductivity silt layers, and completely impermeable clay lenses. The complex geology created complex groundwater flow paths. The complexity of the geology at the EGDY is best illustrated by monitoring well MW-8. MW-8 was located directly between and less than two feet from monitoring wells MW-7 and MW-9, but in contrast to its nearby neighbors, it did not produce sufficient water for groundwater sampling.

Although it was eventually possible to carryout demonstrations at both of these locations, the experiences did corroborate initial concerns that heterogeneous sites can be more challenging and consequently more costly. As a result, the recommendation to conduct field testing in a well defined or relatively homogeneous area was retained in the revised protocol.

5.2.4.2 Administrative Preparations. This section of the revised protocol simply and briefly describes the need to prepare written test plans, obtain regulatory approval, apply for all necessary permits and get all necessary facility clearances required to initiate field work. The section was transplanted from the Test Preparations section of the draft protocol, but otherwise remains unchanged in the revised protocol.

5.2.4.3 System Design. The standardized test system design described in the draft protocol was used effectively at three of the four RABITT demonstration sites; nonetheless, the system has been abandoned because it required the installation and monitoring of a relatively high number of wells, which made it unnecessarily expensive to operate. In addition, the system lacked the flexibility required to satisfy specific regulatory issues that were encountered.

Although the simplicity of a single standardized field testing design is appealing, it may be impossible to design a system that adequately addresses the diverse technical and regulatory issues that could be encountered. For example, legislation in the State of Florida prohibits the use of extract-inject systems like the one described in the draft protocol. It seems unwarranted to restrict the use of this type of system based on legislation in one state, particularly because that design proved to work so effectively at other demonstration sites. As a result, the revised protocol does not specify a standardized testing design, but rather provides users with a flexible set of suggestions that will allow protocol users to design a much simpler, less-costly system that addresses their particular needs.

The goal of the field test system is to create a microbially active low redox potential treatment zone through which chloroethene-contaminated groundwater must pass. In essence, the treatment zone amounts to an in situ bioreactor. A variety of simplified test systems can be used to achieve this objective, and most will require the use of only three or four wells. In general, these systems consist of one groundwater extraction location, one groundwater injection location, one background monitoring well and one treatment zone monitoring well. The revised protocol describes three such systems and makes design recommendations based on experiences at the four RABITT demonstration sites.

The first field testing system described in the revised protocol is the extract-inject system shown in Figure 5-2. This system operates much like the system described in the draft protocol, but with considerably less redundancy. Groundwater is extracted from an extraction well, amended with electron donor, and injected into an injection well. A single monitoring well located close to the injection well is used to monitor contaminant changes in the injected groundwater. A second monitoring well, identified as the background well, located outside the treatment zone is used to verify that changes in chloroethene concentrations are the result of treatment. This type of system should work effectively at most sites.

