FINAL REPORT

Biological Oxidation of DCE through Manganese Addition

ESTCP Project ER-0625

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M. Tony Lieberman
Solutions-IES, Inc.

Robert C. Borden
Solutions-IES, Inc.

Environmental Security Technology Certification Program

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TABLE OF CONTENTS

List of Abbreviations
Acknowledgments
Executive Summary

1.0 INTRODUCTION 1
1.1 Background – Chemistry and Microbiology of Manganese Reduction 1
1.2 Technology Description 2
1.3 Goals and Objectives 3
1.4 Regulatory Drivers 3
1.5 Stakeholder/End-User Issues 4
1.6 Chlorinated Ethene Biodegradation 5
2.0 DEMONSTRATION DESIGN AND METHODS 6
2.1 Site Screening and Selection 6
2.1.1 Site Screening Summary 8
2.2 Biogeochemical Characterization 11
2.3 Laboratory Studies 12
2.3.1 Matrix Collection 12
2.3.2 Microcosm Studies 13
2.3.3 Enrichment Studies 14
3.0 FIELD AND LABORATORY RESULTS–HILL AIR FORCE BASE–OPERATIONAL UNIT-1 15
3.1 Background Information 15
3.1.1 Location and Layout 15
3.1.2 Site Contaminants 17
3.1.3 Site Hydrogeology and Plume Geometry 20
3.2 Biogeochemical Characterization 22
3.3 Microcosm Experimental Design and Results 24
3.4 Summary of Results 25
4.0 FIELD AND LABORATORY RESULTS – Navy Base Kitsap (former Naval Undersea Warfare Center), Division Keyport, Keyport, WA 27
4.1 Background Information 27
4.1.1 Location and Layout 27
4.1.2 Site Contaminants 29
4.1.3 Site Hydrogeology and Plume Geometry 32
4.2 Biogeochemical Characterization 35
4.3 Microcosm Experimental Design and Results 38
4.4 Summary of Results 39
5.0 FIELD AND LABORATORY RESULTS MYRTLE BEACH AIR FORCE BASE – BUILDING 575 – SOLID WASTE MANAGEMENT UNIT 256 41
5.1 Background information 41
5.1.1 Location and Layout 41
5.1.2 Site Contaminants 42
5.1.3 Site Hydrogeology and Plume Geometry 44
5.1.4 Site Remediation Efforts 45

5.2 Biogeochemical Characterization 46
5.3 Microcosm Experimental Design and Results 49
5.4 Summary of Results 50
6.0 FIELD AND LABORATORY RESULTS – LAUNCH COMPLEX 34 – CAPE CANAVERAL AIR FORCE STATION, FLORIDA 52
6.1 Background information 52
6.1.1 Location and Layout 53
6.1.2 Site Contaminants 53
6.1.3 Site Hydrogeology and Plume Geometry 57
6.2 Biogeochemical Characterization 59
6.3 Microcosm Results 61
6.4 Summary of Results 66
7.0 ALAMAC AMERICAN KNITS, LLC 67
7.1 Background Information 67
7.1.1 Location and Layout 67
7.1.2 Site Contaminants 69
7.1.3 Site Hydrogeology and Plume Geometry 72
7.2 Biogeochemical Characterization 74
7.3 Enrichment Study Design and Results 74
7.4 Summary of Results 76
8.0 CONCLUSIONS 77
9.0 REFERENCES 80
10.0 POINTS OF CONTACT 83

TABLES

Table 2-1 Characteristics of Selected Sites 10
Table 3-1 Historical Representative Groundwater Conditions, OU-1 Study Area, Hill AFB, UT 19
Table 3-2 Well Construction Information, OU-1 Study Area, Hill AFB, UT 20
Table 3-3 Summary of Site Characterization Data, OU-1, Hill AFB, UT 23
Table 3-4 Summary of Microcosm Treatments on Matrices from OU-1, Hill AFB, UT 24
Table 4-1 Historical Representative Groundwater Conditions,OU-1, Navy Base Kitsap, WA 31
Table 4-2 Well Construction Information, OU-1, Navy Base Kitsap, WA 32
Table 4-3 Summary of Site Characterization Data, OU-1, Navy Base Kitsap, WA 37
Table 4-4 Summary of Microcosm Treatments on Matrices from Navy Base Kitsap, WA 38
Table 5-1 Historical Groundwater Conditions in Building 575 Groundwater Plume as of December 2005, Myrtle Beach AFB, SC 43
Table 5-2 Well Construction Information, Building 575 Area, Myrtle Beach AFB, SC
Table 5-3 Summary of Site Characterization Data, Building 575 Area, ... 44
Myrtle Beach AFB, SC 47
Table 5-4 Summary of Microcosm Treatments on Matrices from Myrtle Beach AFB, SC 49

Table 6-1 Historical Representative Groundwater Conditions, Launch Complex 34 Groundwater Plume as of Nov. 2004 and Dec. 2006,Cape Canaveral AFS, FL ...54
Table 6-2 Well Construction Information near Engineering Support Building, Launch Complex 34, Cape Canaveral AFS, FL ... 58
Table 6-3 Summary of Site Characterization Data, Cape Canaveral AFS, April 30-May 1, 2007 ... 61
Table 6-4 Summary of Microcosm Treatments on Launch Complex 34 Matrices from IW-51I/ESB-SB-2 ... 63
Table 6-5 Summary of Enrichment Treatments on Launch Complex 34 Matrices from ESB-SB-1 ... 64
Table 7-1 Historical Groundwater Conditions, Alamac American Knits, LLC, Groundwater Plume as of October 2005, Lumberton, NC ... 70
Table 7-2 Well Construction Information, Alamac American Knits, Lumberton, NC ... 72
Table 7-3 Summary of Enrichment Treatments on Matrices from Alamac American Knits, Lumberton, NC ... 74

FIGURES

Figure 1-1 Chlorinated Ethene Distribution at Plattsburgh AFB ... 2
Figure 1-2 Abiotic and Biological Transformation Pathways for Selected Chlorinated Solvents ... 5
Figure 3-1 Operable Unit 1 Study Area and Site Features, Hill AFB, UT ... 16
Figure 3-2 Operable Unit Study Area Monitor Well Locations, Hill AFB, UT ... 17
Figure 3-3 March 1997 Potentiometric Surface and Groundwater Flow Direction at OU-1, Hill AFB, UT ... 21
Figure 3-4 Sampling Locations within OU1, Hill AFB, UT ... 22
Figure 3-5 Hill AFB Microcosm Results for *c*DCE Measurements ... 26
Figure 3-6 Hill AFB Microcosm Results for Dissolved Manganese Measurements ... 26
Figure 4-1 Former Naval Undersea Warfare Center, Operable Unit 1 Site Features ... 28
Figure 4-2 Navy Base Kitsap, Operable Unit 1 Monitor Well Locations ... 30
Figure 4-3a Water Table Elevation and Groundwater Flow Map, Unconfined Surficial Aquifer, Low Tide, September 1996 ... 33
Figure 4-3b Potentiometric Surface, Confined Intermediate Aquifer, Low Tide, September 1996 ... 34
Figure 4-4 N-2 Sample Location, Navy Base Kitsap, WA ... 36
Figure 4-5 Keyport Microcosm Results for *c*DCE Measurements ... 39
Figure 4-6 Keyport Microcosm Results for Dissolved Manganese Measurements ... 39
Figure 5-1 *cis*-1,2-Dichloroethene Concentrations in Groundwater, Myrtle Beach AFB, SC ... 44
Figure 5-2 Groundwater Flow, December 7, 2005 ... 45
Figure 5-3 Building 575 Sampling Locations, Myrtle Beach AFB, SC ... 48
Figure 5-4 Myrtle Beach AFB Microcosm Results for *c*DCE Measurements ... 50
Figure 5-5 Myrtle Beach AFB Microcosm Results for Dissolved Manganese Measurements ... 50
Figure 6-1 Engineering Support Building Site Features, Cape Canaveral AFS, FL ... 55

Figure 6-2 Launch Complex 34 Soil Boring and Monitor Well Locations, Cape Canaveral AFS, FL 56
Figure 6-3 Water Table Elevation Map for Surficial Aquifer from June 1998, Cape Canaveral AFS, FL 59
Figure 6-4 Sample Collection using Geoprobe beside the Engineering Support Building 60
Figure 6-5 Launch Complex IW-51I/ESB-SB-2 Microcosm Results for *c*DCE Measurements 65
Figure 6-6 Launch Complex ESB-SB-1 Enrichment Results for *c*DCE Measurements 65
Figure 6-7 Launch Complex IW-51I/ESB-SB-2 Microcosm Results for Dissolved Manganese Measurements 65
Figure 6-8 Launch Complex 34 ESB-SB-1 Enrichment Results for Dissolved Manganese Measurements 66
Figure 7-1 Alamac American knits, LLC Site Features, Lumberton, NC 68
Figure 7-2 Alamac American Knits, LLC Site Features, Monitor Well Locations and cDCE Plume Limits (October 2005) 71
Figure 7-3 Water Table Elevation Map for Shallow Aquifer from December 2005, Alamac American Knits, Lumberton, NC 73
Figure 7-4 Lumberton Enrichment Results for *c*DCE Measurements 75
Figure 7-5 Lumberton Enrichment Results for Dissolved Manganese Measurements 75

APPENDIX

Appendix A Site Comparison Spreadsheet
Appendix B Manganese Dioxide Synthesis and Media Components
Appendix C Microcosm Data

LIST OF ABBREVIATIONS

ACRONYMS

1. ACE – Army Corps of Engineers
2. AFB –Air Force Base
3. AFS – Air Force Station
4. bgs – Below Ground Surface
5. BOD – Biochemical Oxygen Demand
6. CAH – Chlorinated Aliphatic Hydrocarbons
7. CVOC – Chlorinated Volatile Organic Compound
8. COPC – Compound of Primary Concern
9. DO – Dissolved Oxygen
10. DoD – Department of Defense
11. DOC – Dissolved Organic Carbon
12. EOS® - Emulsified Oil Substrate
13. ESTCP – Environmental Security Technology Certification Program
14. FID – Flame Ionization Detector
15. ft bgs – Feet Below Ground Surface
16. GC – Gas Chromatography
17. gpm – Gallon Per Minute
18. HSWA – Hazardous and Solid Waste Amendments
19. IDW – Investigation-Derived Waste
20. ITRC – Interstate Technology & Regulatory Council
21. MCL – Maximum Contaminant Level
22. MNA – Monitored Natural Attenuation
23. MSL – Mean Sea Level
24. NCSU – North Carolina State University
25. NOD – Natural Oxidant Demand
26. ORP – Oxidation-Reduction Potential
27. OU – Operable Unit
28. PCE – Tetrachloroethene (Tetrachloroethylene)
29. RCRA – Resource Conservation Recovery Act

30. SVOCs – Semivolatile Organic Compounds
31. TOC – Total Organic Carbon
32. USEPA – United States Environmental Protection Agency
33. UST – Underground Storage Tank
34. VOA – Volatile Organic Analysis
35. VOC – Volatile Organic Compound

CHEMICALS

1. 1,1-DCA – 1,1-Dichloroethane
2. 1,2-DCA – 1,2-Dichloroethane
3. *c*DCE – *cis*-1,2-Dichloroethene
4. PCE – Tetrachloroethene
5. *t*DCE – *trans*-1,2-Dichloroethene
6. 1,1,1-TCA – 1,1,1-Trichloroethane
7. 1,1,2-TCA – 1,1,2-Trichloroethane
8. TCE – Trichloroethene
9. VC – Vinyl Chloride
10. NTA – Nitriloacetic acid
11. EDTA – Ethylenediaminetetracetic acid

SITE NAMES, ABBREVIATIONS, ACRONYMS AND SYNONYMS

Alamac American Knits, LLC, Lumberton, NC (Alamac; Lumberton)

Cape Canaveral Air Force Station (CCAFS), Cape Canaveral, FL (Launch Complex 34, LC34)

Hill Air Force Base, Ogden, UT (Hill, Hill AFB)

Myrtle Beach Air Force Base, Myrtle Beach, SC (MBAFB)

Navy Base Kitsap, Keyport, WA (Naval Undersea Warfare Center; Keyport; Navy Base Keyport)

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EXECUTIVE SUMMARY

An apparent stall in the biodegradation of 1,2-*cis*-dichloroethene (*c*DCE) is often observed at many natural attenuation sites where *c*DCE accumulates and is not further degraded. The lack of further breakdown *c*DCE is often attributed to a lack of available hydrogen donor and/or absence of a suitable microbial community to further degrade the contaminant.

Bradley et al. (1998) reported that addition of Mn(IV) could enhance microbial oxidation of *c*DCE under anaerobic conditions. However, the extent to which this process occurs in groundwater and whether it can be enhanced by manganese dioxide (MnO_2) addition in aquifers with persistent *c*DCE is unknown.

This study, funded by the Environmental Security Technology Certification Program (ESTCP Project No. ER-0625), has examined the effect of MnO_2 and other amendments in promoting biological oxidation of *c*DCE under anaerobic, aerobic or cometabolic conditions. Efforts were also made to find and enrich for naturally-occurring microbial populations that could biodegrade *c*DCE using MnO_2 as an electron acceptor.

Solutions-IES examined the historical groundwater data from 16 sites with known CVOC groundwater contamination problems. These included 15 Department of Defense facilities and one commercial location. Although the ESTCP Treatability Work Plan called for evaluation of only four locations, six locations were selected for laboratory testing. Groundwater and/or saturated soil from the water bearing subsurface zone in plumes contaminated with chlorinated ethenes were collected from Hill Air Force Base (Hill AFB) in Utah, Myrtle Beach AFB in South Carolina, Navy Base Kitsap in Keyport, Washington (Keyport), two locations near Launch Complex 34 at Cape Canaveral Air Force Station in Florida (CCAS LC-34 Plume and CCAS LC-34 ESB), and the Alamac American Knits LLC (Alamac) textile manufacturing facility in North Carolina. At each of these locations, there was evidence of a *c*DCE stall. Laboratory microcosm and/or enrichment cultures were constructed at the Shaw Biotechnology Facility in Lawrenceville, NJ, using the matrices collected from these locations to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added manganese and organic substrates. Two indicators were used to measure the effectiveness of the treatments: 1) changes in the *c*DCE and VC concentrations and 2) changes in the concentration of soluble Mn(II).

Changes in the CVOC concentrations (specifically *c*DCE and VC) were recorded over the prescribed incubation period. Concentrations of dissolved Mn(II) were analyzed in solution. An increase in the rate and/or extent of *c*DCE loss in incubations amended with MnO_2 coupled with an increase in dissolved Mn was considered evidence that MnO_2 addition stimulated *c*DCE degradation. Conversely, the disappearance of *c*DCE with concurrent production of VC or ethene was considered evidence that anaerobic reductive dechlorination was the operational biodegradation pathway.

The different microcosm and enrichment studies were incubated and monitored for 2 to 9 months. The microcosm results by site are summarized below:

Hill AFB: Ambient groundwater conditions at the site were generally oxidative. In groundwater used to prepare the microcosms, there was little TOC (2.6 mg/L), virtually no dissolved manganese (.003 mg/L), a low concentration of *c*DCE (0.1 mg/L) and no vinyl chloride (VC). *c*DCE loss relative to controls was greatest (~70%) in the aerobic treatment during the 5-month incubation. Under anaerobic conditions, degradation of *c*DCE was not enhanced by the addition of MnO_2, humic acids, or acetate relative to the background control treatment. Increases in soluble manganese in several treatments was most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources, not *c*DCE biodegradation. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

Navy Base Kitsap at Keyport: *c*DCE was completely depleted in the background controls after four months. By seven months, *c*DCE was completely depleted in the synthesized MnO_2 and humic acid treatments. The aerobic treatment also demonstrated significant loss (~80%) relative to the controls. No VC was reported in the field sample, but there was evidence of approximately 8.9 mg/L TOC in this water and the ORP was in the reducing zone (-38 mV). Vinyl chloride was detected in the background treatment, as well as the commercial, synthesized and humic acid treatments, suggesting reductive dechlorination. The addition of humic acids probably served as an additional electron donor. The addition of MnO_2 appears to inhibit reductive dechlorination based on the lag period associated with treatments receiving MnO_2 compared to the background control treatment. The increase in soluble manganese in several treatments was most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources. Alternatively, some microorganisms can couple the oxidation of H_2 to the reduction of metals such as Fe(III) and Mn(IV) (Lovley *et al.*, 1989). Therefore, some of the Mn(IV) may have been reduced by H_2 derived from indigenous electron donors. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

Myrtle Beach AFB: Conditions in groundwater from 575-MW-12 would generally be considered conducive to anaerobic MNA of chloroethenes, despite previous treatment of the site by *in situ* chemical oxidation (ISCO) using permanganate. Dissolved Mn(II) was present in groundwater at 5.9 mg/L indicating ongoing manganese reduction. In the microcosm study, VC was detected in the commercial, synthesized, background, and humic acid treatments, as well as the in the sterile controls with MnO_2. Based on the detection of VC, *c*DCE loss is attributed to reductive dechlorination, which is consistent with the field observations. The humic acid and acetate amendments did not further stimulate *c*DCE loss beyond that occurring in the control incubations. Dissolved manganese production was greatest in the sterile control amended with MnO_2, presumably due to the presence of formic acid in the formaldehyde used to inhibit microbial activity. The reduction of manganese in the aerobic treatment almost equaled that in the sterile control treatment that was not amended with MnO_2. Manganese reduction under oxic conditions has been observed in other studies (Bratina *et al.*, 1998). Aerobic microorganisms can reduce Mn(IV) via diffusible compounds under oxic conditions (Bratina *et al.*, 1998). Manganese reduction did not occur in any of the other

treatments and was clearly not linked to anaerobic *c*DCE oxidation. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

CCAFS LC-34 Plume: The matrices used in the construction of the LC-34 Plume microcosms contained residual TOC (2.4 mg/L) at low oxygen concentration (0.9 mg/L) and ORP (-209 mV). The background suite of chloroethenes clearly demonstrated the *c*DCE stall in this portion of the plume (i.e., TCE, <20 µg/L; cDCE, 3200 µg/L; VC, 320 µg/L; ethene, BDL). There was no significant loss of *c*DCE in any of the microcosm treatments with or without the addition of MnO_2. Amendments of humic acid, acetate, ethene, NTA and oxalic acid did not stimulate *c*DCE degradation relative to the background control treatment for either site. Although there are *in situ* levels of both *c*DCE and VC in the material, it does not appear as though the microbial community supports *c*DCE degradation. Metals analyses for the microcosms showed that the greatest increase in dissolved manganese (i.e., reduction of Mn^{4+}) occurred in the sterile controls amended with MnO_2. Manganese reduction did occur in the MnO_2 treatment. Nonetheless, the increase in dissolved manganese is most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

The length of the microbial enrichments varied from 2 to 3 months. The enrichment results by site are summarized below:

CCAS LC-34 ESB: The matrices used in the construction of the LC-34 ESB enrichments were collected approximately 100 to 200 ft downgradient of a prior ISCO pilot test using permanganate. There was no significant loss of *c*DCE in any of the treatments with or without the addition of MnO_2. Amendments of humic acid, acetate, ethene, NTA and oxalic acid did not stimulate *c*DCE degradation relative to the background control treatment for either site. The metals analyses for the enrichments showed that the greatest increase in dissolved manganese (i.e., reduction of Mn^{4+}) occurred in the sterile controls amended with MnO_2. In the absence of added MnO_2, the sediment's naturally occurring Mn(IV) was reduced by formic acid present as an impurity and provided a relative measure for background Mn(IV) levels. The addition of the chelators NTA and oxalic acid resulted in the reduction of Mn(IV) and not the solubilization of Mn(IV), and therefore they did not enhance *c*DCE oxidation via MnO_2 reduction. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

Alamac: After 9 weeks, *c*DCE was completely depleted in the background control, and by 4 months it was completely removed from the cometabolism treatment amended with acetate. Significant *c*DCE degradation was observed in the aerobic treatment (72%). VC was detected in the background control, as well as the cometabolism treatment amended with acetate. The addition of humic acids did not enhance *c*DCE degradation. Although there was a lag, the addition of acetate did appear to enhance *c*DCE degradation after several months. Given the assumption that reductive dechlorination is the dominant process removing *c*DCE in site material, acetate probably served as an additional electron donor. The addition of MnO_2 may have inhibited reductive dechlorination based on the lag period associated with treatments receiving MnO_2 compared to the background

control treatment. The metals analysis results showed a significant increase in soluble manganese in the sterile controls amended with MnO_2. Significant manganese reduction was also demonstrated in the treatment that was amended with only acetate as a carbon source. This finding suggests that site material from Alamac supports manganese reducers, and that the lag period associated with *c*DCE loss in the cometabolic treatment may have been attributed to consumption of the electron donor (acetate) during manganese reduction. There was no evidence that MnO_2 addition enhanced *c*DCE biodegradation.

In summary, there was some indication that the background conditions at several sites lead to VC formation by reductive dechlorination. This was more apparent at sites with residual TOC (e.g., Keyport, Myrtle Beach and Alamac) and the addition of additional carbon sources (acetate or humic acids) may have further enhanced this reaction. The presence of an aerobic headspace appeared to promote the best biodegradation of *c*DCE, apparently through aerobic oxidation. MnO_2 addition appeared to inhibit *c*DCE biodegradation in matrices from Keyport and Alamac. There was little evidence that increases in the concentration of soluble Mn(II) from the biological oxidation of *c*DCE occurred.

Multiple treatments were prepared to promote the anaerobic biological oxidation of *c*DCE. None of these treatments were effective in enhancing the anaerobic oxidation of *c*DCE using MnO_2 as an electron acceptor. Based upon these results, there is no evidence that addition of MnO_2 to aquifers will enhance *c*DCE biodegradation. Further pilot testing of MnO_2 addition as a technology to enhance *c*DCE biodegradation is NOT recommended at this time.

1.0 INTRODUCTION

Where suitable conditions exist, natural attenuation processes often result in the relatively rapid dechlorination of tetrachloroethene (PCE) and trichloroethene (TCE) to *cis*-1,2-dichloroethene (*c*DCE). However, at many sites, reductive dechlorination appears to slow or stop at *c*DCE. There are a variety of hypotheses for this apparent 'DCE stall' including the presence of competing electron acceptors or the absence of required microorganisms and/or electron donors. Regardless of the reason, a DCE stall does occur at many monitored natural attenuation (MNA) sites.

The ability of some microorganisms to couple anaerobic oxidation of *c*DCE to Mn(IV) reduction has been reported in the literature. However, the extent to which this process occurs in groundwater and whether it can be enhanced by MnO_2 addition in aquifers is unknown. Mn^{4+} concentrations in soils are typically very low (median = 19 mg/kg as Mn; Chen et al., 1999), in part because manganese dioxide (MnO_2) is relatively easy to reduce (Negra et al., 2005). If *c*DCE oxidation is limited by the amount of bioavailable Mn^{4+}, then the capacity of an aquifer to assimilate *c*DCE and vinyl chloride (VC) could potentially be increased by providing additional MnO_2 as a long-term source of an immobilized electron acceptor. The work described in this treatability report was conducted under funding provided by the Environmental Security Technology Certification Program (ESTCP Project ER-0625).

1.1 Background – Chemistry and Microbiology of Manganese Reduction

Manganese (Mn) can exist in aquifers in a variety of oxidation states including Mn(VII) as MnO_4^-, Mn(IV) as MnO_2, and Mn(II). However, only Mn^{2+} is commonly present in aqueous solution. MnO_4^- will oxidize organic materials, reduced minerals and water at the pH typical of most aquifers, releasing Mn(IV). Mn(IV) does not have any significant aqueous chemistry and will either disproportionate or precipitate out of solution as the extremely insoluble MnO_2 (pyrolusite). At low pH, Mn^{2+} is relatively soluble. However, at higher pH, Mn^{2+} can precipitate as $MnCO_3$ (rhodochrosite), $Mn_2O_3 \cdot H_2O$ (manganite) or $Mn(OH)_2$ (pyrochroite).

Manganese is an important component in many common minerals including biotite mica and amphiboles. Typically, Mn is present in the Mn(II) oxidation state. When present in an oxidized form, Mn often occurs as a mixed oxidation state mineral that has co-precipitated with other oxidized minerals including $Fe(OH)_3$ and has very limited bioavailability.

At present, the microbiology of manganese reduction is much less well understood than other anaerobic processes, in part, because Mn(IV) is typically present at much lower concentrations than other electron acceptors. Current thinking is that dissimilatory Mn(IV) reduction is very similar to dissimilatory Fe(III) reduction (Lovley, 1991; 1993). Most microorganisms that reduce Mn(IV) also reduce Fe(III) and vice versa. However, Fe(III) is not abiotically reduced by common organic materials, while Mn(IV) can be abiotically reduced by a variety of organic acids, reduced sugars, and Fe(II). In natural environments, Mn(IV) could be directly reduced by microorganisms. However, Fe(III) and Mn(IV) reduction could also be coupled where Fe(III) is enzymatically reduced to Fe(II). Mn(IV) would then reoxidize Fe(II) to Fe(III) providing a source of highly reactive electron acceptors for further reduction.

1.2 Technology Description

The purpose of this study was to develop and demonstrate a technology for enhancing **biological oxidation** of *c*DCE and VC under anaerobic conditions by adding highly bioavailable MnO_2. If shown to be feasible, this could be applied to a downgradient portion of an aquifer where TCE had already been depleted and *c*DCE persisted. As an example, Figure 1-1 shows a profile of chlorinated ethene concentrations at an MNA site at Plattsburgh Air Force Base. In the region labeled "Type 3 Behavior", VC is being naturally oxidized by Fe(III) (Bradley et al., 1998b). However, *c*DCE is degraded much more slowly in the aquifer. Assuming this technology could be shown effective, *c*DCE oxidation could be stimulated by distributing MnO_2 in a wide zone between points C and E. In this area, TCE has already been depleted so inhibiting reductive dechlorination of the TCE would not be an issue. The primary objective is to stimulate biological oxidation of *c*DCE and VC to CO_2 and Cl^-. The goal would **NOT** be to enhance reductive dechlorination, so consumption of other electron donors would not be a problem.