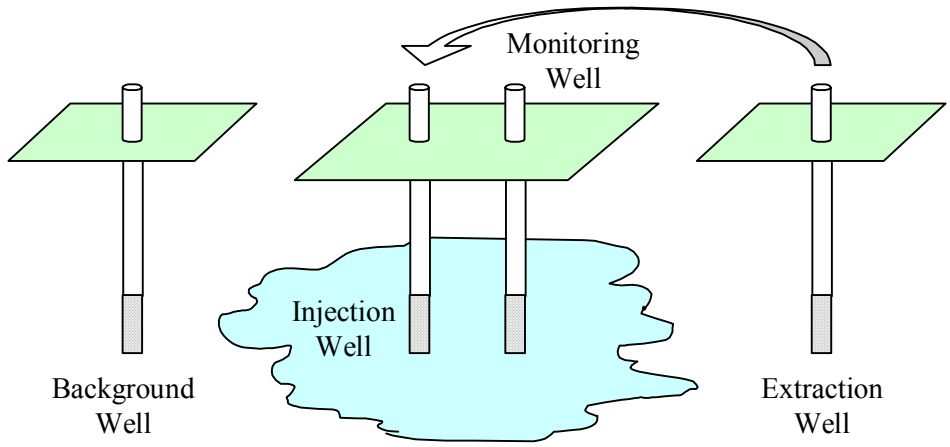


Figure 5-2. Schematic Diagram of Extract-Inject Field Testing System

The limited number of test zone-monitoring wells proposed for this system was prompted by results from the four RABITT demonstration sites. Data revealed that individual monitoring wells located 10 ft or less from the point of electron donor injection were consistently within the active treatment zone and independently demonstrated the sequential reduction of chloroethenes. As a result, all designs suggested in the revised protocol call for the use of only one monitoring well within the treatment zone as long as that well is within 10 ft of the injection location.

A subtle three-well variation of this design also is described in the revised protocol and illustrated in Figure 5-3. This design circulates groundwater between two closely spaced wells. Extracted groundwater is monitored for changes in chloroethene concentrations, amended with electron donor and injected back into the adjacent well. This system was not used at any of the four RABITT demonstration sites, so field data cannot be used to confirm its reliability or effectiveness. It may, however, be a cost-effective option at sites with high drilling costs or small zones of contamination.

The third field test system described in the revised protocol is intended to address regulatory obstacles to the extraction and subsequent injection of contaminated groundwater. The system utilizes one or two dual screen circulation wells to add electron donor to the subsurface without bringing contaminated groundwater to the surface (see Figure 5-4). This type of system was used at the Facility 1381 demonstration site. At that site, two dual screen circulation wells were used to create a subsurface circulation cell (see Figure 3-5). The system effectively mixed electron donor with groundwater in situ to create a biologically active treatment zone that impacted all wells within the 34-ft by 10-ft testing area. The total extent of the system's impact was never determined, but presumably extended beyond the testing area. Based on the results from the Facility 1381 demonstration, this type of system design appears to be a promising alternative for sites with regulatory issues.

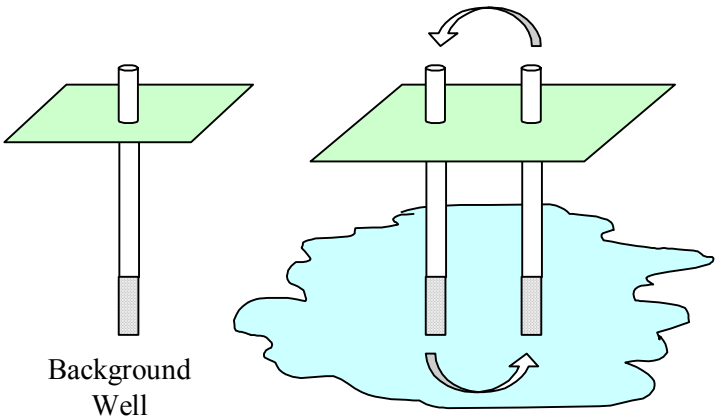


Figure 5-3. Schematic Diagram of an Aboveground Circulation Field Testing System

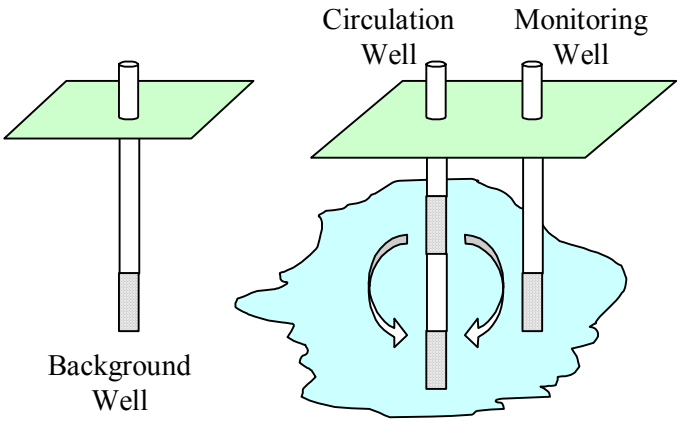


Figure 5-4. Schematic Diagram of an In Situ Circulation Field Testing System

The single circulation well design alternative was not tested at any of the four RABITT demonstration sites; however, it is reasonable to believe that such a system would adequately mix and distribute electron donor in situ at sites with appropriate hydrogeology. The anisotropy at the site is key, communication must occur between the upper and lower screens, but without any short-circuiting that would reduce the radius of influence of the well. Any uncertainty regarding the radius of influence of the circulation well can be countered by locating the system monitoring well very near the circulation well, perhaps within 5 ft, depending on site-specific factors such as the circulation flowrate.