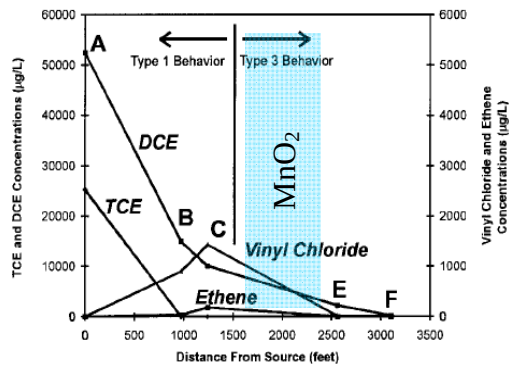

Figure 1-1. Chlorinated ethene distribution at Plattsburgh AFB (Bradley et al., 1998b)

Assuming the presence of MnO_2 in aquifer matrices could be shown to stimulate the desired anaerobic oxidation of *c*DCE and VC in the laboratory, there are two obvious approaches for distributing MnO_2 in aquifers: (1) distribution of solid MnO_2; and (2) injection of permanganate (MnO_4^-) followed by precipitation of MnO_2 as the permanganate reacts with the natural oxidant demand (NOD) of the aquifer material. Solid MnO_2 could be emplaced by conventional excavation techniques similar to an iron wall, or it could be injected as colloidal size particles similar to the injection of nano-scale iron. Both approaches for distributing solid MnO_2 are technically feasible, but would likely be more expensive than simple injection of an aqueous solution of MnO_4^-.

This treatability study was designed to evaluate the potential for MnO_2 addition to stimulate biological oxidation of *c*DCE and VC. In the laboratory, the plan was to bring aquifer material from a variety of sites into contact with MnO_2 either by adding it directly to the microcosm bottles containing aquifer material collected from plumes experiencing DCE stall or by collecting material from aquifers that had already been treated via *in situ* chemical oxidation (ISCO) using $KMnO_4$ and assuming that some of the manganese had already precipitated as MnO_2. Should the technical approach be proven in the laboratory, the project would then consider pilot-scale demonstrations to determine the effectiveness in the field and consider means of introducing MnO_2 for field use. As noted above, the potential advantages of using MnO_4^- compared to MnO_2 might include:

(a) MnO_4^- can generate a more oxidizing environment, enhancing oxidation of DCE and VC;
(b) There is extensive practical and regulatory experience with injection of MnO_4^-. Therefore, obtaining regulatory approval should be relatively straightforward; and
(c) The MnO_2 formed by precipitation of MnO_4^- will be distributed over a wide area providing a large zone for biological oxidation of *c*DCE.

Potential disadvantages of using MnO_4^- include:

(a) MnO_4^- may oxidize some natural organic material that would not react with MnO_2, increasing the amount of reagent required;
(b) Chemical costs per pound of Mn are somewhat higher for MnO_4^- than for MnO_2;
(c) MnO_4^- will chemically oxidize some of the naturally occurring electron donors; and
(d) The strongly oxidizing conditions generated by injection of MnO_4^- could inhibit anaerobic microorganisms that oxidize *c*DCE.

1.3 Goals and Objectives

The goal of this ESTCP project was to demonstrate to environmental managers, regulatory agencies and remediation engineering personnel that biological oxidation of *c*DCE and VC could be implemented as an *in situ* groundwater remedy that is effective for controlling adverse impacts to the environment. The overall objective of this project was to develop and demonstrate a process to enhance the natural attenuation capacity of an aquifer to degrade *c*DCE and VC by increasing the amount of readily bioavailable MnO_2. The technical objectives of the site screening and laboratory treatability studies described in this report included the following:

1. Identify sites where the absence of bioavailable MnO_2 (i.e., Mn^{4+}) and/or required microorganisms limited *c*DCE and/or VC oxidation.
2. Develop and characterize enrichment culture(s) capable of growth on *c*DCE and/or VC using MnO_2 as a terminal electron acceptor.
3. Demonstrate that addition of MnO_2 and/or the enrichment culture to laboratory microcosms could stimulate *c*DCE and/or VC biodegradation.
4. Make a GO/NO GO decision regarding the usefulness of attempting field trials of the technology. If the data from one or more sites indicate that the approach could be promising, subsequent field tests (e.g., small-scale push-pull tests and a full field pilot demonstration) would be implemented.

1.4 Regulatory Drivers

Field studies at numerous sites have shown that PCE and TCE often naturally attenuate to *c*DCE without any human intervention. However, at many of these same sites, *c*DCE persists and low levels of *c*DCE can migrate thousands of feet. The primary Federal water quality Maximum Contaminant Level (MCL) for *c*DCE is 70 µg/L, *trans*-1,2-dichloroethene (*t*DCE) is 100 µg/L and VC is 2 µg/L. In a survey of chlorinated solvent MNA sites, McGuire et al. (2004) reported that a DCE stall was observed at 23 out of 80 sites where DCE information was available and a

DCE stall was reportedly a problem at 2 of the 3 case study sites where the estimated remediation time frame was considered too long for acceptance of MNA.

Because the technology being evaluated involves the possible addition of manganese compounds to an aquifer, it is also important to consider the potential toxicological and regulatory impact of elevated manganese in groundwater. At high levels of manganese exposure, usually as a dust, neurotoxicity can result with ataxia, increase anxiety, dementia and involuntary muscle movements (USEPA 2003), but this is uncommon. Mn is an essential nutrient so reducing Mn concentrations in the water supply could have adverse effects. There is a secondary Federal water quality, non-enforceable MCL for manganese of 50 µg/L (Pontius, 2002). The USEPA (2003) concluded that, "Because manganese ingestion is not known to present adverse health effects at low levels, and because drinking water contributes a small portion of normal oral intake, it is unlikely that regulation of manganese in drinking water would represent a meaningful opportunity for health risk reduction in persons served by public water systems".

From a regulatory perspective, the accumulation of *c*DCE and VC may be an indication that remediation has been incomplete and some environmental and human health risk may remain. Therefore, developing, testing and validating innovative technologies to address this real-world condition will be useful. The successful demonstration of the concept that biological oxidation of these contaminants can be promoted under anaerobic conditions using MnO_2 as an electron acceptor will add to the understanding of these remediation processes and help with regulatory decision making. .

1.5 Stakeholder/End-User Issues

Monitored Natural Attenuation (MNA) is one of the few technologies that is cost-effective over the long-term. The successful demonstration of anaerobic oxidation of *c*DCE and/or VC would provide another biological mechanism and remediation approach that could be considered when evaluating the potential for MNA or *in situ* bioremediation of these contaminants. However, MNA has not been accepted at many chlorinated solvent sites because of *c*DCE accumulation. If a low- cost method could be developed to enhance the *c*DCE attenuation capacity of an aquifer, this could be a tremendous benefit to current property owners, purchasers, and investors as well as regulators in the pursuit of cleaning up chlorinated solvent impacted properties. Once developed, this technology could be applied to a wider variety of reduced contaminants, and this approach could also provide tremendous benefits to the U.S. Department of Defense (DoD) and the remediation community as a whole.

1.6 Chlorinated Ethene Biodegradation

The general sequence of anaerobic reductive dehalogenation of PCE is presented in Figure 1-2.

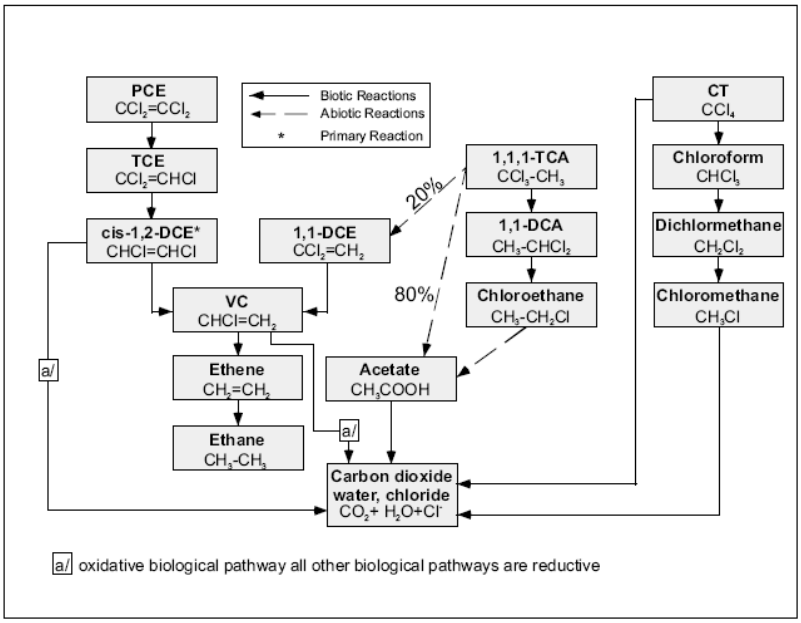

Figure 1-2. Abiotic and Biological Transformation Pathways for Selected Chlorinated Solvents (AFCEE, 2004)

The primary degradation products of PCE dechlorination are TCE, and, in turn, *c*DCE. A small percentage of the biodegradation results in formation of the *trans*-1,2-DCE (*t*DCE) isomer. Because this amount is usually minimal, the term "DCE stall" and "*c*DCE stall" are often used interchangeably. As mentioned above, a DCE stall frequently occurs where the anaerobic reductive dechlorination process is incomplete or stops between the biotransformation of *c*DCE to VC. This study was designed to answer several questions that could show the potential usefulness of the key components of this process:

- Are bacteria available that will utilize the MnO_2 for dechlorination processes?
- Can bioactivity in the soil be increased by the addition of MnO_2?
- Is there a dual effect on the dechlorination process from the breakdown of MnO_2 to Mn^{4+} and O_2?
- Will an increase in bacterial bioactivity add to the reductive dechlorination process (i.e., further enhance and increase the rate of dechlorination of *c*DCE to VC to ethene, etc.)?
- Can the results of this study be applied to other compounds susceptible to dechlorination or similar processes?

2.0 DEMONSTRATION DESIGN AND METHODS

2.1 Site Screening and Selection

The overall objective of this project was to develop and demonstrate a technology for stimulating *c*DCE and/or VC biodegradation by increasing the MnO_2 content of an aquifer. The site selection process was a phased activity. Initially, Solutions-IES compiled a list of potential sites from an internet search, DoD documents and personal contacts in order to identify locations where either: (a) the absence of bioavailable MnO_2 was potentially limiting *c*DCE and/or VC oxidation; or (b) the site had been previously treated by ISCO using permanganate, leaving behind residual MnO_2 which would increase the potential for growth of Mn(IV) reducing microorganisms. Solutions-IES obtained information on site-specific hydrogeology, groundwater geochemistry, and the extent of DCE contamination from on-line source and site personnel. At each of these facilities, the chlorinated solvent plume had been delineated and there was some information on aquifer geochemistry. At each site, PCE and TCE had been reduced to *c*DCE during downgradient transport. However, further degradation of *c*DCE did not appear to be occurring.

This information was reviewed to select locations where MnO_2 addition appears to have good potential for stimulating *c*DCE degradation. This resulting list was biased towards Air Force Bases because the large number of studies conducted by AFCEE on MNA of chlorinated solvents. Information from the following sites was reviewed:

- Myrtle Beach AFB, Myrtle Beach, SC – Building 575 (SWMU 256)
- Naval Air Station Cecil Field, Jacksonville, FL – Site 3
- Cape Canaveral Air Force Station, Cape Canaveral, FL – Site LC-34
- Cape Canaveral Air Force Station, Cape Canaveral, FL – Site Facility 1381 (SWMU 21)
- Orlando Naval Base, Orlando, FL – Site SA-17
- Plattsburgh Air Force Base, Plattsburgh, NY – Site-002
- Shaw Air Force Base, Sumter, SC – Site OU-4, FT-1
- Altus Air Force Base, Altus, OK – OU-1, LF-4
- Columbus Air Force Base, Columbus, MS –Site LF-06
- F.E. Warren Air Force Base, Cheyenne, WY – Site LF-03
- Hill Air Force Base, Ogden, UT – Site OU-1
- Kelly Air Force Base, Kelly AFB, TX – Site S-1, Zone 5
- Offutt Air Force Base, Omaha, NE –Fire Protection Training Area 3
- Tinker Air Force Base, Oklahoma City, OK – Site FTA-2
- Navy Base Kitsap (former Naval Undersea Warfare Center, Division Keyport), Keyport, WA – Site OU-1

A spreadsheet was developed to summarize the available information on site-specific hydrogeology, groundwater geochemistry, extent of TCE, *c*DCE and VC contamination, site accessibility, and willingness of the site manager to participate in a demonstration. The overall spreadsheet is provided in Appendix A. This information was then reviewed along with any site-specific special knowledge and five locations meeting the generally desirable site conditions were considered. These included:

1. Tinker Air Force Base, Oklahoma City, OK – Site FTA-2
2. Naval Air Station Cecil Field, Jacksonville, FL – Site 3
3. Navy Base Kitsap at Keyport (former Naval Undersea Warfare Center, Division Keyport, Keyport, WA;
4. Myrtle Beach Air Force Base, Myrtle Beach, SC;
5. Hill Air Force Base, Operational Unit 1 (OU-1), Hill AFB, UT;

A Treatability Work Plan was prepared and approved by ESTCP for the field sampling and laboratory microcosm studies (Solutions-IES, 2006). Additional details about each site and the conditions that were considered as part of the site-selection process are discussed in individual sections later in this report. A brief rationale for selecting or not selecting promising sites is as follows:

Tinker AFB and NAS Cecil Field:
These bases were named as being under consideration in the Treatability Work Plan based on an initial review of site geochemistry and plume conditions. However, upon further discussion with Mr. Scott Bowen at Tinker AFB and Mr. Cliff Casey of NAVFAC SE regarding Cecil Field, it was decided that neither of these sites was a viable candidate for the demonstration, and therefore, they were removed from further consideration.

Navy Base Kitsap at Keyport:
Bradley et al. (1998a) reported that MnO_2 addition to sediments from Navy Base Kitsap enhanced oxidation anaerobic oxidation of *c*DCE to CO_2. Consequently, Navy Base Kitsap was considered a high probability site for the current demonstration.

Myrtle Beach AFB:
The chlorinated solvent plume at Myrtle Beach AFB had been treated previously by ISCO using potassium permanganate ($KMnO_4$). While the initial ISCO approach was effective, the treated area was experiencing *c*DCE rebound (personal communication, Tarek Ladaa, Shaw Environmental, Inc.). As a result, aquifer material at this site will have been exposed to both MnO_2 and *c*DCE for an extended time, potentially allowing adaptation of the native microbial community. As a consequence, Myrtle Beach AFB was considered a good candidate site for the demonstration.

Hill AFB:
Hill AFB has an extensive *c*DCE plume that is migrating offsite. Consequently, enhancing *c*DCE degradation would have immediate benefits. In addition, historical data indicated that a portion of one chlorinated solvent plume could be isolated where conditions appeared to meet the site-selection criteria.

Cape Canaveral Air Force Station Launch Complex 34:
Solutions-IES investigated the potential to use site matrices from two areas at Launch Complex 34 (LC 34). One area, near the Engineering Support Building (ESB) contains high levels of TCE and *c*DCE. An extensive ISCO pilot test using potassium permanganate had previously been conducted at this site. Consequently, aquifer material at this location would have long-term exposure to *c*DCE and MnO_2 increasing the potential for adaptation of site microorganisms to these conditions.

A second area was identified approximately 2,000 ft downgradient from the ESB. At this location, TCE has naturally attenuated to *c*DCE. However, there is little further attenuation of *c*DCE. ISCO pilot studies were never conducted at this location and there is no evidence of prior exposure of these sediments to MnO_2. After discussions with air station personnel and Mr. Jim Langenbach of Geosyntec Consultants, these two locations were selected as the fourth and fifth locations, replacing Tinker AFB and NAS Cecil Field.

Alamac American Knits, LLC, Lumberton, NC:
A sixth site was added to the testing program to provide an additional source of soil and groundwater that had been exposed to *c*DCE for an extended period of time. Solutions-IES obtained permission from one of its commercial clients, Alamac American Knits, LLC, of Lumberton, NC (Alamac), to collect samples from its site for use in laboratory enrichment studies. The source area at this site was a former PCE aboveground storage tank. In the downgradient portion of the plume, PCE and TCE naturally attenuate to *c*DCE resulting in an extensive *c*DCE plume. However, historical groundwater monitoring suggested that a *c*DCE stall was occurring and the plume discharged at a flood control canal at the property boundary. Including this site in the treatability study was beyond the original scope-of-work, but was included to try to increase the chances of obtaining a successful enrichment culture.

2.1.1 Site Screening Summary

Historical hydrologic and biogeochemical characteristics for each of the five DoD locations selected are summarized in Table 2-1. At each of these sites, there was evidence for anaerobic conditions in some areas including: low dissolved oxygen (DO) and/or nitrate, measurable total organic carbon (TOC), iron, manganese and/or methane, and accumulation of chlorinated solvent degradation products in at least a portion of the plume.

The Treatability Work Plan generally described the methods for collecting site-matrix samples from those sites and the laboratory testing that would be performed. Prior to mobilizing to each location, a site-specific Sampling and Analysis Plan (SAP) was prepared. Each site-specific SAP described methods of sample collection at the particular site and included site-specific health and safety plans (HASPs), sampling and quality assurance project protocols, and laboratory testing methods.

Depending on the available historical site information at each location, one or more of the following studies were conducted for each site:

(1) A preliminary bio-geochemical evaluation of site matrices;
(2) Laboratory microcosm studies to assess the extent of anaerobic oxidation of *c*DCE under ambient conditions and evaluate the potential to stimulate the biological oxidation of *c*DCE under anaerobic conditions by the addition of manganese dioxide (MnO_2).
(3) Laboratory enrichment studies to examine conditions that could promote the growth of indigenous microorganisms capable of anaerobic oxidation of *c*DCE.

Details of the field and laboratory procedures for each site are described in the following sections.

TABLE 2-1 CHARACTERISTICS OF SELECTED SITES		
Site & Location	Myrtle Beach AFB, Myrtle Beach, SC[a] (Bldg 575-SWMU 256)	Hill AFB, Ogden, UT[b] (OU-1)
Characteristics		
TCE	<15 µg/L	Below detection
cis-1,2-Dichloroethene	285 – 900 µg/L	<1 to 469 µg/L
Vinyl Chloride	31 – 124 µg/L	<1 to 274 µg/L
Ethane/Ethene	Not reported[c]	Not reported[c]
Co-contaminants	Not reported[c]	TCA & daughter product; BTEX
Dissolved oxygen	0.63 – 0.72 mg/L	Not reported[c]
Oxidation/reduction potential	+150 to +202 mV	Low in areas with BTEX; higher elsewhere
Nitrate	Not reported[c]	Depleted in plume
Iron-dissolved (Fe^{2+})	Not reported[c]	<.05 to 34.9 mg/L
Manganese-dissolved	Injected >104,000 gal of 2.8% soln. $KMnO_4$ in Sept-Nov 2005	Data available, but not reported[c]
Sulfate	Not reported[c]	Not reported[c]
Methane	Not reported[c]	Not reported[c]
pH	6.6 – 7.0	6.7 – 8.5
TOC	Not reported[c]	<1 to 290 mg/L
Depth to Water (ft below ground surface)	Shallow aq.: 5 – 11 ft bgs; Deep aq.: >40 ft bgs	15 – 30 ft bgs
Seepage Velocity	Not reported[c]	~13 ft/yr; but may be faster
Aquifer Lithology Summary	Not reported[c]	Upper sand & gravel layer comprises upper aquifer = coarse clean to silty sands interbedded with gravel & clay stringers, 0 - 62 ft thick
Other information	Limited to 2 small areas; ISCO treated; may be source of Mn-acclimated microorganisms.	5000 ft; lobes

a. Shaw Environmental, Inc., December 2005 Semiannual Corrective Measure Progress Report (Building 575, SWMU 256), Myrtle Beach Air Force Base, Myrtle Beach, SC., April 2006.

b. Parsons Engineering Science, Inc., Remediation by Natural Attenuation Treatability Study for Operable Unit 1, Hill Air Force Base, Ogden, UT., September 1999.

c. "Not reported" indicates that information was not available in the reference used to create the table.

TABLE 2-1 (Continued) CHARACTERISTICS OF SELECTED SITES			
Site & Location	Navy Base Kitsap, Keyport, WA[d] (OU-1)	Cape Canaveral AFS, Cape Canaveral, FL[e] (SWMU No. 54) LC-34 ESB[f]	Cape Canaveral AFS, Cape Canaveral, FL[f] (SWMU No. 54) LC-34-Plume
Characteristics			
TCE	<1 – 12 µg/L	3.2 – 283,000 µg/L	<500 µg/L
cis-1,2-Dichloroethene	15 – 2300 µg/L	37.6 – 217,000 µg/L	2,760 µg/L
Vinyl Chloride	38 – 370 µg/L	3.7 – 2,060 µg/L	14 -491 µg/L
Ethane/Ethene	1.1 – 33 µg/L	27 µg/L	2.5 – 20.9 µg/L
Co-contaminants	BTEX <1 – 2.4 µg/L	Low level BTEX	
Dissolved oxygen	0.1	0.45 mg/L	0.30 mg/L
Oxidation/reduction potential	-78 to +27 mV	-96.6 mV	-129 mV
Nitrate	<0.06	.240 mg/L	<0.050 mg/L
Iron-dissolved (Fe^{2+})	0.29 -29	2.03-2.24 mg/L	2.24 mg/L
Manganese-dissolved	0.1 – 2.0	0.015 mg/L	0.052 mg/L
Sulfate		25.2 mg/L	95.7 mg/L
Methane	<290 µg/L	.48.3 µg/L	33 µg/L
pH	6.5 – 6.8	8.64	6.84
TOC	8 - 45	3.6 mg/L	10.7 mg/L
Depth to Water (ft below ground surface)	8 - 10 ft bgs	6-9 ft bgs	
Seepage Velocity		0.0023 ft/d	
Aquifer Lithology Summary	Sand and silty sand with marsh, estuary and tidal flats	Sand, silty sands, clay aquitard.	
Other information		DNAPL present	

d. Dinicola, R.S.. Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA. Open-File Report 03-344, USGS, Reston, VA, June 2003; and Dinicola, R.S. 2006. Continued Biodegradation of Chloroethene Compounds in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA; USGS Scientific Investigations Report, 2006-5056, June 2006.

e. Results from most recent data available for wells IW0001S, IW0001I and IW0001D from 2004 and 2005.(CMS LC34)

f. Results from most recent data available for wells IW0051S and IW0051I from 2004 and 2005 (CMS LC34).

2.2 Biogeochemical Characterization

At each of the sites evaluated, up to three groundwater samples were collected to provide a general characterization of biogeochemical conditions in the aquifer. If MnO_4 addition was shown to be effective in stimulating anaerobic oxidation of *c*DCE, this information would be used in planning the field pilot tests. The wells/locations were selected based on historical information provided to Solutions-IES by site representatives and chosen by Solutions-IES to generally cover the range of biogeochemical conditions at the site including highly contaminated locations, moderately contaminated locations, and uncontaminated background locations. The following parameters were measured in the field for each well sampled: depth to water, pH, temperature, oxidation-reduction potential (ORP), dissolved oxygen (DO), dissolved iron, dissolved manganese and turbidity. The following parameters were measured in the laboratory for each well: chemical oxygen demand (COD), total and dissolved iron (Fe) and manganese (Mn), total organic carbon (TOC), permanent gases (methane (CH_4), ethane, ethene), chlorinated volatile organic compounds (PCE, TCE, DCE, 1,1,1-trichloroethane (TCA), dichloroethane (DCA), and VC), and anions (NO_3^-, SO_4^{2-}).

Sample analyses were performed at Prism Laboratories, Inc, in Charlotte, NC. These analyses included chlorinated VOCs (PCE, TCE, TCA, *c/t*DCE, DCA, VC) analyzed by Method 8260B, metals via ICP method 6010B, nitrate via Method SM4500, sulfate via Method 9056, TOC via Method 415.1, and COD via Method SM5220D. Laboratory analysis of light hydrocarbon gases was performed by VaporTech Services, Inc. in Valencia, PA using Method AM20GAX.

2.3 Laboratory Studies

2.3.1 Matrix Collection

Aquifer sediment material and groundwater were collected from one to three locations at each site for potential use in the microcosm studies. The sampling locations were selected based on previous groundwater sampling results indicating the presence of detectable TCE, *c*DCE and VC, previous manganese-based studies or remediation efforts, and biogeochemical monitoring results indicating a combination of low dissolved oxygen and/or low ORP with some organic carbon (Section 2.1).

Sediment samples for the microcosm study were collected in the field using hand augers, hollow stem auger (HSA) drill rigs, or Geoprobe®. When sampling by Geoprobe® or split-spoon samplers, sediment samples were collected in new plastic MacroCore® or split-spoon sleeves. When using a hand auger, the auger was carefully cleaned prior to taking to the field, but was not decontaminated between borings. Sediment samples were collected from a location and depth expected to be representative of groundwater conditions at the location of interest. Sediment samples collected with a hand auger were transferred to new, clean mason jars, covered immediately with groundwater to remove any remaining headspace, and shipped on ice to the Shaw Biotechnology Facility (Shaw) in Lawrenceville, New Jersey, for use in the laboratory studies.

Groundwater samples were collected from wells generally in close proximity to the placement of the soil or sediment sample borings. This was intended to maximize the potential that soil and groundwater were from approximately the same depth and conditions of the aquifer. The selected wells were purged and sampled using low-flow sampling techniques by means of dedicated, peristaltic, Whale™ or Grundfos submersible sampling pump. Field parameters (pH, conductivity, DO, turbidity, ORP and temperature) were recorded every five to ten minutes while purging depending on the flow rate established. After purging and sampling were complete, additional groundwater for use in microcosm and enrichment construction was collected from the monitor well. This water was pumped either directly into 1-liter sterile mason jars or into the appropriate soil jar (as described above). Jars were filled to capacity to eliminate headspace and sustain natural reduced oxygen tensions during shipment.

2.3.2 Microcosm Studies

Laboratory microcosms were constructed using site material from each individual site to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added organic substrates. The microcosm studies were conducted at the Shaw Biotechnology Facility. Set-up conditions common to building microcosms from each site are described below. Additional details specific to treatments established for each site are described in Sections 3 through 7.