In addition to the suggested system designs described above, the revised protocol also recommends the use of existing wells to reduce installation costs. It is particularly sensible to

use an existing well as an extraction well or background monitoring well since neither of these well types is affected by treatability testing. Furthermore, less emphasis is placed on the determination of the HRT. Instead, the revised protocol specifies that changes in the injection flowrate, including a pulsed injection strategy, can be used to observe treatment over longer periods of time.

5.2.4.4 Electron Donor Selection. The draft RABITT protocol used microcosm testing to screen the performance of potential electron donors. The donor ultimately used in the field was selected based primarily on its dechlorination endpoint, but the reaction rate and efficiency also were considered. Results from the four RABITT demonstration sites indicate that butyrate was generally the most effective electron donor tested, and that lactate and yeast extract also were reasonably successful in achieving complete dechlorination (See Table 4-2). The consistently strong performance of these donors and the generally similar dechlorination endpoints of all donors indicated that electron donor screening at every site is not necessary. As a consequence, the revised RABITT protocol has removed microcosm testing as a prerequisite to field testing.

Based on the strong performance of butyric acid supplemented with yeast extract in microcosm and field tests, the revised RABITT protocol suggests its use to protocol users that do not have a strong inclination towards another electron donor. Because butyric acid does have some handling concerns (namely its stench), the use of lactic acid, yeast extract, or an alternative complex donor such as molasses will be discussed; however, protocol users will be urged to use only those donors that consistently performed well during previous testing. Once the ethene endpoint has been achieved, protocol users anxious to use less-expensive donors (e.g., molasses) could consider a donor substitution on a trial basis. Any donor that meets performance goals and cost and handling requirements then could be considered for a larger-scale remedial action.

5.2.4.5 Field System Installation. The field system installation section in the revised protocol contains much of the same material found in the draft protocol. Some relatively minor changes have been made based on experiences at the four RABITT demonstration sites, but the overall layout remains the same. Specific changes that have been made are listed below.

1. Always take a continuous core to make certain the system is not being installed into a previously undiscovered geological heterogeneity.

2. Avoid the use of drilling fluids that can clog the formation and affect groundwater movement.

3. Only one storage container will be required on site, as electron donor and tracer can be added from the same stock solution. In fact, there are advantages doing it this way.

4. Prepared stock solutions do not need to be stripped of oxygen nor do they need to be stored in vessels with an anaerobic headspace.

5.2.4.6 Tracer Testing. Tracer testing is an essential part of the field testing process. The revised protocol builds on information presented in the draft protocol but includes some significant modification and some additional information regarding bromide tracer testing that was learned at the demonstration sites.

The draft protocol recommends the simultaneous injection of tracer and electron donor during "Phase I" injection. The goal of this approach was to save time by exhausting the natural supply of electron acceptors in the testing zone during tracer testing, but results from the demonstration sites showed this approach was unwarranted. Reductive dechlorination was stimulated quickly at the demonstration sites, typically within six weeks, so concerns that dechlorination may not be observed within the six-month testing window were unfounded so the need to save time was deemed unnecessary. In addition, subsurface geochemical changes produced by the electron donor caused interference with the measurement of the bromide tracer selected for all four RABITT demonstration sites. As a result, the simultaneous injection approach described in the draft protocol has been discarded in the revised protocol, which advises users to perform tracer testing independent of electron donor injection.

5.2.4.7 Treatability Testing. The field testing procedures described in the revised protocol bear little resemblance to those presented in the draft protocol. Testing has been scaled back both in terms of the frequency of sampling and the number of analytes examined.

The RABITT demonstrations at Cape Canaveral, Alameda Point, and Fort Lewis were sampled every two weeks, as prescribed in the draft protocol. In a slight deviation from the draft protocol, the sampling at Camp Lejeune was reduced to once every three weeks. In all cases, far more data were collected than was necessary to determine if reductive dechlorination had been stimulated. This was determined by re-examining the data from each of the four sites after removing every other data set. The same conclusions were reached easily with only half the data. As a result, the recommended sampling frequency was reduced to once a month. The data suggest that less frequent sampling may prove to be sufficient, perhaps once every six to eight weeks, but the relatively small amount of money saved (~$4K) may not justify the increased difficulty of assessing system performance with only four data points, and renders the entire test susceptible to erroneous data caused by sampling or analytical problems.

In addition to a reduction in the frequency of sampling, the number of analyses preformed on the samples has also been reduced. The lengthy list of analyses required in the draft protocol has been reduced to the handful of analyses that provided useful diagnostic information at the four RABITT demonstration sites. Table 5-1 shows the analyses critical to the test and those that are recommended due to their diagnostic value.

5.2.4.8 Data Analysis. The simplified nature of the field treatability test described in the revised protocol requires relatively little expertise in the area of bioremediation to analyze the test results. Protocol users are directed to determine the endpoint of the dechlorination process; presumably, the production of ethene will be the desired endpoint for most users. The relative proportion of parent compound to ethene should be calculated on a molar basis. A 10% conversion of parent compound to ethene suggests that the process works well at that particular site.

Table 5-1. Analyses Retained in the Revised Protocol

Critical Analyses	Recommended Analyses
VOCs (laboratory) - PCE, TCE, *cis*-DCE, VC Dissolved gases (laboratory) - Ethene, ethane, methane Tracer (field) - bromide	Redox potential (field) pH (field) Sulfate (field or laboratory) Organic acids (laboratory) - organic acid analytes will depend upon the selected electron donor

Another factor discussed in the revised protocol that may determine the suitability of enhanced reductive dechloration at a site is the production of methane gas. The onset of methanogenesis indicates that subsurface conditions have become highly reduced and that electron acceptors in the testing zone are nearing exhaustion; however, the production of methane requires the consumption of electron donor that could otherwise be used in the dechlorination process. At sites where relatively high levels of electron donor are added, the potential exists for methane to accumulate at potentially hazardous levels. It may be possible to balance methane production and dechlorination activity by adjusting the electron donor dose. Methane production was observed at each of the four demonstration sites, but only at the Camp Lejeune demonstration were the levels high enough to cause concern.

6.0 Cost Assessment

The cost to implement the treatability test described in the revised protocol will depend upon site-specific conditions (e.g., depth of contamination) and the testing methodology selected. Nonetheless, cost estimates to perform both the microcosm testing option and the field testing option described in the revised protocol are outlined below. It was necessary to make several assumptions when estimating the costs, also as outlined below.

6.1 Microcosm Testing Option

The estimated cost to perform the microcosm testing option described in the revised protocol ranges from $77,000 to $94,000. Table 6-1 shows the cost breakdown. It is assumed that five conditions will be tested using triplicate microcosms. The conditions include a killed control, a live control, and three independent electron donors. It has also been assumed that aquifer material and groundwater will be collected from approximately 30 ft bgs. No travel costs have been included.