Microcosms were prepared inside of a COY anaerobic chamber. The chamber was filled with N_2 (i.e., H_2 was not added). A CheckPoint O_2/CO_2 oxygen/carbon dioxide analyzer (PBI Dansensor) was used to measure oxygen levels for sampling events to ensure that the chamber was properly flushed to maintain anaerobic conditions. From Hill AFB, Myrtle Beach AFB, and LC34 Engineering Support Building site, approximately 15 grams of homogenized sediment were added to 60-mL serum bottles. The final volume of groundwater, including amendments, was 50 mL. From Navy Base Kitsap, approximately 30 g of homogenized sediment were added to 160-mL serum bottles. The final volume of groundwater, including amendments, was 140 mL. Bottles were sealed with Teflon stoppers and aluminum seals effectively trapping an anaerobic headspace in each bottle and incubated at 15ºC. Microcosms were not set up using sediments from the soil and groundwater collected downgradient from the ESB at LC34 or the Alamac site.

Nine to ten treatments, prepared in triplicate, were established to evaluate *c*DCE degradation under various conditions. A background control served as a baseline measure of *c*DCE degradation in the absence of MnO_2, and sterile controls with and without MnO_2 were established. In the sterile controls, microbial activity was inhibited by the addition of 1.5% formaldehyde solution. A commercial brand of MnO_2 (Riedel de Hahn) and an amorphous form of MnO_2 (synthesized by Shaw personnel; see Appendix B**)** were used in separate treatments to compare whether the form of MnO_2 affected *c*DCE degradation. With the exception of the commercial MnO_2 treatment and the background control, the in-house Shaw-synthesized form of MnO_2 was used in all other treatments. In all treatments receiving MnO_2, the MnO_2 stock solution was delivered as a slurry to achieve a final concentration of 25 mM (2170 mg/L).

One treatment was amended with humic acids in order to assess whether humic acids facilitate electron shuttling between MnO_2 and *c*DCE (Cervantes et al., 2001). Another treatment was amended with acetate in the event that *c*DCE could be cometabolized. Formaldehyde, *c*DCE, humic acids, and acetate were added as concentrated stocks to give the final concentrations noted in each sites sectional description. One treatment was made aerobic by adding several milliliters of filtered O_2 to the headspace. This step was repeated at each sampling event to maintain aerobic conditions. The aerobic treatment served as a comparison for aerobic versus anaerobic oxidation of *c*DCE.

2.3.3 Enrichment Studies

Laboratory enrichments were constructed using material from the site of the former ISCO pilot study at the Engineering Support Building at LC 34 and the Alamac site. Treatments prepared for the enrichments were mostly the same as for the microcosm studies (Section 2.4.2) although some additional treatments were constructed. General setup conditions are described below. Additional details about the enrichments prepared from these matrices are presented Sections 6 and 7.

Enrichments were prepared inside of a COY anaerobic chamber. The chamber was filled with N_2 (i.e., H_2 was not added). A CheckPoint O_2/CO_2 oxygen/carbon dioxide analyzer (PBI Dansensor) was used to measure oxygen levels for sampling events to ensure that the chamber was properly flushed to maintain anaerobic conditions. One set of enrichments was established using sediment and groundwater from at least one location at each facility. Groundwater and sediment were homogenized separately in the anaerobic chamber prior to establishing the enrichments. To prepare enrichments from the LC34 matrices, approximately 6 g of homogenized sediment were added to 160-mL serum bottles. The final volume of groundwater, including amendments, was 150 mL. In lieu of groundwater from the Alamac facility, an anaerobic medium optimized for iron and manganese-reducers was used (see Appendix B). The final volume of groundwater, including amendments, was 150 mL. Bottles were sealed with Teflon stoppers and aluminum seals, effectively trapping an anaerobic headspace, and incubated at 15ºC.

A background control treatment served as a baseline measure of *c*DCE degradation in the absence of MnO_2, and sterile controls with and without MnO_2 were also established. A commercial brand of MnO_2 (Riedel de Hahn) and an amorphous form of MnO_2 (synthesized by Shaw personnel; see Appendix B) were compared to each other to determine whether the form of MnO_2 influenced *c*DCE degradation. With the exception of the commercial MnO_2 treatment and the background controls, the synthesized form of MnO_2 was used in all other treatments. The MnO_2 stock solution was delivered as a slurry.

Two treatments were amended with humic acids (low and high concentrations) in order to assess whether humic acids facilitate electron shuttling between MnO_2 and *c*DCE (Cervantes et al., 2001). Although chelators usually reduce metals such as Mn(IV), several studies have shown that chelators such as nitrolotriacetic acid (NTA) and oxalic acid can solubilize metals, making them more bioavailable (Lovley et al., 1996; Langenhoff et al., 1997). Therefore, two treatments were established to determine whether *c*DCE degradation, coupled to Mn(IV) reduction, could be enhanced via amendments with these two chelators. Two treatments were also prepared to determine whether *c*DCE could be cometabolized. One treatment was amended with acetate, and the other was amended with ethene, which was added to the headspace. Finally, two treatments were established to assess whether manganese reduction was occurring and could be linked to the utilization of other organic substrates besides *c*DCE (acetate or ethene). Formaldehyde, *c*DCE, humic acids, and acetate were added as concentrated stocks to achieve the final concentrations noted in each site's sectional descriptions. For the aerobic treatment, several milliliters of filtered O_2 were added to the headspace. This step was repeated at each sampling event to maintain aerobic conditions in these treatments.

3.0 FIELD AND LABORATORY RESULTS–HILL AIR FORCE BASE–OPERATIONAL UNIT-1

This section presents the methods and results from the field activities and laboratory studies conducted at Operational Unit 1 (OU-1) at Hill Air Force Base (Hill AFB), near Ogden, UT.

3.1 Background Information

Solutions-IES contacted Mr. Kyle Gorder, Environmental Engineer, at Hill AFB regarding the potential for including OU-1 in the study. Mr. Gorder reviewed the site-specific database from the monitor well network at the base, provided information about the history and site conditions, discussed site conditions with the project's principal investigators and helped to focus the investigation on areas of the site with a higher probability of meeting the criteria established for a successful demonstration. The following report was used as the primary source of information about the site:

> *Air Force Center for Environmental Excellence (AFCEE), 1999. Remediation by Natural Attenuation Treatability Study for Operable Unit 1, Hill Air Force Base, Ogden, UT.*

From the data included in the report, it appeared that several locations around the base might be suitable for the project. At that time, Solutions-IES again contacted Mr. Gorder to discuss the plans. Mr. Gorder sent additional data regarding seven monitor well locations of particular interest. Based on that information, it was decided to focus on three wells for further evaluation and sample collection. These wells were U1-089, U1-103 and U1-307.

3.1.1 Location and Layout

As reported in the 1999 AFCEE report:

> "Hill AFB is located in northern Utah, approximately 25 miles north of Salt Lake City and 5 miles south of Ogden. The Base covers 6,666 acres in Davis and Weber Counties. The western boundary of the Base is near Interstate 15, and the southern boundary is near State Route 193. The western, northern, and northeastern perimeters of the Base are bounded by the Davis-Weber Canal, a privately owned irrigation canal…. The Base is located within the Bonneville Basin subsection of the Great Basin section of the Basin and Range physiographic province."
>
> "Hill AFB is located on a plateau that rises approximately 300 feet above the Weber River Valley on the east and approximately 50 to 100 feet above Sunset and Clinton on the west. …The elevation of the terrace surface in the immediate vicinity of the source areas ranges from approximately 4,780 to 4,810 feet msl. The ground surface to the north and east of this area slopes steeply downward to the Weber River Valley. There is approximately 300 feet of relief between the top of the escarpment at OU-1 and the edge of the valley floor to the north. The portion of OU-1 located in the Weber River Valley slopes gradually to the north, and ranges in elevation from 4,500 feet msl at the south edge of the valley to 4,445 feet msl at the north edge of the investigated area."

A general site map is presented in Figure 3-1**,** and a satellite photograph of the study area is presented in Figure 3-2.

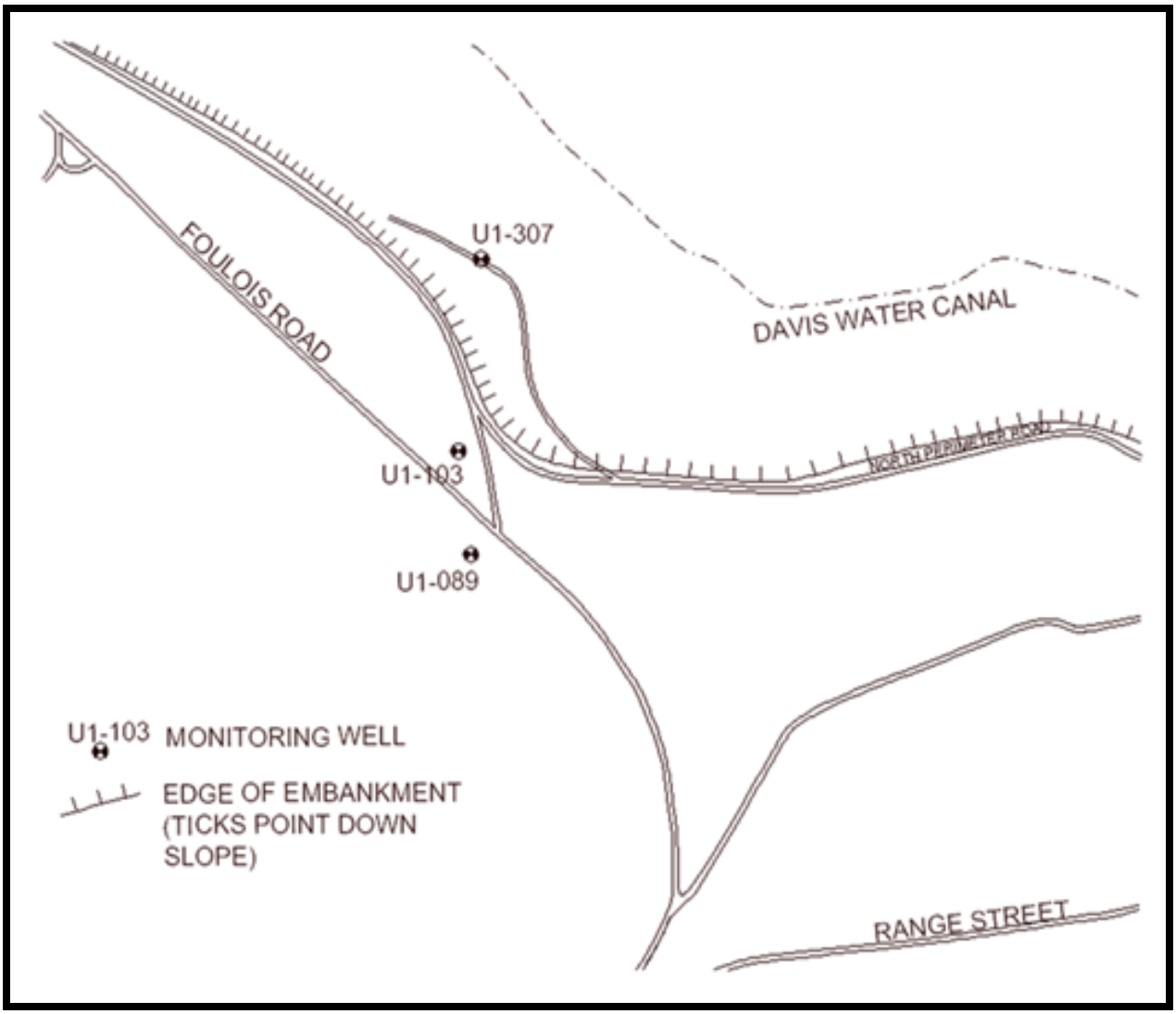

Figure 3-1. Operable Unit 1 Study Area and Site Features, Hill AFB, UT
(from AFCEE, 1999)

Figure 3-2. Operable Unit 1 Study Area Monitor Well Locations, Hill AFB, UT
(Source: Modified from Microsoft TerraServer, Sept, 14, 2003)

3.1.2 Site Contaminants

Table 3-1 provides a summary of historical groundwater conditions in the three selected wells at the site. The data are derived from the OU-1 data set provided by Mr. Kyle Gorder to Solutions-IES. Not all sampling events included all parameters. Where possible, the most recent data are used. The following parameters indicate how Hill AFB fulfills the criteria and why Hill AFB was chosen as a potential MnO_2-enhanced MNA site:

1. The aquifer material is conducive to injection;
2. The depth-to-groundwater is relatively shallow (approximately 26 to 30 ft bgs);
3. Little residual TCE is present, but *c*DCE and VC are present in quantities suitable for this study;
4. A moderate-to-low level *c*DCE stall is noticeable, especially in monitoring well U1-103.
5. The slow degradation of *c*DCE has resulted in offsite migration of *c*DCE. Consequently, an approach that could enhance *c*DCE degradation would have substantial benefits at this site.

6. Co-contaminants found elsewhere on site including BTEX are relatively low or are not present in the study area;
7. Low levels of manganese are present in groundwater;
8. The biogeochemical parameters are variable with some parameters falling within the preferred criteria and some falling outside the preferred criteria. Those falling within the preferred criteria include;
    a) pH
    b) Low nitrate
    c) Low dissolved iron and dissolved manganese
    d) Low methane downgradient
    e) Little to no TCE, and
    f) *c*DCE above 300 μg/L

In addition to the factors cited above, the three wells were selected because of general ease of access, location in relation to the main *c*DCE plume, and a prior comprehensive MNA study at the site (OU-1) indicating naturally attenuation of TCE to *c*DCE (Table 3-1).

TABLE 3-1 HISTORICAL REPRESENTATIVE GROUNDWATER CONDITIONS OU-1 STUDY AREA, HILL AFB, UT				
	Units	**U1-089***	**U1-103****	**U1-307**
Inorganics				
Nitrate/Nitrite – N (Dissolved)	mg/L	<0.1	7.65*/21.1	NA
Iron (Dissolved)	mg/L	14.0/17.5	<.05*/.08	NA
Manganese (Dissolved)	mg/L		.027	NA
Volatile Organic Compounds				
1,1,1-Trichloroethane	µg/L	ND	ND*	ND*
1,1-Dichloroethane	µg/L	10	2.9*	ND*
1,1-Dichloroethene	µg/L	<1	ND*	ND*
cis-1,2-Dichlorothene	µg/L	5.8	335*/10.7	526
trans-1,2-Dichloroethene	µg/L	1.2	1.8*	ND*
Tetrachloroethene	µg/L	<1.0	ND*	ND*
Trichloroethene	µg/L	<1.0	<1.0*/0	ND*
Vinyl Chloride	µg/L	213	ND*	ND*
Ethane	µg/L	NA	NA	NA
Ethene	µg/L	NA	NA	NA
Total BTEX	µg/L	Avg. 23.9	BDL	BDL
Methane	mg/L	NA	NA	NA
Water Quality				
Total Organic Carbon	mg/L	24.8/21	2.62*	NA
pH	SU	6.9	7.01*/7.1	7.42
Dissolved Oxygen	mg/L	0.1/0.17	6.6*/3.7	4.48
Oxidation- Reduction Potential	mV	-209/70	200*/177	361

Notes: 1) * Data from samples collected March 1997; following data collected May 2000
** Data from samples collected March 1997; following data from June 2002
2) ND = Not detected. NR = Not reported in the literature reviewed; date may be available from other sources.
3) BDL = Below Detection Limit

In March 1997, concentrations of TCE were reported as high as 490 µg/L in monitoring well U1-085. During the same period, *c*DCE was detected at concentrations as high as 7,083 µg/L in monitoring well U1-071. These two wells are located east of our area of interest and are central to the main plume in OU-1.

3.1.3 Site Hydrogeology and Plume Geometry

The following information is excerpted from the 1999 AFCEE report: "In the OU-1 area, flow in the surficial aquifer is generally to the north and northeast. …The subsurface features in the vicinity of OU-1 and downgradient areas are consistent with the regional setting of the Provo and Alpine Formations, consisting of fluvial-deltaic deposits of clay, silt, sand and gravel. In general, deposits in the OU-1 area show a downward fining trend. A surficial cap, 2 to 5 feet thick, of silty sand with occasional bentonite intervals covers Landfills 3 and 4 and the LNAPL plume area. The unconsolidated deposits underlying the surficial cap in the on-Base portion of OU-1 are described below:

> "Upper Sand and Gravel Unit – consists of fine to coarse to silty sands interbedded with gravel and some clay stringers. This unit ranges in thickness from 0 to 62 feet and has an average thickness of approximately 30 feet. This unit (the Provo Formation) comprises the shallow aquifer underlying the on-Base terrace."
>
> "Silty Clay Unit" – consists primarily of silty clay interbedded with fat clays and silts containing thin stringers of very fine sand (0 to 10 inches thick). This unit (the Alpine Formation) is potentially 200 feet thick and appears to be saturated from its top to the depth it has been penetrated by drilling (approximately 150 to 200 feet)".
>
> "The depth to groundwater is approximately 15 to 30 feet bgs in the on-Base OU-1 area, and ground water emerges at the surface in the form of seeps and springs along the escarpment north of the on-Base terrace."

The construction of the monitor wells of interest and depth to groundwater measured in March 1997 are reported in Table 3-2.

TABLE 3-2
WELL CONSTRUCTION INFORMATION
OU-1 STUDY AREA, HILL AFB, UT

Well ID	Total Depth (ft)	Screen Interval (ft)	Depth to Water (ft bgs)
U1-089	34.0	24.0-34.0	24.51
U1-103	40.0	23.0-33.0	29.11
U1-307	NA	NA	Surface Seep

Notes: Depth to water measured March 1997
NA = not applicable

The groundwater levels and flow directions in the unconfined aquifer at OU-1 (March 1997) are shown in Figure 3-3. The hydraulic gradient at the site ranges from 0.007 to 0.04 ft/ft, depending on the exact location within OU-1, and averages approximately 0.015 ft/ft across the site. The hydraulic conductivity at the site varies from 103 to 113 ft/day. Although calculations using these data suggest a high groundwater flow velocity, practical experience and site-specific conditions result in a prevailing estimate of approximately 131 ft/yr.

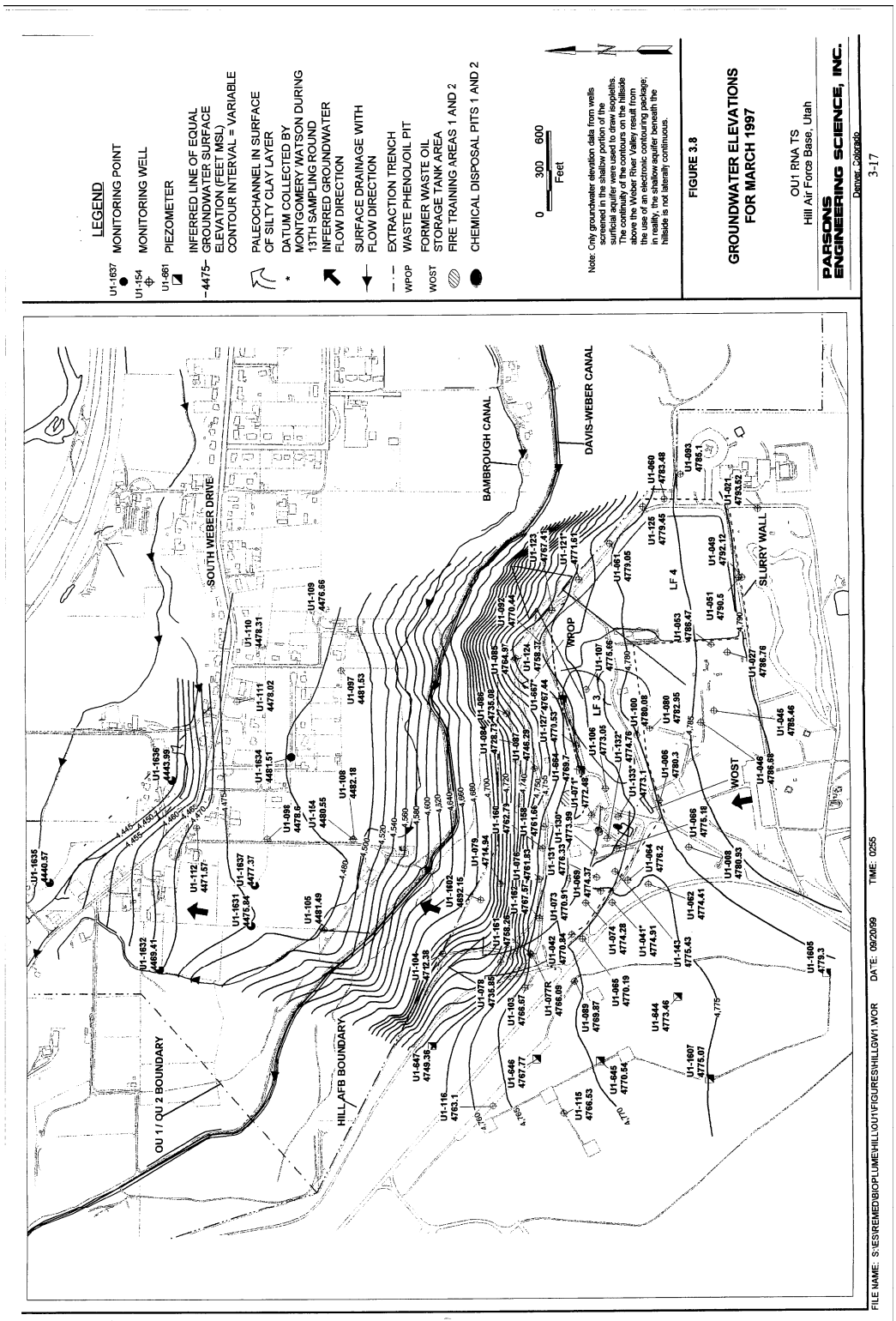

Figure 3-3. March 1997 Potentiometric Surface and Groundwater Flow Direction at OU-1, Hill AFB, UT (AFCEE, 1999)

3.2 Biogeochemical Characterization

Sample collection and groundwater monitoring activities were conducted by Solutions-IES on February 5-6, 2007, in accordance with the site-specific Sampling and Analysis Plan. Sediment samples (SB-1-U1-103) were collected from near monitoring well U1-103 utilizing hollow stem auger drilling procedures (ASTM D 1586-84) conducted by the local office of ConeTec, Inc. of West Berlin, NJ. Cores from the depth intervals at 26 to 28, 28 to 30, 30 to 32 ft and 32 to 34 ft bgs were collected in jars and sent to Shaw Lab.

Groundwater samples were collected from monitoring wells U1-089, U1-103 and U1-307 using dedicated low-flow bladder sampling pumps (U1-089 and U1-103) or a submersible pump (U1-307). Field parameters (pH, conductivity, temperature, and ORP) were measured through a flow-through cell during the low-flow sampling process. Additional volume from well U1-103 was collected for use in the microcosm studies.

Locations of the three monitor wells within the CVOC plume at the OU-1 site is shown in Figure 3-4. Table 3-3 summarizes the field and current groundwater laboratory results for each of the three representative wells along the OU-1 groundwater plume sampled during the February 2007 event. Monitoring results from February 2007 were generally consistent with historical information. The groundwater was aerobic with low levels of TOC, dissolved iron and manganese, and *c*DCE. The ___ day natural oxidant demand (NOD) of the sandy material was 5.25 g/kg dry soil; the NOD of the clayey deeper material was 15.65 kg/dry soil. These measurements indicate the aquifer material does have some appreciable NOD and MnO_4 injection could be used to distribute MnO_2 throughout the treatment zone, if required.

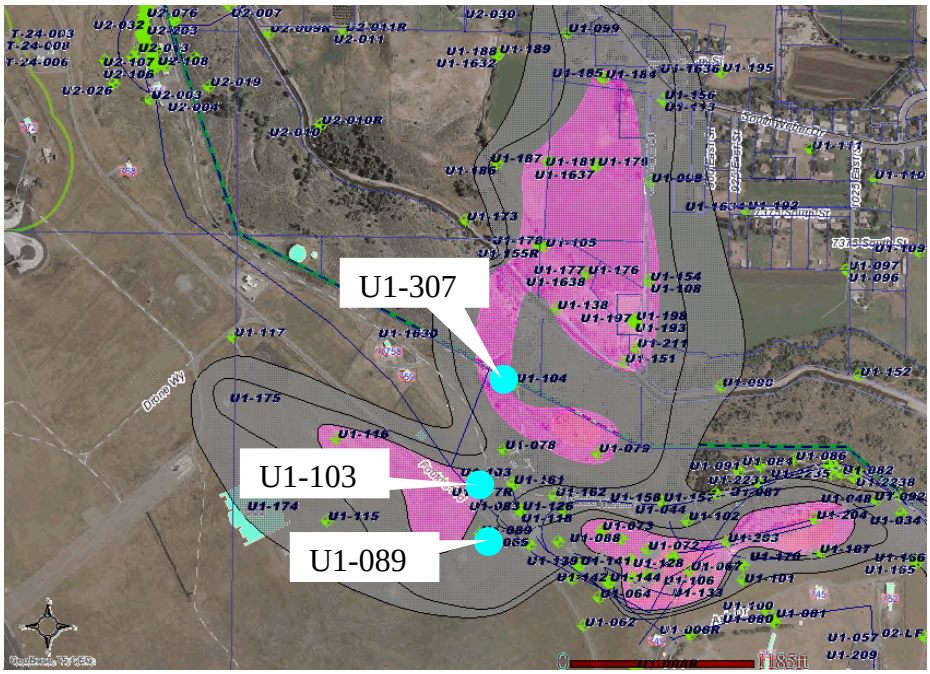

Figure 3-4. Sampling Locations within the OU-1 Plume
(Plume map provided by Mr. Kyle Gorder Hill AFB)

TABLE 3-3
SUMMARY OF SITE CHARACTERIZATION DATA (FEB. 5 - 6, 2007)
OU-1 STUDY AREA, HILL AFB, UT

		U1-089	U1-103	U1-307
Volatile Organic Compounds (EPA Method 8260B)				
Benzene	µg/L	<1.0	<1.0	<1.0
Chlorobenzene	µg/L	320	<1.0	<1.0
1,3-Dichlorobenzene	µg/L	5.1	<1.0	<1.0
1,4-Dichlorobenzene	µg/L	31	<1.0	<1.0
Chloroethane	µg/L	<5.0	<5.0	<5.0
Isopropylbenzene	µg/L	<1.0	<1.0	<1.0
sec-Butylbenzene	µg/L	<1.0	<1.0	<1.0
Naphthalene	µg/L	<1.0	<1.0	<1.0
Tetrachloroethene	µg/L	<1.0	<1.0	<1.0
Trichloroethene	µg/L	<2.0	<2.0	<2.0
trans-1,2-Dichloroethene	µg/L	<2.0	1.5[J]	0.67[J]
cis-1,2-Dichloroethene	µg/L	12	60	100
1,1-Dichloroethene	µg/L	<1.0	0.90[J]	<1.0
Vinyl chloride	µg/L	67	<2.0	0.97[J]
Light Hydrocarbon Gases (Method AM20GAX)				
Ethane	µg/L	0.10	<0.01	<0.01
Ethene	µg/L	2.44	<0.01	0.05
Methane	µg/L	678.6	0.6	1.3
Metals (ICP)				
Iron (Total)	mg/L	0.59	1.3	0.34
Iron (Dissolved)	mg/L	0.35	0.12	0.18
Manganese (Total)	mg/L	0.62	0.033	0.0037[J]
Manganese (Dissolved)	mg/L	0.6	0.010	0.0030[J]
Anions				
Nitrate (Method SM4500)	mg/L	0.018[J]	4.1	2.3
Sulfate (Method 9056)	mg/L	17	30	42
Chemical Oxygen Demand (Method SM5220 D)				
Chemical Oxygen Demand	mg/L	20[J]	30[J]	<50
Total Organic Carbon (Method 415.1)				
Total Organic Carbon	mg/L	6.84	2.66	1.89
Field Measurements				
Temperature	C	12.6	12.7	9.5
pH	SU	5.74	7.68	6.2
Specific Conductance	µS/cm	14.4	17.8	19.1
Dissolved Oxygen	mg/L	0.9	4.05	7.9*
Redox Potential	mV	52.9	223.1	103.8
Turbidity	NTU	3.99	21.4	7.07

* = Water coming from recovery sump with pump running at all times.

J = Estimated value between the Reporting Limit and the Method Detection Limit.

3.3 Microcosm Experimental Design and Results

Groundwater from monitor well U1-103 and sediment from SB1-U1-103 cores from the depth intervals at 26 to 28, 28 to 30, and 30 to 32 ft bgs were homogenized separately inside the anaerobic chamber. Sediment from the 32 to 34 ft bgs depth interval consisted of sandy material, whereas the other sediment cores consisted of clayey material. A separate treatment was established using the sandy material; all other treatments contained clay. A sample of composited sandy material and a sample of clayey material were shipped to the Shaw Laboratory in Knoxville, TN for analysis of NOD.

Approximately 15 grams of homogenized sediment were added to 60-mL serum bottles. The final volume of groundwater, including amendments, was 50 mL. Bottles were sealed with Teflon stoppers and aluminum seals and incubated at 15ºC. Ten treatments, prepared in triplicate, were established to evaluate *c*DCE degradation under various conditions (Table 3-4). Formaldehyde, *c*DCE, humic acids, and acetate were added as concentrated stocks to give the final concentrations noted in Table 3-4.

TABLE 3-4
SUMMARY OF MICROCOSM TREATMENTS ON MATRICES FROM OU-1, HILL AFB, UT

Treatment Descriptions	**Soil (30%)**	***c*DCE (2 ppm)**	**Formal-dehyde (1.5%)**	**MnO_2 (25 mM)**	**Humic Acids (2 ppm)**	**Acetate (200 ppm)**	**O_2 (Added to Headspace)**
Sterile Control Without MnO_2	**X**	**X**	**X**				
Sterile Control With MnO_2	**X**	**X**	**X**	**X**			
Unamended	**X**						
Background Control	**X**	**X**					
Commercial MnO_2	**X**	**X**		**X**			
Synthesized MnO_2 (Clay microcosms)	**X**	**X**		**X**			
Synthesized MnO_2 (Sandy microcosms)	**X**	**X**		**X**			
Aerobic	**X**	**X**		**X**			**X**
Humic Acid Amendment	**X**	**X**		**X**	**X**		
Cometabolism (*c*DCE and Acetate)	**X**	**X**		**X**		**X**	

Aqueous samples were collected over the course of five months and analyzed for VOCs (EPA Method 8260). Dissolved manganese (Mn^{2+}) was analyzed at 0 weeks and 2 months via EPA Method SW-846 6010.

The analytical data for the Hill AFB microcosm study are included in Appendix C1 and C2. In Figure 3-5, *c*DCE is represented as the percentage remaining relative to the sterile controls that did not contain MnO_2 (i.e., the average of the triplicate values for each treatment was divided by the average of the triplicate values for the sterile control treatment that did not contain MnO_2). In Figure 3-6, the dissolved manganese values are averages of the triplicate values for each treatment for each timepoint.

3.4 Summary of Results

Groundwater used to prepare the microcosms contained little TOC (2.6 mg/L), virtually no dissolved manganese (.003 mg/L), a low concentration of *c*DCE (0.1 mg/L) and no VC. Ambient groundwater conditions at the site were generally oxidative.

The microcosm results are shown in Figures 3-5 and 3-6. Overall, *c*DCE degradation was very limited in the microcosm incubations. Under anaerobic conditions, degradation of *c*DCE was not enhanced by the addition of MnO_2, humic acids, or acetate relative to the background control treatment. *c*DCE loss relative to controls during the 5-month incubation was greatest (~70%) in the aerobic treatment suggesting some potential for aerobic biodegradation of *c*DCE in the downgradient portion of the plume at OU-1.

The results of the metals analysis showed that the greatest reduction of MnO_2 (i.e., chemical reduction from Mn^{4+} to Mn^{2+}) occurred in the sterile controls amended with MnO_2. Reduction of *in situ* Mn(IV) also occurred in the sterile control that was not amended with MnO_2. Commercial formaldehyde added to the sterile controls contains low concentrations of formic acid, which can reduce Mn(IV). Although there appears to have been some reduction of Mn(IV) in the other treatments, reduction cannot be clearly linked to anaerobic *c*DCE oxidation. Stoichiometrically, the dissolved manganese concentrations exceed the predicted Mn(II) concentrations that would result from reduction of Mn(IV) coupled solely to the anaerobic oxidation of *c*DCE (analytical data in Appendix C). Therefore, the increase in soluble manganese in several treatments is most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources, not the result of utilization by microbial populations present in the matrices.

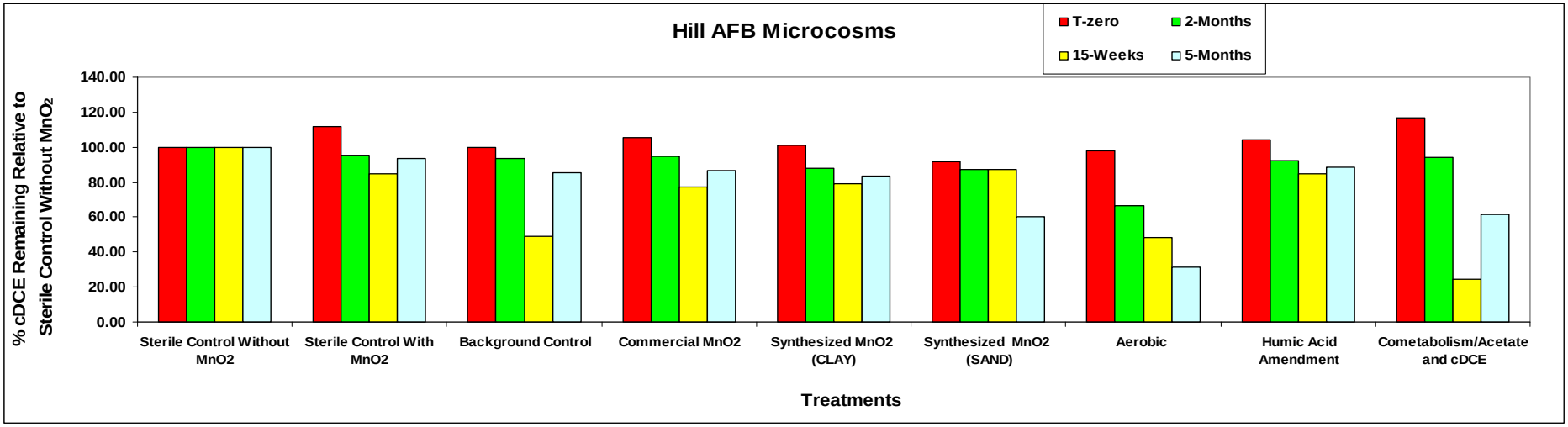

Figure 3-5. Hill AFB Microcosm Results for *c*DCE Measurements

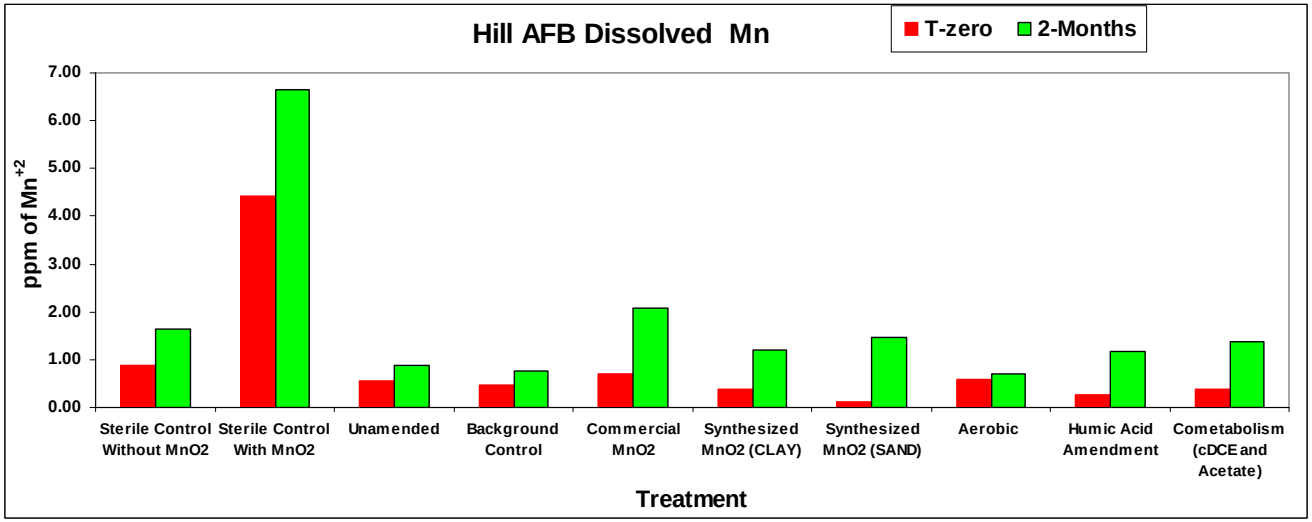

Figure 3-6. Hill AFB Microcosm Results for Dissolved Manganese Measurements

4.0 FIELD AND LABORATORY RESULTS – Navy Base Kitsap (former Naval Undersea Warfare Center), Division Keyport, Keyport, WA

This section presents the methods and results from the field activities and laboratory studies conducted at Operational Unit 1 (OU-1) of Navy Base Kitsap former Naval Undersea Warfare Center (NUWC), near Keyport, WA. This site is alternatively referred to as NUWC Keyport and Navy Base Keyport.

4.1 Background Information

Solutions-IES obtained several reports prepared for the Navy by the United States Geological Survey (USGS) regarding the soil and groundwater conditions at the Navy Base Kitsap at Keyport (formerly the Naval Undersea Warfare Center, Keyport Division) Keyport, WA. These reports included:

> *Dinicola, R.S. 2003. Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA. Open-File Report 03-344, USGS, Reston, VA, June 2001.*
>
> *Dinicola, R.S. 2006. Continued Biodegradation of Chloroethene Compounds in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA. USGS Scientific Investigations Report, 2006-5056, June 2006.*
>
> *Dinicola, R.S. and R.L. Huffman, 2003. Selected Natural Attenuation Monitoring Data, Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, WA. Open-File Report 2004-1330, USGS, Reston, VA, June 2003*

Solutions-IES then contacted Mr. Douglas Thelin (360-396-0206, douglas.thelin@navy.mil) at the base regarding the potential for including Operable Unit 1 (OU-1) in the study. After expressing his willingness to participate, Mr. Thelin recommended contacting Sealaska Environmental Services, LLC to assist with the logistics of collecting samples at the base.

4.1.1 Location and Layout

As reported in Dinicola, 2001:

> "The NUWC is located mostly on a small peninsula in Kitsap County, Washington, in an extension of Puget Sound called Liberty Bay. The 9-acre former landfill at OU-1 is on the narrow strip of connecting land and is adjacent to some tidal flats that are an extension of Dogfish and Liberty Bays. The OU-1 landfill is unlined at the bottom and is constructed in a former marshland. The landfill was the primary disposal area for domestic and industrial wastes generated by NUWC Keyport from the 1930s through 1973. Paints, thinners, solvents, acids, dried sludge from a wastewater-treatment plant, and other industrial wastes were disposed of at various locations in the landfill. The most concentrated disposal area for waste paints and solvents was at the southern end of the landfill."

Figure 4-1 shows the overall layout of the former NUWC Keyport (Navy Base Kitsap) base.

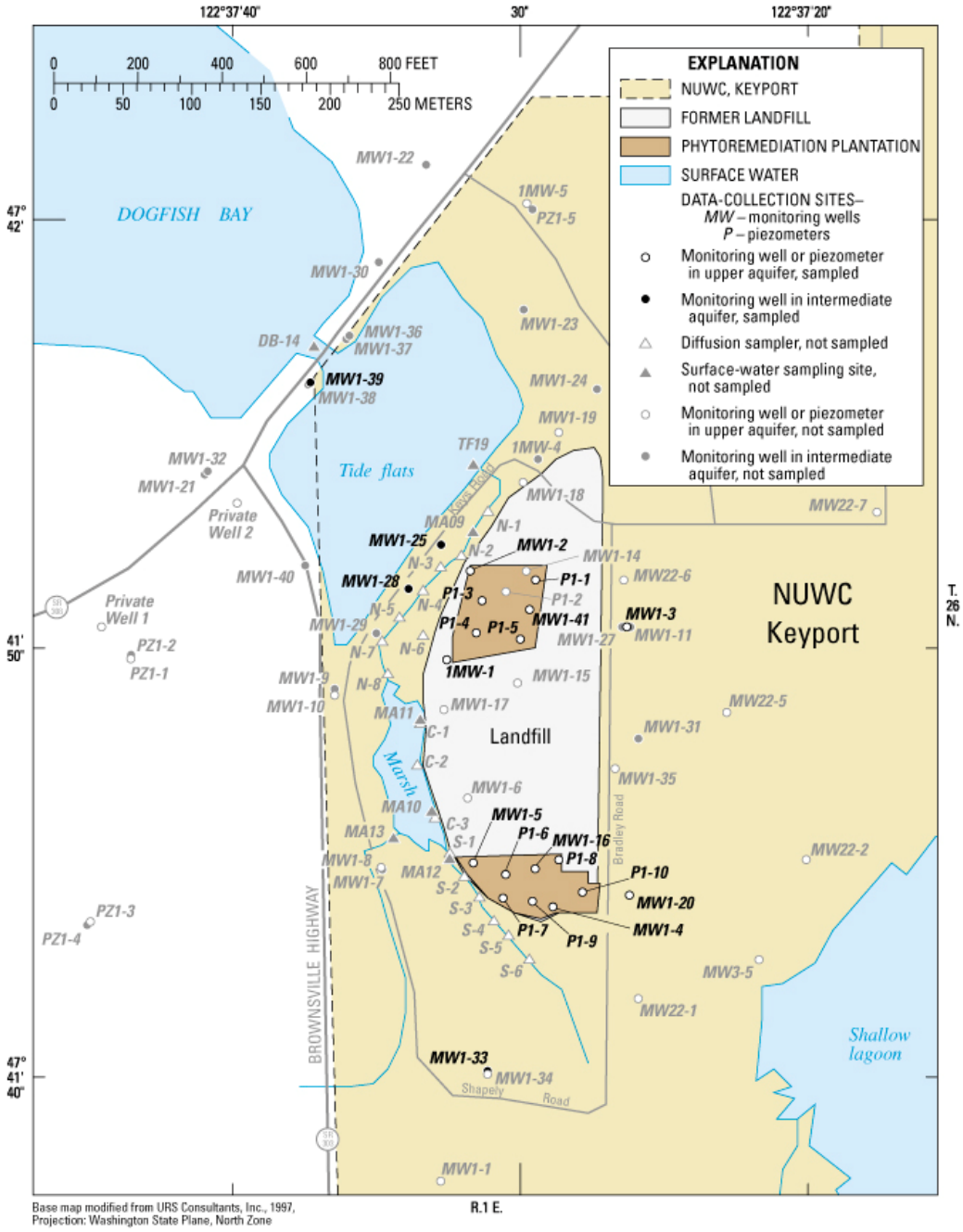

Figure 4-1. Former Naval Undersea Warfare Center, Operable Unit 1 Site Features (Dinicola, 2003)

4.1.2 Site Contaminants

Table 4-1 provides a historical summary of groundwater conditions in selected wells and surface water sampling areas at the site. The data were derived from the reports cited above. Not all sampling events included all parameters. The data cover a three-year span from 2001 to 2004. Where possible, the most recent data are shown.

The following parameters indicate how Navy Base Kitsap fulfills the criteria as a potential MnO_2-enhanced MNA site:

1. The aquifer material is conducive to injection;
2. The depth-to-groundwater is relatively shallow (approximately 4 to 7 ft. bgs);
3. Little residual TCE is present; however, *c*DCE and VC are present in quantities suitable for this study;
4. A moderate-to-low level *c*DCE stall is noticeable, especially in the upgradient well, P1-4;
5. Co-contaminants such as BTEX are in very low concentrations or are not present in the study area;
6. Low levels of manganese are present in groundwater;
7. The biogeochemical parameters are variable, with some parameters falling within the preferred criteria and some falling outside the preferred criteria. Those falling within the preferred criteria include;
    a) pH
    b) Low-to-moderate nitrate concentrations
    c) Low-to-moderate dissolved iron and dissolved manganese concentrations
    d) Low methane downgradient
    e) Little to no TCE, and
    f) *c*DCE above 300 μg/L.

In addition to the above factors, Bradley et al. (1998a) observed enhanced mineralization of radiolabeled DCE in microcosm constructed with sediment collected near location N-2 at Navy Base Kitsap and amended with MnO_2. These prior laboratory studies suggested that there was a good potential that MnO_2 addition could stimulate DCE degradation.

Four locations were chosen from Navy Base Kitsap because of the above referenced factors, as well as for logistical reasons including: general ease of access, location in relation to the main *c*DCE plume, and a prior comprehensive MNA study at the landfill site (OU-1) indicating naturally attenuation of TCE to *c*DCE. The four locations are shown on Figure 4-2.

Figure 4-2. Navy Base Kitsap Operable Unit 1 Monitor Well Locations
(Source: Modified from Google™ Earth)

Table 4-1 provides a historical summary of groundwater conditions in selected monitoring wells and passive diffusion samplers installed at surface water sampling location N-2. Data from the June 2004 sampling event reported concentrations of TCE as high as 12 µg/L in monitoring well MW1-2. However, *c*DCE was detected at concentrations up to 2,300 µg/L in monitoring well P1-4 during the same sampling event

TABLE 4-1 HISTORICAL GROUNDWATER CONDITIONS OU-1, NAVY BASE KITSAP, WA					
	Units	**P1-3**	**P1-4**	**MW1-2**	**N-2**
Inorganics					
Nitrate/Nitrite – N (Dissolved)	mg/L	<.06	<.06	<.06	NR
Iron (Dissolved)	mg/L	29	4.1	0.29	NR
Manganese (Dissolved)	mg/L	2.0	0.43	0.10	NR
Volatile Organic Compounds					
1,1,1-Trichloroethane	µg/L	<1.0	<130	<50	<2.0
1,1-Dichloroethane	µg/L	0.38	<130	<50	0.76
Chloroethane	µg/L	6.9	<270	<100	<4.0
1,1-Dichloroethene	µg/L	<1.0	<130	<50	<2.0
cis-1,2-Dichlorothene	µg/L	15	2,300	630	83
trans-1,2-Dichloroethene	µg/L	2.4	29	13	3.4
Tetrachloroethene	µg/L	<1.0	<130	<50	<2.0
Trichloroethene	µg/L	<1.0	<130	12	1.6
Vinyl Chloride	µg/L	41	370	110	38
Ethane	µg/L	33	7.1	5.9	3.6
Ethene	µg/L	27	29	1.1	12
Total BTEX	µg/L	2.4	BDL	BDL	BDL
Methane	mg/L	NA	NA	NA	290
Water Quality					
Total Organic Carbon	mg/L	45	8.0	45	NR
Dissolved Organic Carbon	mg/L	19	7.0	6.0	NR
pH	SU	6.8	6.9	6.5	NR
Dissolved Oxygen	mg/L	0.1	0.1	0.1	NR
Oxidation-Reduction Conditions	mV	-78	Iron-Reducing	+27	NR

Notes:
1) VOC data reported represents samples collected June 17, 2004; inorganics and metals collected June 18, 2003; TOC collected June 11, 2002.; pH and ORP collected June 12, 2001.
2) NR = Not reported in the literature reviewed. May be available from other sources.
3) BDL = Below detection limit
4) NA = Not Analyzed

4.1.3 Site Hydrogeology and Plume Geometry

"Chlorinated VOCs are present in the upper and intermediate aquifers and in surface water at OU-1. Ground water beneath OU-1 occurs within a series of aquifers that are composed of permeable sand, gravel, or fill materials separated by finer grained silt or clay layers. Contamination at OU-1 is known to occur only in about the top 60 feet of the unconsolidated deposits in the hydrogeologic units referred to as the unsaturated zone, the upper aquifer, the middle aquitard and the intermediate aquifer. Ground water in the unconfined upper aquifer generally flows from east to west towards Dogfish Bay. Ground water in the predominantly confined intermediate aquifer generally flows from south and west to beneath the landfill, and then to the northwest towards Dogfish bay. Two perennial freshwater creeks drain the marsh adjacent to the landfill" (Dinicola, 2003).

"The upper aquifer consists primarily of sand or silty-sand and gravel with localized zones of marsh, estuary, and tide flat deposits. The unit is nearly continuous across OU-1 and ranges from about 4 to 22 feet thick. The permeability of the upper aquifer is variable and scattered deposits of finer grained materials indicate that preferential flow pathways are likely over short distances. Estimated hydraulic conductivity for the upper aquifer ranges from 0.2 to 4.1 ft/d" (Dinicola, 2006).

The construction details of the monitor wells of interest and depth to groundwater measured on June 16, 2004 are presented in Table 4-2.

TABLE 4-2
WELL CONSTRUCTION INFORMATION
OU-1, NAVY BASE KITSAP, WA

Well ID	Total Depth (ft)	Screen Interval (ft)	Depth to Water (ft bmp)
MW1-2	18.5	12.5 – 17.5	9.75
P1-3	15.0	10 – 15	9.57
P1-4	15.0	10 – 15	8.20

Note: 1) Depth to water measured June 17, 2004
2) bmp = below measuring point

The upper-aquifer water levels and flow directions beneath the northeastern one-third of the landfill are influenced by tidal changes" (Dinicola, 2006). Figure 4-3a and Figure 4-3b show the ground water levels and flow directions in the unconfined and confined aquifer zones, respectively, during low tide at OU-1.