Table 6-1. Estimated Cost of Microcosm Testing Option

Activity	Unit Cost	Quantity	Cost
Component 1 – Site Assessment	$5-10K	1	**$5-10K**
Component 2 – Select Testing Methodology	$1-3K	1	**$1-3K**
Component 3a – Microcosm Testing			**$61-67K**
Select testing location	$2-4K	1	$2-4K
Collect aquifer core material and groundwater	$8-$10K	1	$8-10K
Labor	$2-4K	1	$2-4K
Drilling costs			
Mobilization	$0.5K	1	$0.5K
Boreholes (2 holes drilled to 30 ft)	$25/lf	60 lf	$1.5K
Waste disposal	$2K	1	$2K
Misc. (decontamination, etc.)	$1K	1	$1K
Consumables and supplies	$1K	1	$1K
Conduct testing	$48.3K	1	$48.3K
Operation and maintenance	$550/bottle	15 bottles	$8.3K
Analytical services			
VOCs	$100/sample	200 samples	$20K
Organic acids	$100/sample	200 samples	$20K
Data analysis	$3-5K	1	$3-5K
Reporting	$10-14K	1	$10-14K
Total Cost for Microcosm Testing Option			**$77-94K**

6.2 Field Testing Option

The estimated cost to complete the field testing option described in the revised protocol ranges from $84,000-$111,000. This estimate is based on the four well extract-inject system shown in Figure 5-2, and assumes that three 1-inch PVC monitoring wells will be installed to a depth of 30 feet bgs. It is assumed an existing well will be used to collect the required background samples, and that all wells may be left intact following the demonstration. No decommission costs have been included. Table 6-2 shows the cost breakdown.

Table 6-2. Estimated Cost of Field Testing Option

Activity	Unit Cost	Units	Cost
Component 1 – Site Assessment	$5-10K	1	**$5-10K**
Component 2 – Select Testing Methodology	$1-3K	1	**$1-3K**
Component 3b – Field Testing			**$68-84K**
Select testing location	$2-4K	1	$2-4K
Prepare work plan/design system	$12-17K	1	$12-17K
Install system			$18-21K
Labor	$3-5K	1	$3-5K
Drilling costs			
Mobilization	$0.5K	1	$0.5K
Three system wells (30-ft deep)	$45/lf	90 lf	$4K
Two 1-inch PVC MWs			
One 2-inch PVC extraction well			
Waste disposal	$2K	1	$2K
Misc. (decontamination, etc.)	$1K	1	$1K
Materials	$2K	1	$2K
Equipment (pumps, tanks, etc.)	$6K	1	$6K
Conduct testing			$33-37K
Labor	$10-14K	1	$10-14K
Analytical services			
VOCs	$120/sample	32 samples	$3.8K
Organic acids	$125/sample	32 samples	$4K
Gases	$100/sample	32 samples	$3.2K
Consumables and supplies	$10K	1	$10K
Field office rental	$400/month	6 months	$2.4K
Data analysis	$3-5K	1	$3-5K
Reporting	$10-14K	1	$10-14K
Total Cost for Field Testing Option			**$84-111K**

The selection of an alternative system design (for example, the belowground circulation system shown in Figure 5-4) should not seriously impact the overall cost of the field test. The fundamental cost difference between the three proposed system designs is the number of wells installed. The amount spent on materials, equipment, and monitoring should not be significantly affected. To estimate the costs in Table 6-2, it was assumed that three wells would be installed

to a depth of 30 feet. If only two wells are installed, as would be the case in the other two designs, the difference in cost would be approximately $1,350 less. It is assumed that a background well will always be available at a site, presumably one of the wells that initially demonstrated there to be a chlorinated solvent problem.

6.3 Cost Drivers and Potential Cost Impacts

The costs provided for each testing option (i.e., microcosm or field test) were calculated under assumptions that were developed to describe a "typical" site. As mentioned above, the actual costs for both microcosm testing and field testing will depend on site-specific requirements/ logistics, so a cost comparison between the two approaches should be made during the process of selecting a test methodology. The variables that affect each approach and their potential impact are summarized in the following sections.