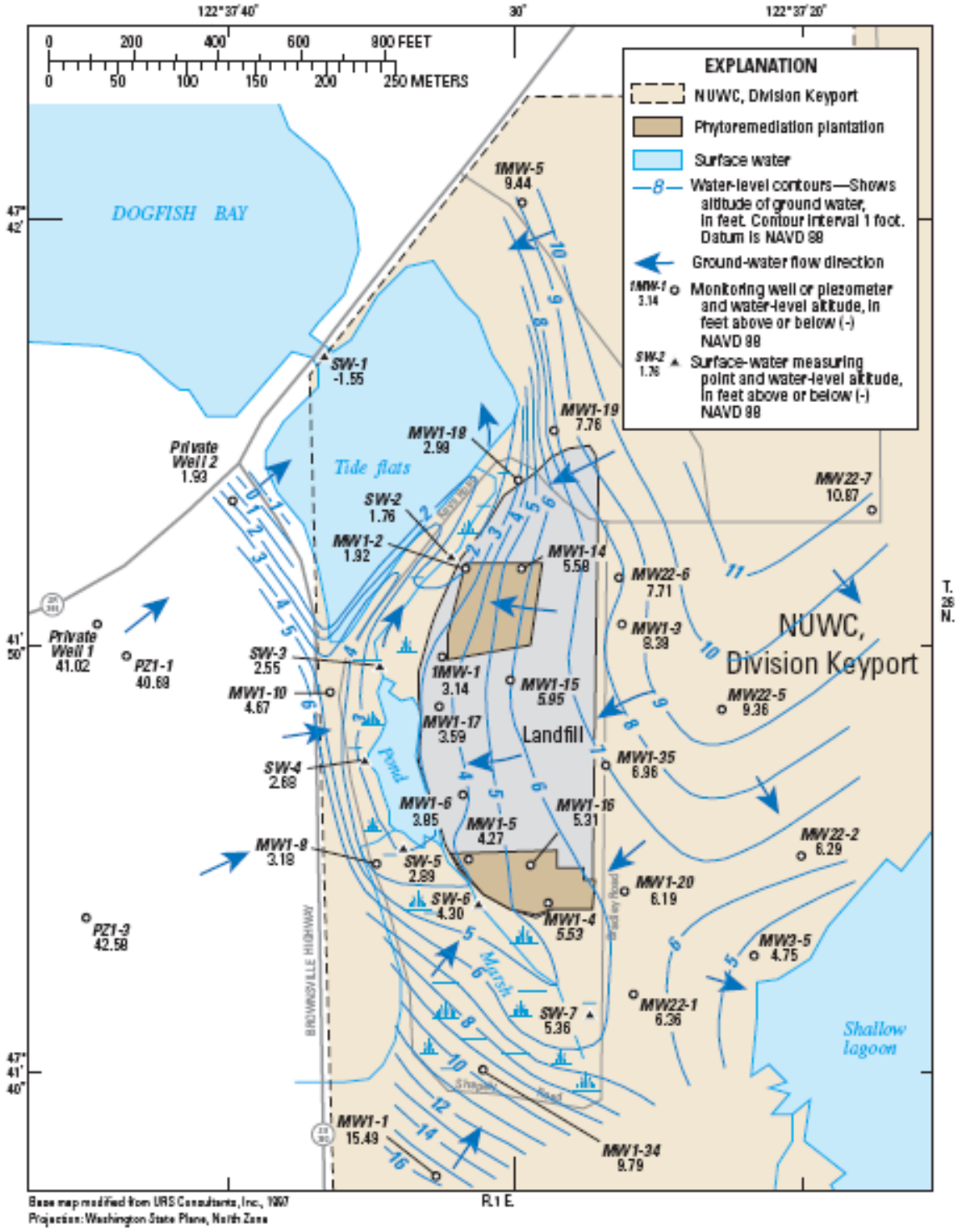

Figure 4-3a. Water Table Elevation and Groundwater Flow Map, Unconfined Surficial Aquifer, Low Tide, September 1996
(Dinicola, 2006)

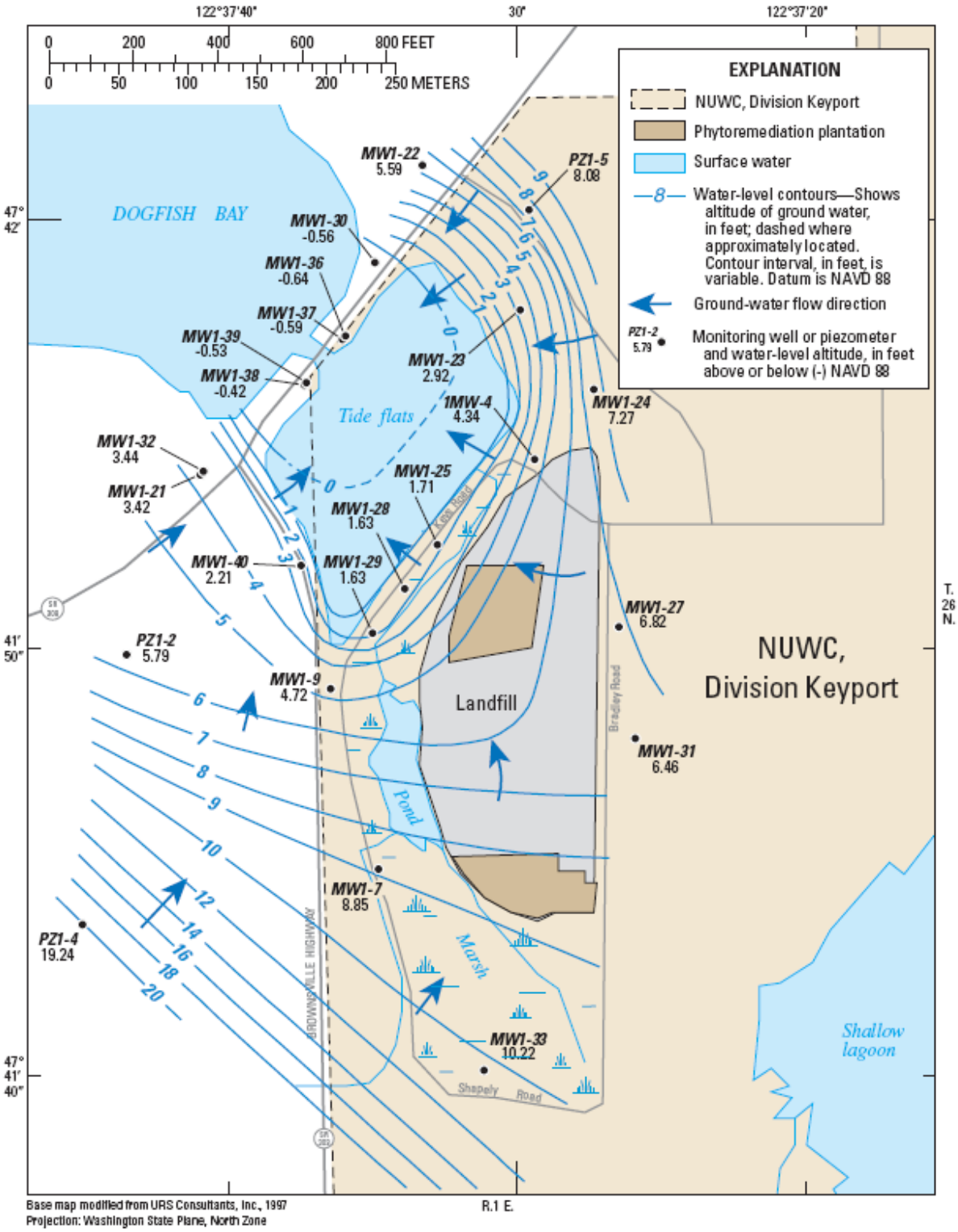

Figure 4-3b. Potentiometric Surface, Confined Intermediate Aquifer, Low Tide, September 1996 (Dinicola, 2006)

4.2 Biogeochemical Characterization

The Sampling and Analysis Plan for this site described steps to collect aquifer sediment from 6 to 14 ft bgs adjacent to monitoring well P1-4 and shallow soil from near surface water seep N-2 (Figure 4-2). Sample collection and groundwater monitoring activities were conducted by Sealaska Environmental Services (Sealaska) of Bellevue, WA on November 29, 2006. Sealaska used their Geoprobe to try to penetrate to the desired depths, but encountered refusal at 2 to 3 ft bgs at multiple locations near well P1-4. Therefore, soils were not collected from beneath the landfill. Groundwater samples were collected from monitoring wells MW1-2, P1-3 and P1-4 using a peristaltic pump with disposable tubing. Field parameters (pH, conductivity, temperature, and ORP) were measured through a Horiba flow through cell during the low-flow sampling process. The field and laboratory results for each location or well that were sampled are presented in Table 4-3.

Because of the difficulty obtaining soils from beneath the landfill near P1-4, soil and water samples for the microcosm study were collected from the vicinity of the groundwater seep at surface water sampling location N-2 (Figure 4-4). The soil sample was collected using a hand auger advanced to 3 ft bgs. Shallow groundwater was collected from a short piece of ¾-inch well casing placed in the same hand auger boring. This seep was immediately downgradient of the OU-1 landfill and the Northern Plantation phytoremediation treatment plot. In 2004, 83 µg/L of *c*DCE and 38 µg/L VC were reported at this location. As shown in Table 4-3, CVOCs were not detected in the groundwater samples collected for this project. However, water samples collected at N-2 did contain trace levels of benzene, chlorobenzene and naphthalene. Groundwater in MW1-2, which was upgradient of the seep, was reported to contain both *c*DCE and VC and conditions generally beneath the landfill appeared more conducive to anaerobic reductive dechlorination. Water samples contained 1.2 mg/L dissolved iron and 1.0 mg/L dissolved manganese with ORP = -38 mV indicating moderately reducing conditions appropriate for this study. However, the dissolved oxygen concentration in the field sample was ~ 5 mg/L suggesting mixing with surface water. Based on these results, it appeared there was a reasonable potential for *c*DCE degradation in samples collected at N-2 and the samples from N-2 were processed for use in the microcosm studies.

The 27-day NOD of the homogenized sediment used in the microcosms was 125 g/kg dry soil indicating this material has a relatively high NOD and MnO_4 injection could be used to distribute MnO_2 throughout the treatment zone, if required.

Figure 4-4. N-2 Sample Location, Navy Base Kitsap, WA

TABLE 4-3
SUMMARY OF SITE CHARACTERIZATION DATA (NOV. 29, 2006)
OU-1, NAVY BASE KITSAP, WA

		N-2	MW1-2	P1-3	P1-4
Volatile Organic Compounds (EPA Method 8260B)					
Benzene	µg/L	1.2	<1	2.3	0.71[J]
Chlorobenzene	µg/L	3.1	<1	11	<1
1,3-Dichlorobenzene	µg/L	<1	<1	0.84[J]	<1
1,4-Dichlorobenzene	µg/L	<1	<1	7.8	<1
Chloroethane	µg/L	<5	<5	4.0[J]	<5
Isopropylbenzene	µg/L	<1	<1	2.3	<1
sec-Butylbenzene	µg/L	<1	<1	1.7	<1
Naphthalene	µg/L	2.6	<1	<1	<1
Tetrachloroethene	µg/L	<1	<1	<1	<1
Trichloroethene	µg/L	<2	13	<2	<2
trans-1,2-Dichloroethene	µg/L	<2	15	<2	31
cis-1,2-Dichloroethene	µg/L	<1	560	<1	1,600
1,1-Dichloroethene	µg/L	<1	2.0	<1	4.1
Vinyl chloride	µg/L	<2	95	<2	330
Light Hydrocarbon Gases (Method AM20GAX)					
Ethane	µg/L	NA	1.10	15.0	29.0
Ethene	µg/L	NA	0.079	0.08	84.0
Methane	µg/L	NA	2.90	14,000	4,400
Metals (ICP)					
Iron (Total)	mg/L	51	0.91	52	4.3
Iron (Dissolved)	mg/L	1.2	0.68	0.94	3.6
Manganese (Total)	mg/L	1.5	0.11	2.9	0.39
Manganese (Dissolved)	mg/L	1.0	0.11	2.7	0.39
Anions					
Nitrate (Method SM4500)	mg/L	0.15	0.023	0.11	0.035[J]
Sulfate (Method 9056)	mg/L	21	4.0	8.7	6.9
Organic Carbon (Method 415.1)					
Total Organic Carbon	mg/L	8.89	6.08	25.1	7.16
Field Measurements					
		N-2	**MW1-2**	**P1-3**	**P1-4**
Temperature	C	9.3	11.7	12.2	12.3
pH	SU	6.04	6.38	6.27	6.72
Specific Conductance	µS/cm	1070	1510	1590	1140
Dissolved Oxygen	mg/L	5.1	0.5	0.8	0.8
Redox Potential	mV	-38	-4	-92	-89
Turbidity	NTU	850	4	19	7

J = The estimated value is between the Reporting Limit and the Method Detection Limit.

4.3 Microcosm Experimental Design and Results

Sediment from the hand-auger boring near surface water monitoring location N-2 (depth interval 1 to 3 ft bgs) and groundwater from the temporary well emplaced in the boring were homogenized separately in the anaerobic chamber prior to establishing the microcosms. A sub-sample of the homogenized soil was shipped to Shaw Laboratory in Knoxville, TN for NOD analysis. Approximately 30 g of homogenized sediment were added to 160-mL serum bottles. The final volume of groundwater, including amendments, was 140 mL (Section 2.4.2). The treatments prepared in these microcosm bottles are summarized in Table 4-4.

TABLE 4-4
SUMMARY OF MICROCOSM TREATMENTS ON MATRICES FROM NAVY BASE KITSAP, WA

Treatments	Soil (~20%)	*c*DCE (2 ppm)	Formal-dehyde (1.5%)	MnO_2 (25 mM)	Humics (2 ppm)	O_2 (Added to headspace)
Sterile controls without MnO_2	X	X	X			
Sterile controls with MnO_2	X	X	X	X		
Unamended	X					
Background controls	X	X				
Commercial MnO_2	X	X		X		
Synthesized MnO_2	X	X		X		
Aerobic	X	X		X		X
Humic acids	X	X		X	X	

Aqueous samples were collected over the course of nine months and analyzed for VOCs (EPA Method 8260). After two months, one bottle from each treatment was sampled for dissolved manganese, and all bottles were sampled for dissolved manganese after 8 months (EPA Method SW-846 6010).

The analytical results for the Naval Base Kitsap microcosm study are included in Appendix C3 and C4. In Figure 4-5, *c*DCE is represented as the percentage remaining relative to the sterile controls that did not contain MnO_2 (i.e., the average of the triplicate values for each treatment was divided by the average of the triplicate values for the sterile control treatment that did not contain MnO_2). Some treatments were re-spiked with *c*DCE when the *c*DCE was depleted. See Appendix C3 for additional details. Re-spiked values were not graphed for the purpose of comparing when complete loss of *c*DCE was observed across treatments. In Figure 4-6, the dissolved manganese values are represented as single measurements (for 2-month timepoint) or averages of the triplicate values for each treatment (8-month timepoint) for each timepoint.

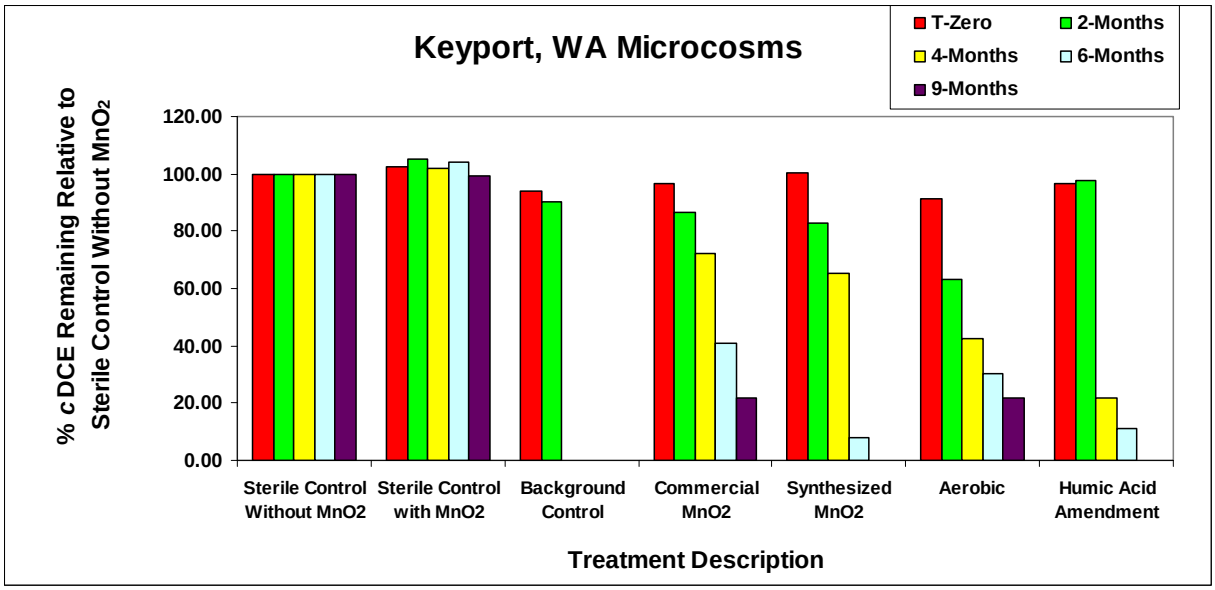

Figure 4-5. Navy Base Kitsap Microcosm Results for *c*DCE Measurements

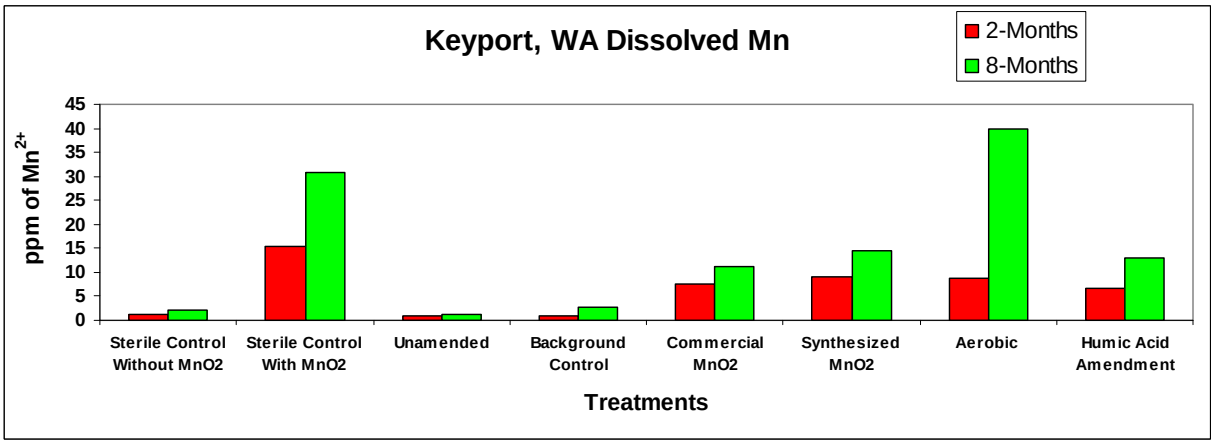

Figure 4-6. Navy Base Kitsap Microcosm Results for Dissolved Manganese Measurements

4.4 Summary of Results

*c*DCE was completely depleted in the background controls over a 4-month incubation period. By seven months, *c*DCE was completely depleted in the synthesized MnO_2 and humic acid treatments (see Appendix C3). The aerobic treatment also demonstrated significant loss (~80%) relative to the controls. No VC was reported in the field sample from temporary seep well N-2, but there was evidence of approximately 8.9 mg/L TOC in this water and the ORP was in the reducing zone
(-38 mV). VC was detected in the background treatment, as well as the commercial, synthesized and humic acid treatments, suggesting reductive dechlorination (data not included). The addition of humic acids appears to have had an early effect on *c*DCE degradation. Almost 80% of the *c*DCE was degraded within 4 months. Given the assumption that reductive dechlorination is the dominant process removing *c*DCE in site material, the humic acids probably served as an additional electron donor. The addition of MnO_2 appears to have inhibited reductive

dechlorination based on the lag period associated with treatments receiving MnO_2 compared to the background control treatment.

The results of the metals analysis showed a significant increase in soluble manganese in the sterile controls amended with MnO_2. This increase was likely associated with addition of commercial formaldehyde to these bottles which contain low concentrations of formic acid that can reduce MnO_2. The shift from Mn(IV) to Mn(II) (i.e., reduction) of manganese in the aerobic treatment exceeded that in the sterile control treatment that was amended with MnO_2. Manganese reduction under oxic conditions has been observed in other studies (Bratina et al., 1998). Aerobic microorganisms can reduce Mn(IV) via diffusible compounds under oxic conditions (Bratina et al., 1998). MnO_2 reduction was also demonstrated in several other treatments. However, stoichiometrically, the soluble manganese concentrations exceed the predicted Mn(II) concentrations that would result from reduction of Mn(IV) coupled solely to the anaerobic oxidation of *c*DCE (analytical data in Appendix C). Therefore, the increase in soluble manganese in several treatments is most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources. Alternatively, some microorganisms can couple the oxidation of H_2 to the reduction of metals such as Fe(III) and Mn(IV) (Lovley et al., 1989). Therefore, some of the Mn(IV) may have been reduced by H_2 derived from indigenous electron donors.

As discussed above, MnO_2 addition did not stimulate cDCE. This was surprising given that Bradley et al. (1998a) had observed enhanced mineralization of radiolabeled DCE in microcosm constructed using sediment collected near location N-2 and amended with MnO_2. The reason for the different results obtained by Bradley et al. and in this study is not known.

5.0 FIELD AND LABORATORY RESULTS MYRTLE BEACH AIR FORCE BASE – BUILDING 575 – SOLID WASTE MANAGEMENT UNIT 256

This section presents the methods and results from the field activities and laboratory studies conducted near Building 575, Solid Waste Management Unit 256 (SWMU 256) on Myrtle Beach Air Force Base (MBAFB), near Myrtle Beach, SC.

5.1 Background information

Solutions-IES contacted Mr. Tarek Ladaa, a Remediation Scientist at Shaw Environmental, Inc., regarding the conditions at Myrtle Beach AFB and the potential for using the Building 575 site (SWMU 256) in the study. After consulting with the Base Environmental Coordinator, Ms. Cathy Jerrard, representing the Air Force Real Property Agency, Mr. Ladaa provided Solutions-IES with a report entitled:

> *Shaw Environmental, Inc., April 2006. December 2005 Semiannual Corrective Measure Progress Report, Building 575 (SWMU 256), Myrtle Beach Air Force Base, Myrtle Beach, SC. Total Environmental Restoration Contract DACW45-93-D-0044 (Shaw, 2006).*

The report discussed the remediation efforts conducted at the site and summarized the recent findings from the monitor well network at the base. Mr. Ladaa also discussed site conditions with the project's principal investigators, helping to focus the investigation on areas of the site with a higher probability of meeting the criteria established for a successful demonstration.

From the data included in the report, it appeared that several locations around the site might be suitable for the project. Three wells were identified as potentially useful: B575-MW03, B575-MW08 and B575-MW12.

5.1.1 Location and Layout

As reported in the 2006 Shaw Environmental report that was reviewed,

> "Myrtle Beach AFB is located in northeastern South Carolina, approximately 85 miles north of Charleston and 70 miles south of Wilmington, NC. MBAFB occupies an area of approximately 3,800 acres in Horry County and is contained within the city limits of Myrtle Beach, between the Intracoastal Waterway to the northwest and the Atlantic Ocean to the east. MBAFB lies in an area referred to as the Grand Strand, an established resort area on the East Coast, and is an inactive U.S. Air Force base that officially closed on March 31, 1993."

> "Building 575 is located in the northwest quadrant of MBAFB. … Building 575 …. was used as a munitions maintenance and inspections shop from 1985 until Base closure in 1993. The site included a small, self-contained part cleaning vat, which was utilized for system and trailer maintenance. The vat originally used PD-680 solvent and later Safety Kleen™ solvent…"
>
> "A portion of the Base, including this site, (has) been transferred to the South Carolina Public Service Authority prior to the discovery of Solid Waste Management Unit 256."

Figure 5-1 presents the general layout and features of the SWMU 256 area.

5.1.2 Site Contaminants

The site was previously treated by ISCO using $KMnO_4$. Two phases of injection were performed in 2005. The remedy was initially effective, however, groundwater currently shows evidence of a *c*DCE rebound effect. Because the indigenous microbial population had been exposed to MnO_2 and *c*DCE for an extended period, Solutions-IES was optimistic that microorganisms present in aquifer from this site would be pre-acclimated to degrade *c*DCE using MnO_2 as an electron acceptor.

Table 5-1 provides a summary of historical groundwater conditions in selected wells at the site. The data are derived from the Shaw Environmental 2006 report. Where possible, the most recent data are used. The following parameters indicate how Myrtle Beach AFB fulfills the criteria and why it was chosen as a potential MnO_2-enhanced MNA site:

1. The aquifer material is conducive to injection;
2. The depth-to-groundwater is relatively shallow (approximately 6 to 10 ft bgs);
3. Little residual TCE is present; however *c*DCE and VC are present in quantities suitable for this study;
4. A moderate-to-low level *c*DCE stall is noticeable, especially in the upgradient well (and one suspected source area), B575-MW-03 (Figure 5-1);
5. Measureable manganese is present in groundwater;
6. The biogeochemical parameters are variable with some parameters falling within the preferred criteria and some falling outside the preferred criteria. Those falling within the preferred criteria include;
    a) pH
    b) Relatively low methane downgradient
    c) Little to no TCE, and
    d) *c*DCE above 300 μg/L

Three wells were chosen from MBAFB because of the above-referenced factors as well as for logistical reasons including: general ease of access and location in relation to the main *c*DCE plume.

TABLE 5-1 HISTORIC GROUNDWATER CONDITIONS IN BUILDING 575 GROUNDWATER PLUME AS OF DECEMBER 2005 MYRTLE BEACH AFB, SC				
	Units	**B575-MW03**	**B575-MW08**	**B575-RW01**
Inorganic Compounds				
Manganese (Dissolved)	mg/L	24.8	0.195	6.9
Volatile Organic Compounds				
Carbon Disulfide	µg/L	<1	1.19	3.94
Chloroethane	µg/L	<1	<1	<1
Chloroform	µg/L	<1	<1	1.72
1,1-Dichloroethane	µg/L	<1	<1	<1
1,1-Dichloroethene	µg/L	1.55/.734	<1/<1	<1/1.63
cis-1,2-Dichlorothene	µg/L	904/348	19.5/0.39	285/953
trans-1,2-Dichloroethene	µg/L	90/44.3	21.7/<1	35.5/142
Trichloroethene	µg/L	9.99/3.35	0.267/.442	2.08/33.7
Vinyl Chloride	µg/L	124/15.6	31.3/2	31.1/20.1
BTEX	µg/L	<1	<1	<1/
Water Quality				
pH	SU	6.58/6.61	7.03/6.92	7.32/6.91
Dissolved Oxygen	mg/L	0.63/0.2	0.72/.26	7.65/5.2
Oxidation-Reduction Potential	mV	149.5/-142.8	202/-157.4	252.2/139.7

Notes: Manganese data from April 2005; VOC and water quality data from samples collected December 2005/May 2006.

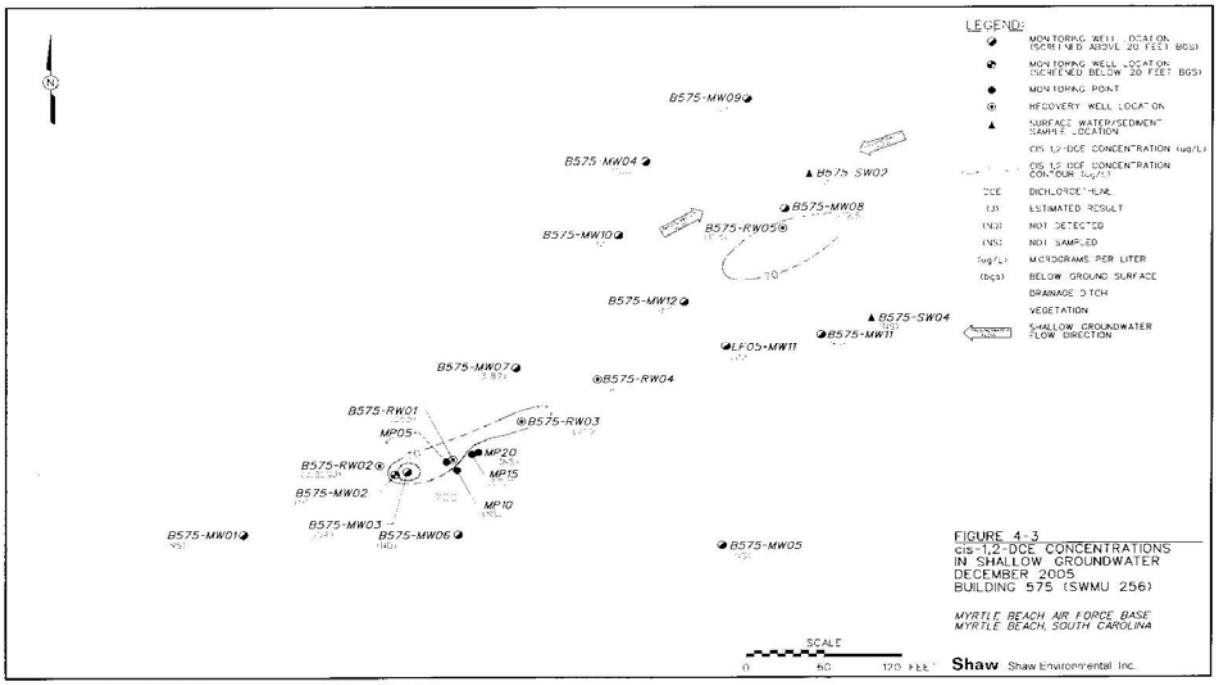

Figure 5-1. *cis*-1,2-Dichloroethene Concentrations in Groundwater, Myrtle Beach AFB, SC (Shaw, 2006)

Groundwater sampling in May 2006 detected concentrations of TCE as high as 5.4 µg/L in monitoring well B575-MW12. *c*DCE was reported at concentrations up to 348 µg/L in monitoring well B575-MW03. B575-MW03 is located upgradient (east-southeast) of our area of interest, and B575-MW12 is central to the main study area plume.

5.1.3 Site Hydrogeology and Plume Geometry

No information regarding the site hydrogeology was contained in the Shaw Environmental report. The construction of the monitor wells of interest and depth to groundwater measured in December 2005 are presented in Table 5-2.

TABLE 5-2
WELL CONSTRUCTION INFORMATION,
BUILDING 575 AREA, MYRTLE BEACH AFB, SC

Well ID	Total Depth (ft bgs)	Screen Interval (ft bgs)	Depth to Water (ft bgs)
B575-MW03	15	5 to 15	3.62
B575-MW08	15	5 to 15	4.79
B575-RW01	19	4 to 19	4.76

Note: Depth to water measured December 2005

The ground water elevations and flow direction in the unconfined aquifer (December 2005) at B575 are shown in Figure 5-2 from the Shaw 2006 report. Groundwater flow is to the northeast

with a shallow hydraulic gradient across the site measuring approximately 0.011 ft/ft. The depth to groundwater is approximately 3 to 5 feet bgs in the B575 area.

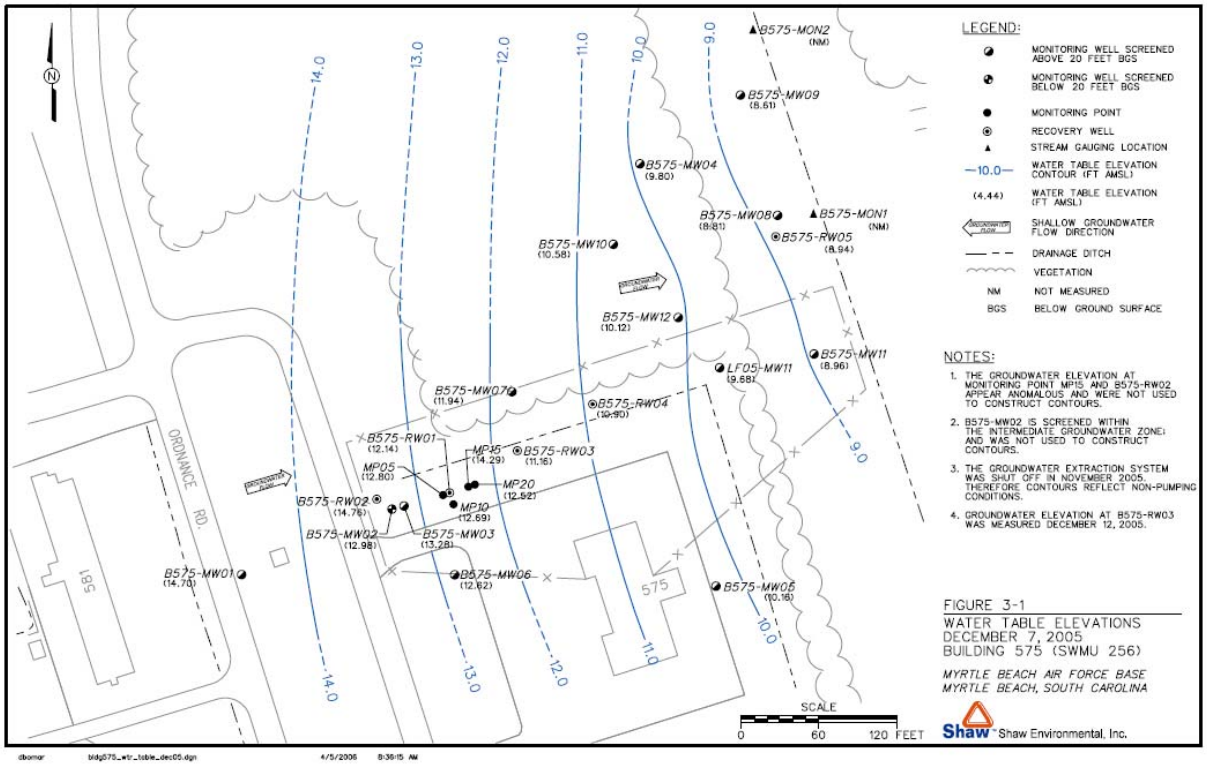

Figure 5-2. Groundwater Flow, December 7, 2005 (Shaw, 2006)

5.1.4 Site Remediation Efforts

The following paragraphs are paraphrased from the 2006 Shaw report. Some portions are directly quoted:

> Shaw Environmental, under direction of the U.S. Army Corps of Engineers-Omaha District, has executed a corrective measures implementation (CMI) work plan and long-term monitoring of contaminated groundwater for Building 575 (SWMU 256). The CMI consists of groundwater *in situ* chemical oxidation (ISCO) using potassium permanganate ($KMnO_4$), groundwater extraction with direct discharge to the publicly owned treatment works for off-site treatment, and land-use controls to achieve groundwater corrective action objectives at Building 575. Phases I through IV of the treatment were completed between January and March 2005. Phases V and VI were completed from September through November 2005. Sixty-four injection wells have been installed at the site.

During Phases V and VI, approximately 24,308 pounds (11,026 kg) of remediation-grade $KMnO_4$ were injected into the shallow aquifer via 12 new and 52 existing injection wells. The $KMnO_4$ was injected into the surface as a 2.8 percent solution, prepared on site using potable water from a fire hydrant. The solution was injected at the rate of approximately 0.1 gpm per foot of well screen. Four recovery wells were operated to maintain hydraulic control of the injected solution and the displaced groundwater. The recovery wells were operated until $KMnO_4$ was detected, indicating adequate distribution. Upon detection of $KMnO_4$ in a recovery well, that specific well was turned off to allow ample time for the $KMnO_4$ to react with the soil oxidant demand and the contaminants, and to avoid the extraction and discharge of $KMnO_4$ from the subsurface. Following consumption of the $KMnO_4$, the recovery wells were turned on. The on-off cycling continued throughout the injection, until delivery of the target amount of $KMnO_4$ solution was achieved.

The flowmeters at the extraction wells were plagued by fouling with manganese dioxide, a byproduct of the $KMnO_4$ injections.

The December 2005 detection of total chlorinated ethenes revealed that the $KMnO_4$ injections were successful in reducing the extent of the chlorinated ethene plume to generally below 100 µg/L. As shown in Figure 5-1 above, as of December 2005, *c*DCE concentrations were at or above approximately 100 µg/L in only two small plume areas: near B575-MW03 and RW01 (near the suspected source area) and around B575-RW-05 (downgradient).

During the injections, $KMnO_4$ was observed in all the monitoring and recovery wells within the treatment zones. Following the injections, the $KMnO_4$ concentrations were monitored until all of the oxidant was consumed. At the time of groundwater sample collection in December 2005, only B575-MW12 contained measurable levels of $KMnO_4$. Nevertheless, a VOC sample was collected from that well, but as anticipated, all chlorinated ethenes were non-detect. During a subsequent monitoring event in April 2006, the $KMnO_4$ in B575-MW12 had been consumed, and VOC results in that well indicated a rebound in *c*DCE and VC concentrations, rendering the well a suitable candidate for sample collection for this study (personal communication with Mr. Tarek Ladaa, Shaw Environmental).

5.2 Biogeochemical Characterization

Sample collection and groundwater monitoring activities were conducted by Solutions-IES on January 25-29, 2007. Soil borings were characterized as mostly silty clay throughout the 16-foot deep profile. Based on the site information provided by Shaw, sediment samples were collected from near monitoring well 575-MW-12 utilizing Geoprobe direct push equipment supplied by Atlas Geo Sampling Company of Alpharetta, GA. Groundwater samples were also collected from monitoring wells 575-MW08, 575-MW03, and 575-MW12 using low-flow techniques and dedicated, disposable tubing in a peristaltic sampling pump. Sampling locations are shown on Figure 5-3. Field parameters (pH, conductivity, temperature, and ORP) were measured through a flow through cell during the low-flow sampling process. Extra groundwater was collected

from 575-MW-12 for use in the microcosm studies. The NOD of the homogenized soil used in the microcosms was 16.7 g/kg dry soil indicating permanganate injection could be used to distribute MnO_2 through the target treatment zone.

TABLE 5-3
SUMMARY OF SITE CHARACTERIZATION DATA (JAN. 25, 2007)
BUILDING 575 AREA, MYRTLE BEACH AFB, SC

		MW-03	MW-08	MW-12
Volatile Organic				
Benzene	µg/L	<1.0	<1.0	<1.0
Chlorobenzene	µg/L	<1.0	<1.0	<1.0
1,3-Dichlorobenzene	µg/L	<1.0	<1.0	<1.0
1,4-Dichlorobenzene	µg/L	<1.0	<1.0	<1.0
Chloroethane	µg/L	<5.0	<5.0	1.0[J]
Isopropylbenzene	µg/L	<1.0	<1.0	<1.0
sec-Butylbenzene	µg/L	<1.0	<1.0	<1.0
Naphthalene	µg/L	<1.0	<1.0	<1.0
Tetrachloroethene	µg/L	<1.0	<1.0	<1.0
Trichloroethene	µg/L	1.9[J]	0.51[J]	2.4
trans-1,2-	µg/L	27	8.2	260
cis-1,2-Dichloroethene	µg/L	350	28	270
1,1-Dichloroethene	µg/L	0.75[J]	<1.0	0.79[J]
Vinyl chloride	µg/L	6.1	21	83
Light Hydrocarbon Gases (Method AM20GAX)				
Ethane	µg/L	0.02	0.31	0.03
Ethene	µg/L	0.72	6.80	30.98
Methane	µg/L	49.2	290.5	388.1
Metals (ICP)				
Iron (Total)	mg/L	0.37	1.2	0.46
Iron (Dissolved)	mg/L	0.15	0.81	0.045[J]
Manganese (Total)	mg/L	9.1	7.7	6.3
Manganese (Dissolved)	mg/L	8.6	7.0	5.9
Anions				
Nitrate (Method	mg/L	<0.10	0.010[J]	<0.010
Sulfate (Method 9056)	mg/L	41	660	190
Organic Carbon (Method 415.1)				
Total Organic Carbon	mg/L	<1.0	15.2	3.1
Chemical Oxygen Demand (Method SM5220D)				
Chemical Oxygen Demand	mg/L	23[J]	62	30[J]
Temperature	C	17.4	16.55	18.57
pH	SU	6.54	6.82	6.9
Specific Conductance	µS/cm	0.686	1.890	1.696
Dissolved Oxygen	mg/L	0.52	0.47	0.53
Redox Potential	mV	-91.2	-150.0	-89.4
Turbidity	NTU	2.3	4.8	8.9

J = The estimated value is between the Reporting Limit and the Method Detection Limit.

Table 5-3 summarizes the January 2007 groundwater field measurements and laboratory analytical conditions at three representative wells (Figure 5-2) along the OU-1 groundwater plume.

The groundwater was moderately reducing as indicated by the negative ORP and low dissolved oxygen concentrations. Elevated levels of dissolved manganese were observed in all wells indicating significant amounts of bioavailable Mn were present (presumably from the prior MnO_4 injections).

Figure 5-3. Building 575 Sampling Locations, Myrtle Beach AFB, SC
(Modifed from Google™ Earth)

5.3 Microcosm Experimental Design and Results

Groundwater from monitor well B575-MW-12 and sediment cores SB-MW-12-1 (10-12'), SB-MW-12-2 (10-12'), and SB-MW-12-3 (8-10', 10-12', 12-14') were homogenized separately inside the chamber. The microcosm bottles were constructed as described in Section 2.4.2 and subjected to the treatments summarized in Table 5-4. A sample of the homogenized soil was shipped to the Shaw Laboratory in Knoxville, TN for NOD analysis.

TABLE 5-4
SUMMARY OF MICROCOSM TREATMENTS ON MATRICES FROM MYRTLE BEACH AFB, SC

Treatment Descriptions	Soil (30%)	*c*DCE (2 ppm)	Formaldehyde (1.5%)	MnO_2 (25 mM)	Humics (2 ppm)	Acetate (200 ppm)	O_2 (Added to Headspace)
Sterile Control Without MnO_2	X	X	X				
Sterile Control With MnO_2	X	X	X	X			
Unamended	X						
Background Control	X	X					
Commercial MnO_2	X	X		X			
Synthesized MnO_2	X	X		X			
Aerobic	X	X		X			X
Humic Acid Amendment	X	X		X	X		
Cometabolism (*c*DCE and acetate)	X	X		X		X	

Aqueous samples were collected over the course of seven months and analyzed for VOCs (EPA Method 8260). Bottles were sampled at 0 weeks and 2 months for dissolved manganese via EPA Method SW-846 6010.

The analytical results for the Myrtle Beach microcosm study are included in Appendix C5 and C6. In Figure 5-4, *c*DCE is represented as the percentage remaining relative to the sterile controls that did not contain MnO_2 (i.e., the average of the triplicate values for each treatment was divided by the average of the triplicate values for the sterile control treatment that did not contain MnO_2). In Figure 5-5, the dissolved manganese values are averages of the triplicate values for each treatment at each timepoint.

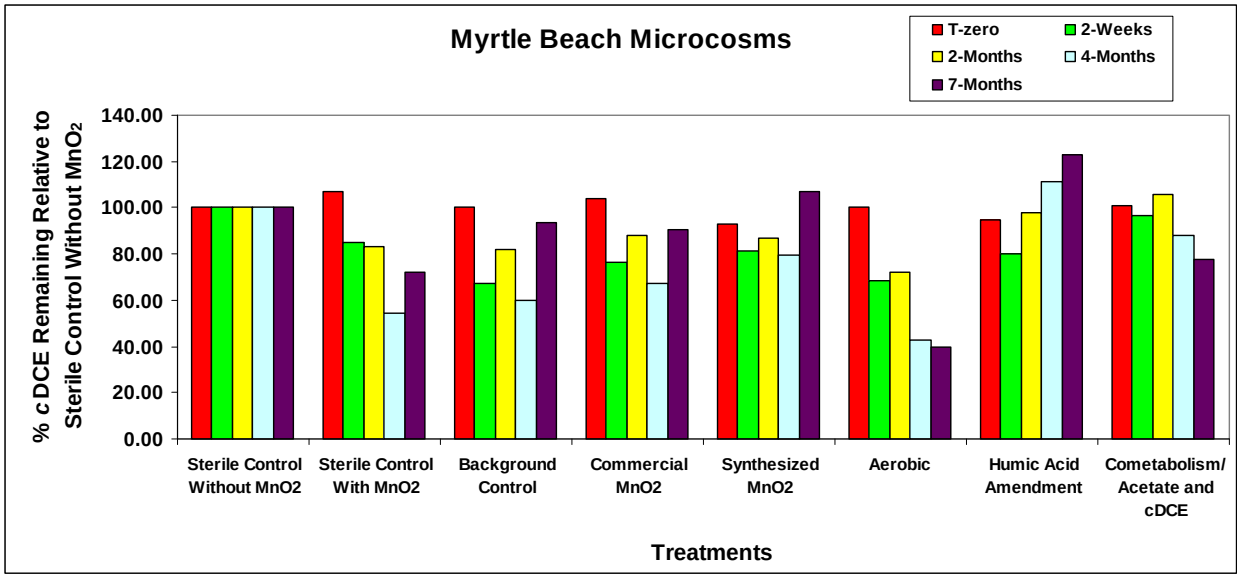

Figure 5-4. Myrtle Beach AFB Microcosm Results for *c*DCE Measurements

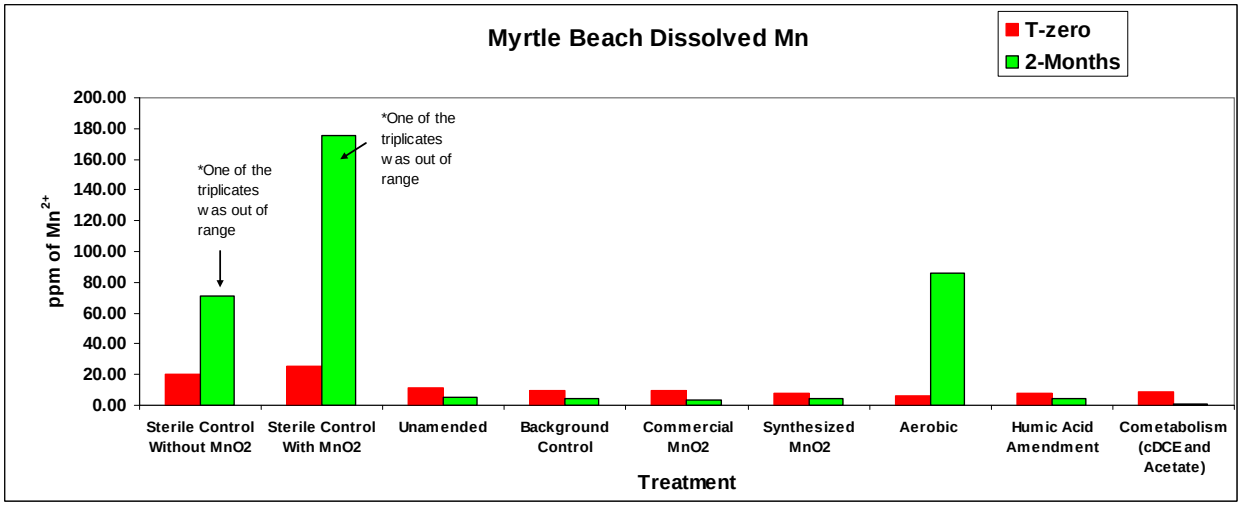

Figure 5-5. Myrtle Beach AFB Microcosm Results for Dissolved Manganese Measurements

5.4 Summary of Results

Conditions in groundwater from 575-MW-12 would generally be considered conducive to anaerobic MNA of chloroethenes, i.e., residual TOC (3.1 mg/L) at low oxygen tension with reducing ORP (-89.4 mV) (Table 5-3). The presence of a low concentration of TCE (2.4 µg/L) with measurable *c*DCE (270 µg/L), VC (83 µg/L) and ethene (31 µg/L) also suggests that this process is occurring despite having previously been treated by ISCO with permanganate. Elevated levels of dissolved Mn(II) were detected indicating conditions were appropriate for Mn reduction. In the microcosm study, VC was detected in the commercial, synthesized, background, and humic acid treatments, as well as the in the sterile controls (with MnO_2) (data not included). Based on the detection of vinyl chloride, it appears as though *c*DCE loss is

attributed to reductive dechlorination, which is consistent with the observations in the field. Amendments of humic acid and acetate did not further stimulate *c*DCE loss beyond that which appears to have been naturally occurring.

The aerobic microcosms demonstrated the greatest loss (60%) of *c*DCE relative to the sterile controls that were not amended with MnO_2. Interestingly, there was some loss of *c*DCE in the sterile controls that were amended with MnO_2, suggesting that the formaldehyde did not kill the entire microbial population.

The results of the metals analyses showed that the greatest reduction of manganese was demonstrated in the sterile control amended with MnO_2. In the absence of added MnO_2, the sediment's *in situ* Mn(IV) was also reduced by formic acid and provided a relative measure for background Mn(IV) levels. The reduction of manganese in the aerobic treatment almost equaled that in the sterile control treatment that was not amended with MnO_2. Manganese reduction under oxic conditions has been observed in other studies (Bratina et al., 1998). Aerobic microorganisms can reduce Mn(IV) via diffusible compounds under oxic conditions (Bratina et al., 1998). Manganese reduction did not occur in any of the other treatments and is clearly not linked to anaerobic *c*DCE oxidation.

6.0 FIELD AND LABORATORY RESULTS – LAUNCH COMPLEX 34 – CAPE CANAVERAL AIR FORCE STATION, FLORIDA

This section presents the methods and results activities from the field and laboratory studies conducted at Launch Complex 34 (LC-34) of Cape Canaveral Air Force Station (Cape Canaveral AFS), near Titusville, FL.

6.1 Background information

Solutions-IES contacted Mr. Jim Langenbach of GeoSyntec Consultants, the Base Operational Contractor conducting site investigations at the Launch Complex 34. Mr. Langenbach identified Mr. Michael Deliz as the Base Environmental Coordinator. Solutions-IES then contacted Mr. Deliz regarding the conditions at Cape Canaveral AFS and the potential for using the LC34 site (Figure 6-1) in the study. Mr. Deliz and Mr. Langenbach provided Solutions-IES with copies of selected reports and data sets including the following:

> *Azadpour-Keeley, Ann, Wood, Lynn A., Lee, Tony R., and Mravik, Susan C., 2004. Microbial Responses to In Situ chemical Oxidation, Six-Phase Heating, and Steam Injection remediation Technologies in Groundwater. Remediation Journal: Autumn 2004, pp 5-17.*
>
> *Battelle, 2004. Demonstration of Biodegradation of Dense, Nonaqueous-Phase Liquids (DNAPL) through Biostimulation and Bioaugmentation at Launch Complex 34 in Cape Canaveral Air Force Station, Florida. Superfund Innovative Technology Evaluation Program, USEPA, National Risk Management Research Laboratory, September 30, 2004.*
>
> *Leonard, W.C., E. Mott-Smith, R. Lewis, W.S. Clayton and J. Ramirez. In Situ Oxidation of DNAPL Using Permanganate: IDC Cape Canaveral Demonstration.*
>
> *National Aeronautics and Space Administration, 2003. RCRA Facility Investigation Addendum Report, Launch Complex 34, SWMU No. CC054, Cape Canaveral Air Force Station, Florida (KSC-TA-6356). Prepared by HSA Engineers & Scientists, Titusville, FL, July 2003.*

The reports discussed the remediation efforts conducted at the site and summarized the recent findings from the monitor well network at the base. Mr. Deliz and Mr. Langenbach also discussed site conditions with the project's principal investigator, helping to focus the investigation on areas of the site with higher probability of meeting the criteria established for a successful demonstration. Mr. Langenbach also offered to facilitate on-site logistics of the sampling activities.

6.1.1 Location and Layout

A described in the Battelle report (Battelle 2004):

> "Launch Complex 34 is located at Cape Canaveral Air Force Station, FL. Launch Complex 34 was used as a launch site for Saturn rockets from 1960 to 1968. Historical records and worker accounts suggest that rocket engines were cleaned on the launch pad with chlorinated organic solvents such as TCE. Other rocket parts were cleaned on racks at the western portion of the Engineering Support Building and inside the building. Some of the solvents ran off to the surface or discharged into drainage pits. The site was abandoned in 1968; since then, much of the site has been overgrown by vegetation, although several on-site buildings remain operational."

The following was excerpted from the 2003 RFI Addendum submitted by HSA Engineers & Scientists cited above:

> "LC-34, which has no marked or legally designated property boundaries, lies in Section 6, Township 23 South, and Range 38 East. The facility is bordered (1) to the north by Launch Complex 37, (2) to the south by Launch Complex 20, (3) to the west by ICBM Road, and (4) to the east by the Atlantic Ocean. LC-34 was constructed in the late-1950s and early-1960s for the launch of Saturn I and IB rockets, which served as launch vehicles during the Apollo manned space program. A total of ten Saturn launches were successfully completed at LC-34 from 1960 through 1968. After terminating launch operations at LC-34, most operational equipment (service towers, fuel storage tanks, piping, etc.) was dismantled, and the majority of the on-site buildings and structures were abandoned-in-place. Native shrubbery, trees, and other vegetation overgrew the majority of the site; however, maintenance activities at LC-34 in 1998 resulted in the clearing of much of the vegetation in the Launch Pad area. Dense, mature forest surrounds the site to the north, south, and west."

A general site map is presented in Figure 6-1.

6.1.2 Site Contaminants

Two locations were identified as possible sampling sites for the project. The first area was in the vicinity of the well cluster designated LC34-IW0051 located approximately 2,000 ft west-southwest of the Engineering Support Building (ESB). For the purpose of this report, this area is designated as the "LC-34 Plume". The second area was alongside the ESB, about 200 ft east of the northeast corner of the building where an ISCO pilot test was performed. This area is designated as "LC-34 ESB".

Table 6-1 provides a summary of historical groundwater conditions in the two areas of interest. The data are derived from the RFI (HSA Engineers & Scientists, 2003) and the Battelle 2004 report. Where possible, the most recent data are used. According to these data collected between 2004 and 2006, the LC-34 Plume area contains little TCE, significant amounts of *c*DCE and some VC. Concentrations were substantially higher in the well screened in the shallow zone

(1 to 11 ft bgs) compared to the intermediate depth (23 to 28 ft bgs). The apparent DCE stall in this location of the plume was accompanied by low levels of manganese in groundwater, neutral pH and low DO and ORP, suggesting conditions indicative of anaerobic MNA. Low methane concentrations suggested some residual carbon in the formation, but information on other key parameters such as TOC was not available. The complete conversion of TCE to *c*DCE along with the apparent *c*DCE stall indicate this site would be a good candidate for enhancing MNA through MnO_2 addition.

Most of the wells in the ISCO pilot test area (LC-34 ESB area) were previously abandoned according to Mr. Mike Deliz and Mr. Jim Langenbach. However, the area was still accessible and still heavily contaminated. Table 6-1 shows data compiled from reports prepared between 2004 and 2006 for IW-001I and IW-001D , which are along the eastern side of the ESB about 120 to 200 ft downgradient of the ISCO test plot. The monitoring data indicates that IW-0001I continues to be contaminated with very high concentrations of TCE and *c*DCE. MnO_2 concentrations in soil are expected to be high due to prior treatment of this area by ISCO using permanganate. As a consequence, there was thought to be a good potential for prior acclimation of the microbial community at this location to degrade *c*DCE using MnO_2 as an electron acceptor.