6.3.1 Cost Variables for Microcosm Testing. The single variable that could significantly impact the cost of conducting the microcosm tests is the depth of the contamination, which has a direct effect on the costs associated with collecting the aquifer core material, specifically the drilling, waste disposal, and labor costs. The costs presented in Section 6.1 assume a depth of 30 feet. Collection of cores from shallower sites would be somewhat less expensive. For example, the total drilling costs at $25/foot would be decreased by a total of $1,100. The cost savings associated with waste disposal would depend on the agreement with the waste hauler but would be expected to be on the order of 20% or approximately $400. Because less time is required at the shallower site, the labor costs could be expected to decrease by approximately 15%, which is a savings of between $300 and $600. The remaining microcosm cost variables would not be significantly impacted by the difference in contaminant depth. Adding up the cost impacts of reducing the depth by 20 feet results in a range of total costs for implementing the microcosm approach between $78,800 and $96,199.

A more dramatic effect is realized in a situation where the contamination is at 200 feet. Again, the impacted cost variables would be the same but the difference in magnitude would be significant. The costs associated with drilling the two boreholes would increase to $10,000. The impact to the cost for waste disposal again is dependent on disposal requirements, the volume of soil that must be handled as waste, and the agreement with the waste hauler, and could run as high as $10,000, which is an $8,000 increase. Finally, the labor cost associated with drilling two 200-foot boreholes would increase by approximately $1,000. This results in a cost differential of +$17,500, resulting in a range of costs between $94,500 and $111,500.

Another area where cost savings may be realized is the cost for analysis. Laboratories that have automated in-house analytical capabilities should be able to provide those services for lower costs than an outside analytical laboratory. Depending on the costing practices of the lab, a savings of as much as $20,000 could be expected.

6.3.2 Cost Variables for Field Testing. Similar to the microcosm approach, the most significant cost variable for the field approach is the depth to the contamination. The impact that depth has on the costs, however, is much more pronounced. Not only is the system installation

cost impacted, but the cost of conducting the test is impacted as well. The potential magnitude of the impact is illustrated using the same two scenarios presented in Section 6.3.1. First, for a 10-foot-deep site, the drilling costs for the three system wells would decrease to $1,350, a $2,650 cost savings, and waste disposal costs would decrease by approximately 20%, resulting in a savings of $400. Labor costs associated with system installation could be reduced by 15%, resulting in a labor cost range of $2,550 to $4,250, but labor costs associated with the operation and maintenance of the system would not be affected significantly. Based on these cost impacts, the cost of implementing RABITT at a 10-foot-deep site would range from $80,500 to $107,200.

Implementing RABITT at a 200-foot-deep site would result in a more dramatic cost impact. The cost of labor for system installation would double to between $6,000 and $10,000. The costs of the three wells and waste disposal would increase almost seven times to $26,700 and $13,500, respectively. The labor costs for conducting the test would increase approximately 30%, primarily because of the need for bailing the wells, to between $13,000 and $18,200. Adding up all of these cost impacts shows that the cost of implementing RABITT at a 200-foot-deep site likely would range between $124,200 to $154,000.

6.4 Cost Comparison

The RABITT protocol is unique in that it is a screening technology rather than a remediation technology; therefore, it is inappropriate to compare its associated costs with those of conventional chlorinated solvent remediation technologies.

7.0 Regulatory Issues

The main regulatory issue associated with the implementation of a RABITT treatability test is the injection of contaminated groundwater. Regulations, and in some cases legislation, have been created to protect aquifers from the introduction of hazardous substances. Although the benefits of these regulations are numerous, they have had the unintended consequence of complicating the use of in situ remedial systems that require the extraction and subsequent injection of contaminated groundwater. As a result, individuals or organizations considering the use of in situ remedial technologies must sometimes navigate a complex web of federal, state and local regulations prior to receiving regulatory approval for this type a system.

Despite these regulatory obstacles, approval was granted to allow injection of contaminated groundwater amended with the electron donor and nutrients for the RABITT demonstrations at Alameda Point, California; Fort Lewis, Washington; and Camp Lejeune, North Carolina. Approval was typically granted on the grounds that the addition of the electron donor and nutrients amounted to "substantial treatment" of the groundwater, as required in the regulations. Only in the State of Florida, where injection is prohibited by statute, was it impossible to install an extract-inject system.