TABLE 6-1
HISTORICAL REPRESENTATIVE GROUNDWATER CONDITIONS
LAUNCH COMPLEX 34 GROUNDWATER PLUME
AS OF NOV. 2004 AND DEC. 2006
CAPE CANAVERAL AFS, FL

		LC-34 Plume		**LC-34-ESB**	
	Units	**IW0051I**	**IW0051S**	**IW-0001I**	**IW-0001D**
Inorganics					
Manganese (Dissolved)	mg/L		0.052*		14.8
Volatile Organic Compounds					
Methane	µg/L		33*		48.3
Ethane	µg/L		1.92*		0.6^{U}
Ethene	µg/L		13.2*		27
cis-1,2-Dichlorothene	µg/L	2,760	29,600	217,000	608
trans-1,2-Dichloroethene	µg/L	27.5^{I}	500^{U}	$5{,}000^{U}$	25^{U}
Trichloroethene	µg/L	25^{U}	500^{U}	283,000	25^{U}
Vinyl Chloride	µg/L	385	2,390	$5{,}000^{U}$	2,060
Water Quality					
pH	SU		6.84*		8.64
Dissolved Oxygen	mg/L		0.30		0.45
Oxidation-Reduction Condition	mV		-81.2*		-96.6

Notes: *Data from November 17, 2004; VOC data from samples collected 2005 and 2006; U = Not detected at associated detection limit.

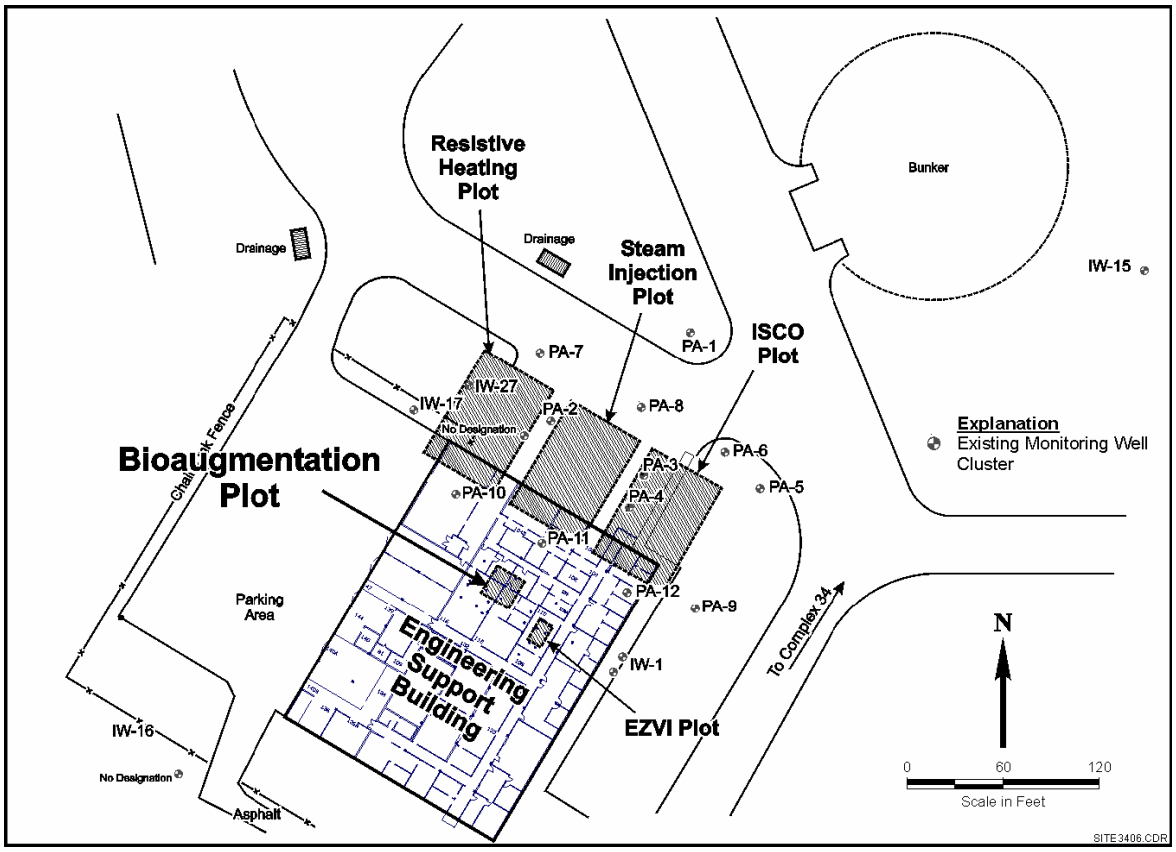

Figure 6-1. Engineering Support Building Site Features, Cape Canaveral AFS, FL (Battelle, 2004)

Monitor wells PA-27I and PA-28I, were located northeast and southwest, respectively, of the Battelle bioaugmentation plot that is shown inside the ESB on Figure 6-1. TCE concentrations as high as 1,110,000 µg/L (June 2003 Battelle data were recorded in monitoring well PA-27I. The TCE degradation product *c*DCE has been detected at concentrations up to 225,000 µg/L (June 2003 Battelle data) in monitoring well PA-28I. .

The locations of the soil sampling points and the monitoring wells sampled are presented on Figure 6-2. These locations were selected to represent two distinct areas of the same plume.

Figure 6.2. Launch Complex 34 Soil Borings and Monitor Well Locations, Cape Canaveral AFS, FL

6.1.3 Site Hydrogeology and Plume Geometry

The subsurface in the Launch Complex 34 area has been described in terms of three aquifers "…reflecting a barrier island complex overlying coastal sediments." These are:

- The Floridan Aquifer (bedrock aquifer, confined, greater than 105 feet MSL elevation);
- The Hawthorne Formation Semi-confined Aquifer (between approximately 47 ft. MSL to 105 ft. MSL); and
- The Surficial Aquifer (land surface to approximately 47 ft. MSL).

The Hawthorne Formation includes a confining clay that immediately overlies the top of the Floridan Aquifer. A semi-confining layer is present at the top of the Hawthorne Formation and separates the Hawthorne Aquifer from the overlying Surficial Aquifer. This semi-confining layer is approximately 1.5 to 3 ft thick and is pervasive across the LC-34 area.

The Surficial Aquifer has been subdivided into an Upper Sand Unit (the "S" zone, unconsolidated, gray fine sand and shell fragments-ground surface to 20 to26 ft bgs), a Middle Fine-Grained Unit (the "I" zone, gray, fine-grained silty/clayey sand from 26 to 36 ft bgs) and a Lower Sand Unit (the "D" zone, gray fine to medium-sized sand and shell fragments with some isolated fine grained silt and/or clay lenses). The Surficial Aquifer receives direct recharge from the surface infiltration of rainfall. In the RFI, three hydrogeologic/stratigraphic zones beneath and to the south/southwest of the ESB are described as follows:

- "S" Zone: Approximately 1 to 11 ft bgs; encompasses water table and represents shallow groundwater conditions in the surficial sand sediments.
- "I" Zone: Approximately 25 to 30 ft bgs; intermediate groundwater conditions in the fine-grained, clayey sand sediments.
- "D" Zone: Approximately 35 to 40 ft bgs; groundwater conditions in sands and silty sands at the base of the surficial aquifer…" and overlying the semi-confining layer on top of the Hawthorne Formation.

The groundwater elevations and flow directions in the Surficial Aquifer at LC-34 are shown in Figure 6-3 from the Battelle 2004 report for June 1998. Groundwater flow in the Surficial Aquifer tends to be radial away from the Engineering Support Building with the building overlying the highest groundwater elevations. The horizontal gradient in the Surficial Aquifer is relatively flat ranging from 0.00009 to 0.0007 ft/ft (1997 to 1998). Battelle (2004) noted that groundwater flow and gradients were variable over time with flow directions ranging from north-northeast to south-southwest.

The construction of the monitor wells of interest (or near areas of interest) and depth to groundwater measured in July 2006 are presented in Table 6-2:

TABLE 6-2 WELL CONSTRUCTION INFORMATION NEAR ENGINEERING SUPPORT BUILDING, LAUNCH COMPLEX 34 CAPE CANAVERAL AFS, FL			
Well ID	**Total Depth (ft)**	**Screen Interval (ft)**	**Depth to Water (ft TOC)**
IW0051S	11	1 to 11	8.09
IW0051I	28	23 to 28	8.04
IW0001I	30	25 to 30	7.00
IW0001D	40	35 to 40	6.75

Notes: Depth to water measured July 24, 2006
Ft TOC = feet below top of casing

In general, the plumes of chlorinated compounds range from the Atlantic Ocean to the east-northeast towards the southwest with the ESB near the center of the plume.

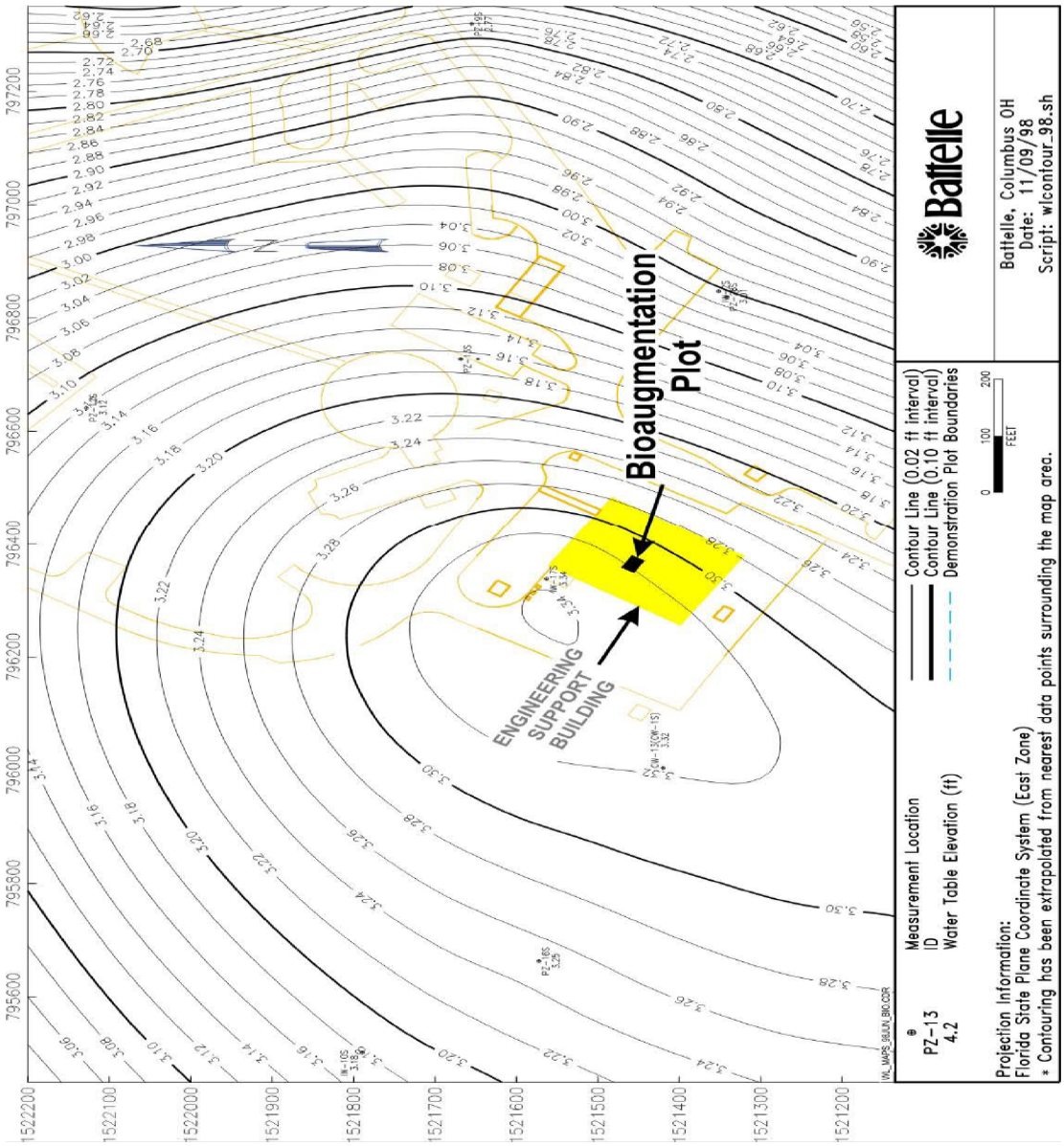

Figure 6-3. Water Table Elevation Map for Surficial Aquifer from June 1998, Cape Canaveral AFS, FL (Battelle, 2004)

6.2 Biogeochemical Characterization

Soil and groundwater collection and groundwater monitoring activities were conducted by Solutions-IES personnel on April 30 and May 1, 2007 in accordance with the site-specific Sampling and Analysis Plan. Initially, work commenced alongside the ESB using a Geoprobe direct push rig operated by Environmental Drilling Service, Inc., of Orlando, FL (Figure 6-4). A boring was advanced by hand auger to a depth of 4 ft bgs to clear utilities and then further advanced to about 6 ft bgs with the Geoprobe at which point refusal was encountered. After twice moving and repeating, the Geoprobe successfully reached 12 ft bgs and the drive rod became jammed with the Macrcore sleeve. The remaining 14 to 16 ft bgs were collected using a

hand auger. Then a 1-inch diameter PVC well was placed into the boring. Collapsing sand required the well to be driven in with a hammer from 13 to 16 ft bgs. This temporary well was designated as ESB-SB-1, the same as the soil boring. Purging with a peristaltic pump for less than 1 hour cleared up the groundwater. Field parameters were measured and a sample was collected. Because of previous exposure of this area to $KMnO_4$ during the ISCO pilot test, this soil and groundwater were packaged for use in enrichment studies at the laboratory.

Figure 6-4. Sample Collection using Geoprobe beside the Engineering Support Building

The Geoprobe moved to the LC-34 Plume area and successfully advanced a soil boring to the depth of 24 ft bgs to collect the soil samples from location ESB-SB-2 as specified in the Sampling and Analysis Plan (Figure 6-2). Groundwater samples were collected from adjacent monitoring wells IW-51S and IW-51I using a peristaltic sampling pump. Field parameters (pH, conductivity, temperature, and ORP) were measured through a flow through cell during the low-flow sampling process. Table 6-3 summarizes the current groundwater analytical conditions at the three representative wells along the LC-34 ESB groundwater plume.

TABLE 6-3
SUMMARY OF GROUNDWATER SITE CHARACTERIZATION DATA (APRIL 30 – MAY 1, 2007)
CAPE CANAVERAL AFS, FL

		LC-34 Plume		LC-34 ESB
		IW-51S	IW-51I	ESB-SB-1
Volatile Organic Compounds (EPA Method 8260B)				
Tetrachloroethene	µg/L	<100	<10	<1.0
Trichloroethene	µg/L	<200	<20	0.73[J]
trans-1,2-Dichloroethene	µg/L	370	36	8.5
cis-1,2-Dichloroethene	µg/L	23,000	3,200	120
1,1-Dichloroethene	µg/L	53[J]	<10	<1.0
Vinyl chloride	µg/L	1,600	320	120
Light Hydrocarbon Gases (Method AM20GAX)				
Ethane	µg/L	1.40	NS	0.78
Ethene	µg/L	11.90	NS	2.29
Methane	µg/L	37.3	NS	527.2
Metals (ICP)				
Iron (Total)	mg/L	1.9	0.030[J]	0.0095[J]
Iron (Dissolved)	mg/L	0.67	0.0053[J]	0.0092[J]
Manganese (Total)	mg/L	0.039	0.0055[J]	0.91
Manganese (Dissolved)	mg/L	0.035	0.0046[J]	0.84
Anions				
Nitrate (Method SM4500)	mg/L	0.011[J]	0.012[J]	<0.20
Sulfate (Method 9056)	mg/L	61	35	49
Chemical Oxygen Demand (Method SM5220 D)				
Chemical Oxygen Demand	mg/L	35[J]	37[J]	16[J]
Total Organic Carbon (Method 415.1)				
Total Organic Carbon	mg/L	7.78	2.43	<1.0
Field Measurements				
Temperature	C	24.2	23.9	25.0
pH	SU	7.04	7.66	7.54
Specific Conductance	µS/cm	1,416	2,212	641
Dissolved Oxygen	mg/L	1.67	0.90	2.01
Redox Potential	mV	-98.7	-209	-2.8
Turbidity	NTU	0.53	0.53	0.65

J = The estimated value is between the Reporting Limit and the Method Detection Limit.

6.3 Microcosm Results

Groundwater from monitoring well IW-51I and sediment from ESB-SB-2 cores (18 to 24 ft bgs) were used for the set of microcosms from the LCF-34 Plume. These microcosms were designed to evaluate the effect of MnO_2 addition on biogeochemical processes in the downgradient portion of the plume where there is evidence of an obvious *c*DCE stall. Groundwater from temporary monitor well ESB-SB-1 and sediment from ESB-SB-1 cores (4 to 16 ft bgs) were used to construct enrichment cultures from LC-34 ESB. These cultures were designed to enrich for

microorganism that could degrade *c*DCE using MnO_2 since the microbial community at this location has been exposed to *c*DCE and MnO_2 from the prior ISCO project.

Groundwater and sediment were homogenized separately in the anaerobic chamber prior to establishing the microcosms and enrichments. For IW-51I/ESB-SB-2 microcosms, approximately 15 g of homogenized sediment was added to 60-mL serum bottles. The final volume of groundwater, including amendments, was 50 mL. For ESB-SB-1 enrichments, approximately 6 g of homogenized sediment was added to 160-mL serum bottles. The final volume of groundwater, including amendments, was 150 mL. Bottles were sealed with Teflon stoppers and aluminum seals, effectively trapping an anaerobic headspace, and incubated at 15ºC. Several treatments, prepared in triplicate for IW-51I/ESB-SB-2 and as single bottles for ESB-SB-1, were established to evaluate *c*DCE degradation under various conditions (see Tables 6-4 and 6-5**)**. Two treatments were amended with humic acids (low and high concentrations) in order to assess whether humic acids facilitate electron shuttling between MnO_2 and *c*DCE (Cervantes et al., 2001). Although chelators usually reduce metals such as Mn(IV), several studies have shown that chelators such as nitrolotriacetic acid (NTA) and oxalic acid can solubilize metals, making them more bioavailable (Lovley et al., 1996; Langenhoff et al., 1997). Therefore, two treatments were established to determine whether *c*DCE degradation, coupled to Mn(IV) reduction, could be enhanced via amendments with these two chelators. Two treatments were established to determine whether *c*DCE could be cometabolized. One treatment was amended with acetate, and the other was amended with ethene, which was added to the headspace. Finally, two treatments were established to assess whether manganese reduction was occurring and could be linked to the utilization of other organic substrates besides *c*DCE (acetate or ethene). However, as reported below, those treatments that were established with the site material from IW-51I/ESB-SB-2 contained background levels of *c*DCE and vinyl chloride. Formaldehyde, *c*DCE, humic acids, and acetate were added as concentrated stocks to give the final concentrations noted in Tables 6-4 and 6-5.

TABLE 6-4
SUMMARY OF MICROCOSM TREATMENTS ON LAUNCH COMPLEX 34 MATRICES FROM IW-51I/ESB-SB-2

Treatment	Sediment (30%)	*c*DCE (2 ppm)	Formald. (1.5%)	MnO_2 (25 mM)	Low Humic (2 ppm)	High Humic (20 ppm)	Ethene Added to Headspace	Acetate (200 ppm)	NTA (2 mM)	Oxalic (4 mM)	Oxygen Added to Headspace
Sterile Control Without MnO_2	**X**	**X**	**X**								
Sterile Control With MnO_2	**X**	**X**	**X**	**X**							
Unamended	**X**										
Background Control	**X**	**X**									
Commercial MnO_2	**X**	**X**		**X**							
Synthetic MnO_2	**X**	**X**		**X**							
Low Humic Acid Amendment	**X**	**X**		**X**	**X**						
High Humic Acid Amendment	**X**	**X**		**X**		**X**					
NTA Amendment	**X**	**X**		**X**					**X**		
Oxalic Acid Amendment	**X**	**X**		**X**						**X**	
Cometab. (DCE and Ethene)	**X**	**X**		**X**			**X**				
Cometab. (DCE and Acetate)	**X**	**X**		**X**				**X**			
Ethene	X			X			X				
Acetate	X			X				X			
Aerobic	**X**	**X**		**X**							**X**

TABLE 6-5
SUMMARY OF MICROBIAL ENRICHMENT TREATMENTS ON LAUNCH COMPLEX 34 MATRICES FROM ESB-SB-1

Treatment	Sediment (4%)	*c*DCE (2 ppm)	Formald. (1.5%)	MnO_2 (25 mM)	Low Humic (2 ppm)	High Humic (20 ppm)	Ethene Added to Headspace	Acetate (200 ppm)	NTA (2 mM)	Oxalic (4 mM)	Oxygen Added to Headspace
Sterile Control Without MnO_2	X	X	X								
Sterile Control With MnO_2	X	X	X	X							
Background	X	X									
Unamended	X										
Commercial MnO_2	X	X		X							
Synthesized MnO_2	X	X		X							
Low Humic Acid Amendment	X	X		X	X						
High Humic Acid Amendment	X	X		X		X					
NTA Amendment	X	X		X					X		
Oxalic Acid Amendment	X	X		X						X	
Cometab. (DCE and Ethene)	X	X		X			X				
Cometab. (DCE and Acetate)	X	X		X				X			
Ethene	X			X			X				
Acetate	X			X				X			
Aerobic	X	X		X							X

Aqueous samples were collected over the course of two months and analyzed for VOCs (EPA Method 8260). Bottles were sampled at 0 weeks and 2 months for dissolved manganese via EPA Method SW-846 6010.

The analytical results for the LC-34 microcosm and enrichment studies are included in Appendix C7 through C10. In Figures 6-5 and 6-6, *c*DCE is shown as the percentage remaining relative to the sterile controls that did not contain MnO_2 (i.e., for the IW-51I/ESB-SB-2 microcosms, the average of the triplicate values for each treatment was divided by the average of the triplicate values for the sterile control treatment that did not contain MnO_2; for the ESB-SB-1 enrichments, single values were evaluated). In Figures 6-7 and 6-8, the dissolved manganese values are averages of the triplicate values for each treatment for the IW-51I/ESB-SB-2 microcosms and single values for the ESB-SB-1 enrichments at each timepoint.

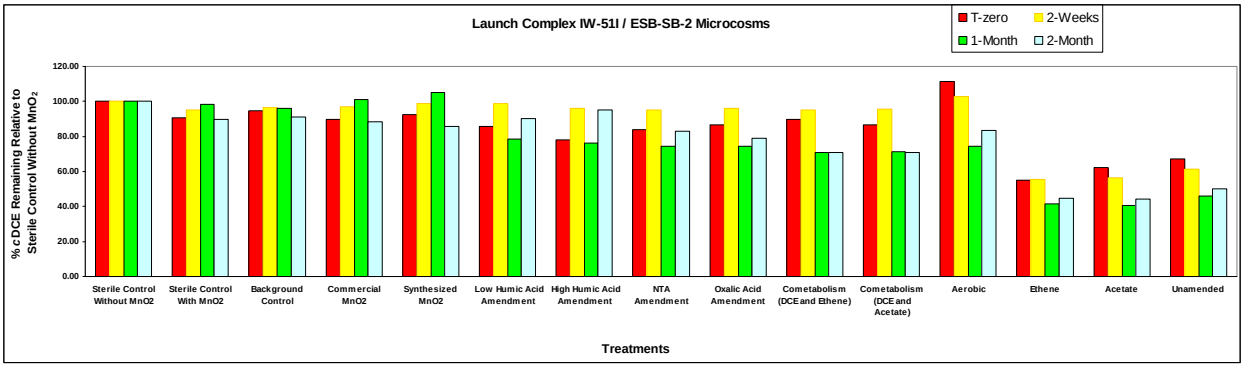

Figure 6-5. Launch Complex 34 IW-51I/ESB-SB-2 Microcosm Results for *c*DCE Measurements

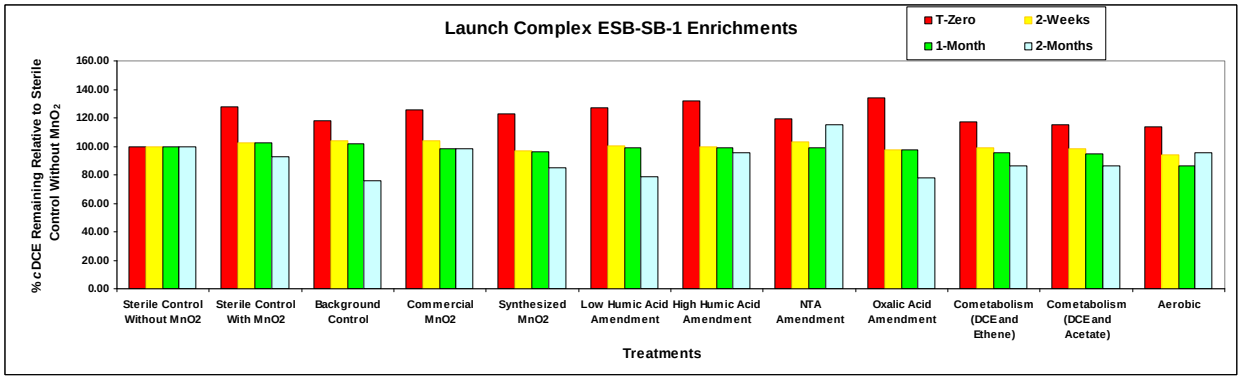

Figure 6-6. Launch Complex 34 ESB-SB-1 Enrichment Results for *c*DCE Measurements

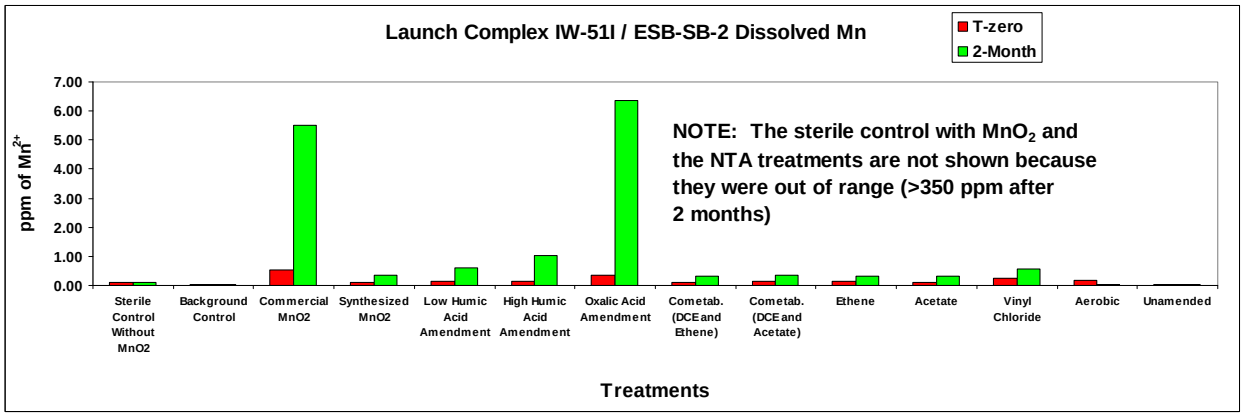

Figure 6-7. Launch Complex 34 IW-51I/ESB-SB-2 Microcosm Results for Dissolved Manganese Measurements

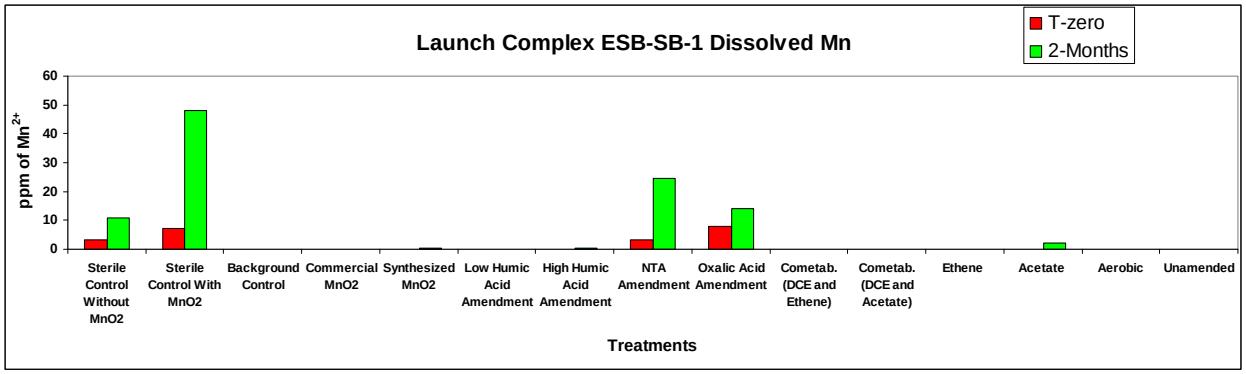

Figure 6-8. Launch Complex 34 ESB-SB-1 Enrichment Results for Dissolved Manganese Measurements

6.4 Summary of Results

The matrices used in the construction of the LC-34 Plume microcosms (IW-51I/ESB-SB-2 site material) were collected from over 2000 ft downgradient from the ESB pilot test area. The groundwater used in the microcosms contained residual TOC (2.4 mg/L) at low oxygen concentration (0.9 mg/L) and ORP (-209 mV) (Table 6-3). The background suite of chloroethenes clearly demonstrates the *c*DCE stall in this portion of the plume (i.e., TCE, <20 µg/L; *c*DCE, 3200 µg/L; VC, 320 µg/L; ethene, BDL). If MnO_2 addition were effective in stimulating biodegradation, then this would be a good location to evaluate this technology.