In December of 1998 the Interstate Technology Regulatory Cooperation (ITRC) published a document entitled, "Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater." The document provides a useful discussion of regulatory issues associated with in situ bioremediation and outlines regulations in 24 states on a state-by-state basis. The document can be accessed on-line at http://www.itrcweb.org.

8.0 Technology Implementation

8.1 DoD Need

A 1997 report estimated that DoD owned over 3,000 sites in the United States contaminated with chlorinated hydrocarbons, and that TCE is one of the two most common contaminants (U.S. EPA, 1997). In 2001, the Navy alone was reported to have 867 chlorinated solvent sites, with an estimated cleanup cost of $1.83 billion (SERDP/ESTCP, 2001). Many sites are fairly old, but new spills continually add to the problem. Almost 500 new chlorinated hydrocarbon spills at DoD sites were reported to the EPA between 1987 and 2000 (U.S. EPA, 2001). The Department of Defense goals for Installation Remediation Program (IRP) sites like these is to have all of the 27,000 IRP locations (high, medium, and low-risk) cleaned up, or in the process of being cleaned up, by 2014 (DERP, 2001). Technologies that target recalcitrant contaminants, such as TCE, can assist in meeting these cleanup goals.

8.2 Transition

Technology transfer can take place through various mechanisms including distribution of the final RABITT protocol, presentation at technical conferences and symposia, and training workshops conducted at DoD-sponsored forums. The final protocol produced as a deliverable document for this project is the primary method of technology transfer and will serve as the basis for the other transfer mechanisms. The protocol can be distributed to selected organizations and individuals and made available online to reach a wider audience. Additional forums for technology transfer include ITRC training courses, Remediation Innovative Technology Seminars (RITS), the SERDP/ESTCP technical symposium and workshop, and other environmental remediation conferences. A brief description of each of these forums and their applicability to the RABITT project follows.

The Interstate Technology Regulatory Council (ITRC) was created to promote the use of innovative technologies for environmental remediation and treatment of hazardous wastes and to help states maximize resources in the process. The ITRC consists of more than 35 states, multiple federal partners, industry participants, and other stakeholders that work together to advance and achieve regulatory compliance of new technologies. Both classroom and Internet-based training courses are developed by ITRC technical work teams, and they are already conducting training related to chlorinated solvents. A training program on the use of the RABITT protocol could help raise awareness of the document as well as ensure that it is used effectively. The provision of training courses through the ITRC will result in even further technology transfer due to the large network of representatives from the environmental community.

RITS seminars are sponsored by the Naval Facilities Engineering Command (NAVFAC) with the purpose of providing guidance and training on new and innovative technologies. Technology transfer provided by the program is intended to facilitate faster and more effective site remediation at lower costs. The seminar is offered twice per year at each of the Navy field

divisions; each seminar consists of new presentations that are selected on the basis of current challenges to the Navy and DoD environmental cleanup programs and policies.

Another potential forum for technology transfer is the annual SERDP/ESTCP technical symposium and workshop. SERDP supports environmental research and development for the DoD. The Cleanup Thrust Area of SERDP seeks to support research for more effective remediation of soil, sediment, groundwater, and surface water. ESTCP demonstrates and validates innovative technologies that address urgent needs of the DoD. The SERDP/ESTCP technical symposium and workshop would be an appropriate technology transfer mechanism because of its technical merit and because it attracts attendees interested in the advancement and utilization of innovative technologies.

Additional opportunities for training programs include various environmental remediation conferences. For example, Battelle sponsors conferences in alternating years entitled *In Situ and On-Site Bioremediation Symposium and International Conference on the Remediation of Chlorinated and Recalcitrant Compounds*. The conferences are widely attended by representatives from the regulatory community, DoD, and the private sector. Participants include a large international contingency, thereby resulting in more widespread technology transfer. Both conferences provide opportunities for platform presentations as well as participatory workshops.

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Appendix B: Data Archive and Demonstration Plans