The matrices used in the construction of the LC-34 ESB enrichments (ESB-SB-1 site material) were collected 100 to 200 ft downgradient of the prior ISCO pilot test area. Geochemical data collected at this location indicate the groundwater was moderately reducing (ORP = -3 mV) with some dissolved Mn (0.84 mg/L), but very low levels of dissolved iron (<0.01 mg/L). Methane and ethene were also measurable. Some *c*DCE was detected (120 µg/L) indicating the microbial community at this location had been exposed to *c*DCE and moderately reducing conditions consistent with Mn reduction.

There was no significant loss of *c*DCE in any of the treatments with or without the addition of MnO_2 for both the plume microcosms and ESB area enrichments. Amendments of humic acid, acetate, ethene, NTA and oxalic acid did not stimulate *c*DCE degradation relative to the background control treatment for either site. Although there are *in situ* levels of both *c*DCE (see treatments that were amended with ethene and acetate as sole carbon sources) and VC (data not included) in the IW-51I/ESB-SB-2 site material, there was no evidence of *c*DCE degradation on the timescale investigated.

The results of the metals analyses for the plume microcosms (IW-51I/ESB-SB-2) and ESB area enrichments (ESB-SB-1) showed that the greatest increase in dissolved manganese (i.e., reduction of Mn^{4+}) occurred in the sterile controls amended with MnO_2. In the absence of added MnO_2, the sediment's *in situ* Mn(IV) was likely reduced by formic acid and provided a relative measure for background Mn(IV) levels. The addition of the chelators NTA and oxalic acid resulted in the reduction of Mn(IV) and not the solubilization of Mn(IV), and therefore they did

not enhance *c*DCE oxidation via MnO_2 reduction. Manganese reduction did occur in the commercial MnO_2 treatment for the plume (IW-51I/ESB-SB-2) site. Stoichiometrically, the soluble manganese concentrations exceed the predicted Mn(II) concentrations that would result from reduction of Mn(IV) coupled solely to the anaerobic oxidation of *c*DCE (analytical data in Appendix C). Therefore, the increase in dissolved manganese is most likely due to Mn(IV) reduction being coupled to the oxidation of indigenous carbon sources.

7.0 ALAMAC AMERICAN KNITS, LLC

This section presents the methods and results activities from the field and laboratory studies conducted on matrices obtained from the Alamac American Knits, LLC, (Alamac) site in Lumberton, Robeson County, NC. Solutions-IES has worked on this site for ten years conducting groundwater assessment, remediation, long-term monitoring and reporting for a PCE release from an aboveground PCE storage tank located behind the textile manufacturing building.

7.1 Background Information

Solutions-IES contacted Mr. Mark Cabral, President of Alamac American Knits to obtain permission to collect soil samples for enrichment studies. Solutions-IES visited the site (Figure 1) during February 2007 to collect samples. Because Solutions-IES has been conducting sampling activities at the site since 2001, historical information and multiple reports were readily available including various semi-annual and annual *Groundwater Monitoring Reports* prepared between December 2000 and December 2006.

Solutions-IES has implemented several remediation technologies to treat the PCE source area including excavation of shallow soil and low-temperature thermal treatment groundwater recovery and discharge to control plume migration, and *in situ* bioremediation using molasses and neat NAPL soybean oil. In the downgradient portions of the plume, natural attenuation processes are converting PCE and TCE to *c*DCE with a small amount of VC produced. The reports that were reviewed discuss the historical remediation efforts conducted at the site and summarize the findings from the monitor well network and the continuing remediation efforts at the facility.

7.1.1 Location and Layout

The Alamac site is located in the Coastal Plain Physiographic Province of North Carolina. The topography is flat and has a relatively shallow water table (based only on the wells measured during sampling) varying between 2.86 and 8.51 below the top of the casing in November 2006. The impacts to groundwater and soil were caused by PCE formerly used at the facility's dry cleaning operation. The suspected source area of chlorinated impacts (PCE and its daughter products) is located near a former PCE tank containment pad and piping on the east side of the manufacturing building. The site is bordered on the south by Jacob Swamp Canal. Land surface at the site lies at approximately 110 feet above mean sea level (ft msl). The subsurface zones of interest have been delineated into a shallow aquifer, 0 to 20 ft bgs, and a deep aquifer, 20 to 75 ft bgs. Groundwater flow is to the south towards Jacob Swamp Canal. A recovery system

consisting of three recovery wells was installed in July 1999 and has operated continuously since system startup. A general site location map is presented in Figure 7-1.

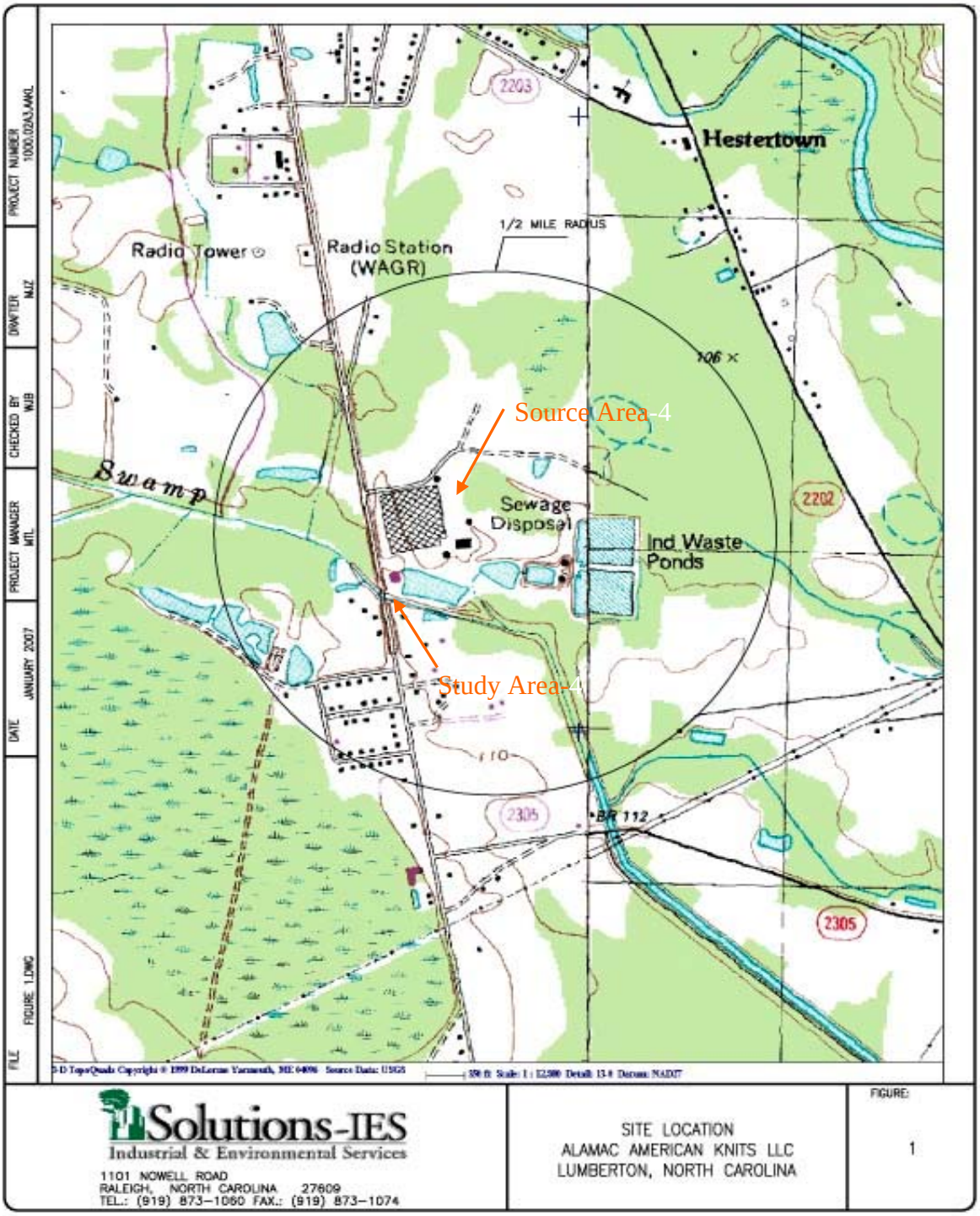

Figure 7.1. Alamac American Knits, LLC Site Features, Lumberton, NC
(Solutions-IES, 2005)

7.1.2 Site Contaminants

The multiple remediation approaches implemented in the source area have substantially reduced the PCE and TCE concentrations over time. Initial groundwater investigations in November 1999 measured up to 32,000 µg/L PCE and 24,000 µg/L *c*DCE in monitoring well MW-11 which is located southwest of the former PCE AST outside the Manufacturing Building **(Figure 7-1).** This is the area where active and passive remediation technologies were applied. In 2007, this well contained 35 µg/L PCE and 1,000 µg/L *c*DCE. The locations of the soil sampling points and the monitoring wells sampled are presented on Figure 7-2. However, in the downgradient portion of the plume, there are indications of the DCE stall. One location near Jacob Swamp Canal was identified as a possible area suitable for the enrichment project. This area is approximately 450 to 500 ft downgradient of the source and in the vicinity of the monitoring wells designated MW-6, MW-8 and MW-12 located west-southwest of the PCE source area (Figure 7-2). This area of the groundwater plume contains little PCE, measurable *c*DCE and some VC. The following parameters indicate how the Alamac site fulfills the criteria and why it was chosen as a potential MnO_2-enhanced MNA site:

1. The aquifer material is conducive to injection;
2. The depth-to-groundwater is relatively shallow (approximately 2 to 9 ft. bgs.);
3. Little residual PCE or TCE is present, but *c*DCE and VC are present in quantities suitable for this study;
4. A moderate-to-high level *c*DCE stall is noticeable, especially in nearby deep well MW-12;
5. The biogeochemical parameters are variable with some parameters falling within the preferred criteria and some falling outside the preferred criteria. Those falling within the preferred criteria include;
    a) Slightly acidic to neutral pH
    b) No nitrate
    c) Low dissolved iron
    d) Relatively low methane downgradient

Table 7-1 provides a summary of historical groundwater conditions in the general area of interest. The data are derived from the 2000 through 2005 groundwater sampling reports. Where possible, the most recent data are used.

TABLE 7-1 HISTORICAL GROUNDWATER CONDITIONS GROUNDWATER PLUME AS OF OCTOBER 2005 ALAMAC AMERICAN KNITS, LUMBERTON, NC				
	Units	**MW-6**	**MW-8**	**MW-12**
Inorganics				
Iron (Dissolved)	mg/L	0.60*[1]	3.5	2.0*[1]
Volatile Organic Compounds				
Tetrachloroethene	μg/L	<0.5	<0.5	<.5
Trichloroethene	μg/L	<0.5	0.84	6.8
cis-1,2-Dichlorothene	μg/L	3.2	140	2400
trans-1,2-Dichloroethene	μg/L	<0.5	2.7	27
Vinyl Chloride	μg/L	2.5	79	230
Ethene	μg/L	0.49	NA	NA
Methane	μg/L	998	690*[3]	640*[3]
Water Quality				
pH	SU	6.5	6.3	5.7
Dissolved Oxygen	mg/L	15.6	0.20	0.18
Oxidation-Reduction Potential	mV	-93	<-100	-38
Dissolved Organic Carbon	mg/L	15.6	12*[2]	5.1*[2]
Sulfate	mg/L	15.0	62*[2]	<5*[2]
Nitrate	mg/L	<.05*[2]	<.05*[2]	<.05*[2]
Alkalinity	mg/L	200	210*[2]	44*[2]

Notes: *[1]data from April 26, 2000; unmarked other data from October 26, 2005.
*[2] data from November 1, 1999
*3 data from October 24, 2000
NA = Not analyzed

MW-6, MW-8 and MW-12 are located 450 to 500 ft downgradient of the source area. As shown in Table 7-1, limited biogeochemical data have been obtained from the downgradient portions of the plume, but there has been evidence of prolonged exposure of aquifer matrices in these areas to *c*DCE.

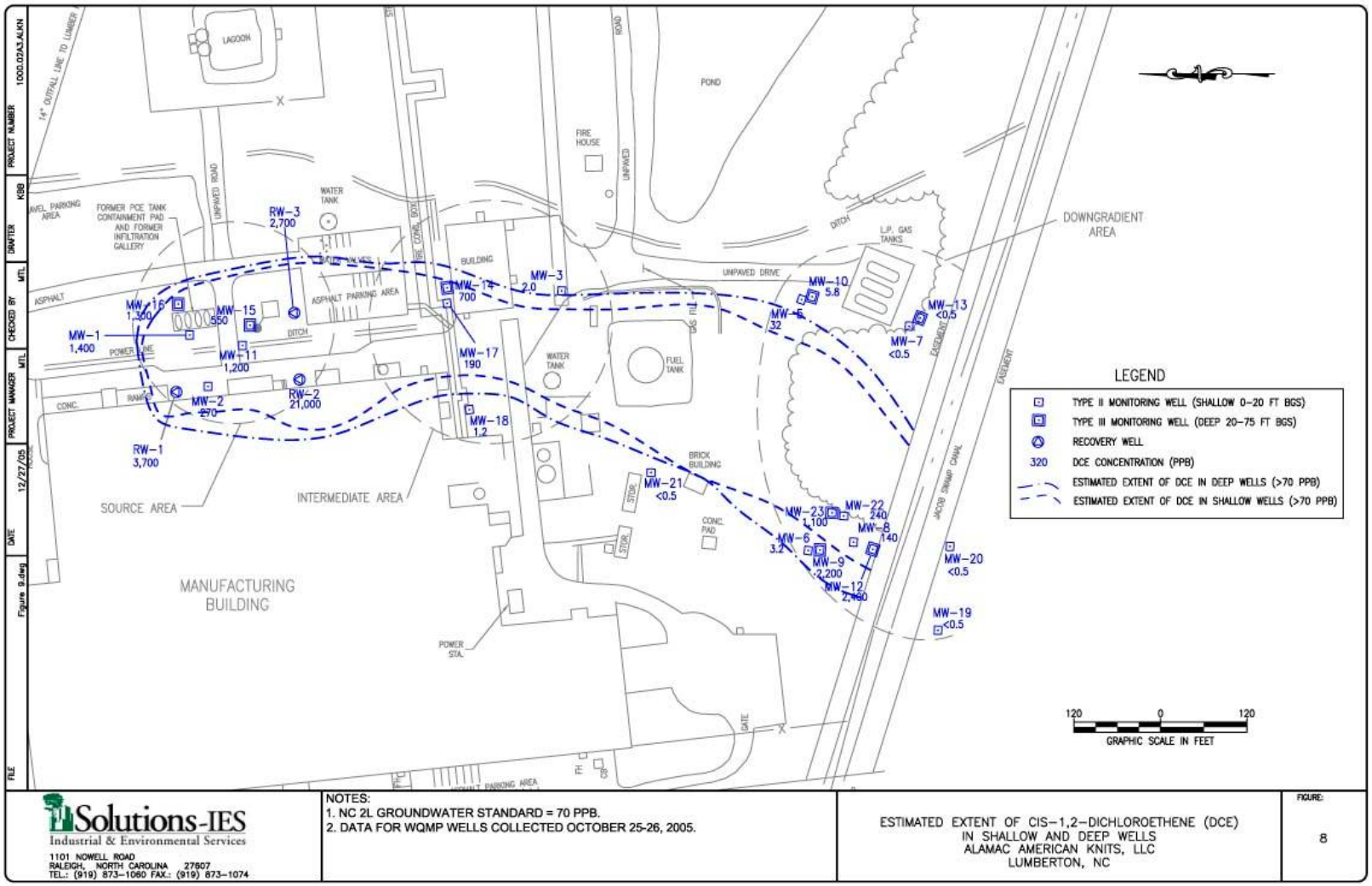

Figure 7.2. Alamac American Knits, LLC. Monitor Well Locations and *c*DCE Plume Limits (October 2005),
(Solutions-IES, 2005)

7.1.3 Site Hydrogeology and Plume Geometry

The subsurface in the Lumberton area has been described in terms of at least two shallow aquifers. The Site is underlain by the Duplin Formation, a shelly, medium-to coarse-grained sand, sandy marl and limestone.

The groundwater elevations and flow directions in the surficial aquifer at the site are shown in Figure 7-3 from the Solutions-IES 2005 report for December 2005. Groundwater flow in the surficial aquifer tends to be south, away from the former PCE tank containment pad.

The construction of the monitor wells of interest (or near areas of interest) and depth to groundwater measured in October 2005 or November 2006 are presented in Table 7-2.

TABLE 7-2
WELL CONSTRUCTION INFORMATION
ALAMAC AMERICAN KNITS, LUMBERTON, NC

Well ID	Total Depth (ft)	Screen Interval (ft bgs)	Depth to Water (ft below top of casing)
MW-6[1]	18	7.8-17.8	9.48
MW-8[1]	20	9.6-19.6	9.67
MW-12[1]	31	26.0 – 31.0	9.23

Note: 1 Depth to water measured October 25, 2005

In general, the plumes (shallow and deep) of *c*DCE lie in a relatively narrow region approximately 270 ft wide and ranging from the east side of the manufacturing building to the south towards the Jacob Swamp Canal. Monitoring wells across Jacob Swamp Canal do not show any impacts from *c*DCE. Discharge of groundwater to Jacobs Swamp Canal is suspected.

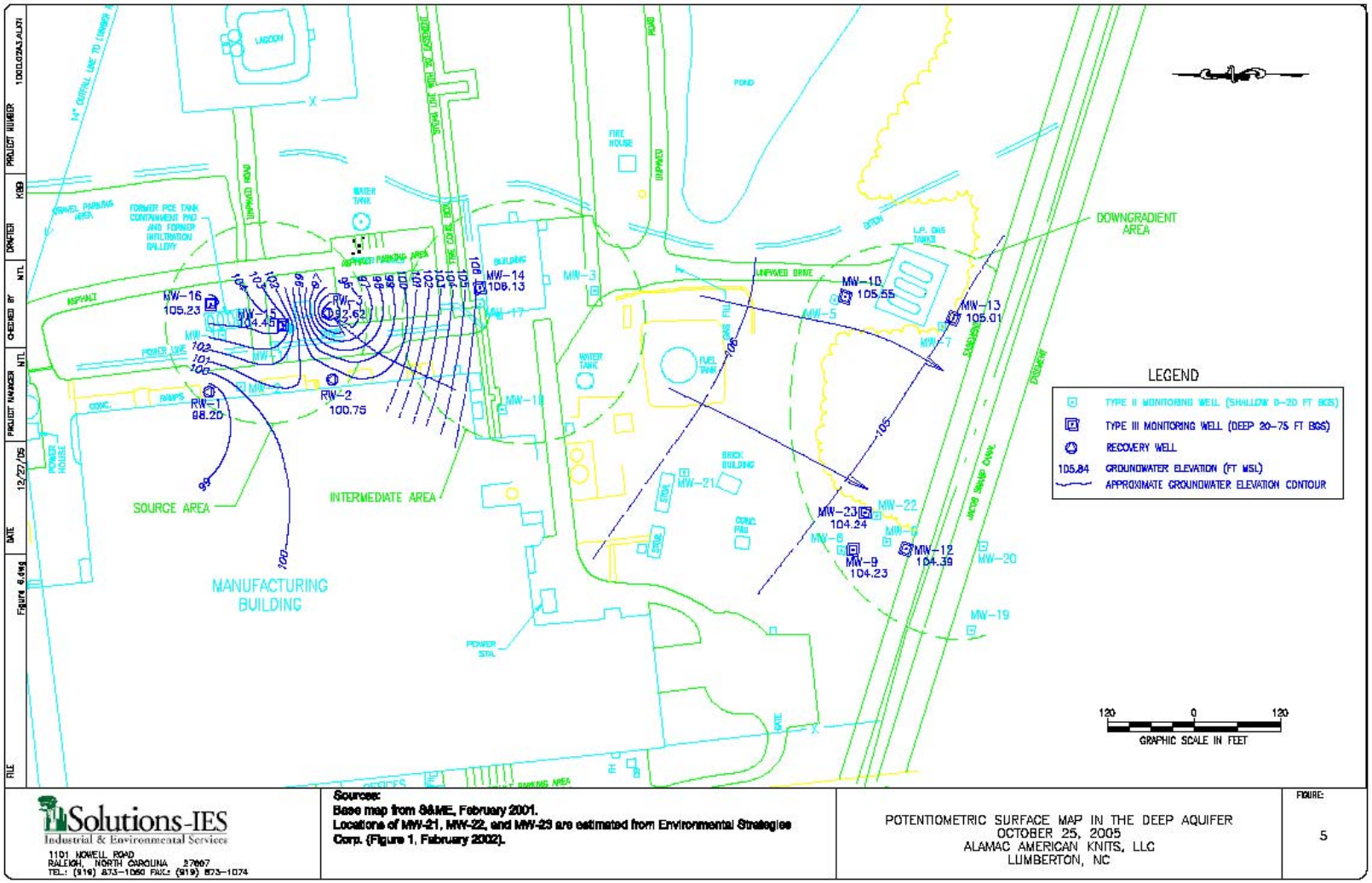

Figure 7-3. Water Table Elevation Map for Shallow Aquifer from December 2005, Alamac American Knits, Lumberton, NC (Solutions-IES, 2005)

7.2 Biogeochemical Characterization

For the enrichment studies in this area, three composite soil samples (SB-1, SB-2 and SB-3) were collected along Jacobs Swamp Canal (Figure 7-2). The canal is a flood control channel through a wooded riparian buffer zone that forms the property boundary. The hand auger locations were about 50 to 100 ft apart depending upon access to the sediments near the water line in the canal. The locations were chosen based on the assumption that *c*DCE contaminated groundwater naturally discharged to the canal and that soils from the edge of the stream would have the best opportunity for natural enrichment by long-term exposure to *c*DCE. The soils were not submitted for laboratory analysis and no groundwater was collected from any nearby wells.

7.3 Enrichment Study Design and Results

Sediment from SB-1, SB-2, and SB-3 cores (depth 0-0.5') was homogenized inside the anaerobic chamber. In lieu of groundwater, an anaerobic medium optimized for iron and manganese-reducers was used (see Appendix B). Approximately 3 grams of homogenized sediment were added to 160-mL serum bottles. The final volume of the medium, including amendments, was 150 mL. Several treatments (single bottles) were established to evaluate *c*DCE degradation under various conditions. Two treatments were established to determine whether *c*DCE could be cometabolized. One treatment was amended with acetate, and the other was amended with ethene, which was added to the headspace. One treatment was amended with humic acids in order to assess whether the addition of humic acids facilitates electron shuttling between MnO_2 and *c*DCE (Cervantes *et al.*, 2001). Finally, two treatments were established to assess whether manganese reduction was occurring and could be linked to the utilization of other organic substrates besides *c*DCE (acetate or ethene). Formaldehyde, *c*DCE, humic acids, and acetate were added as concentrated stocks to give the final concentrations noted in Table 7-4.

TABLE 7-3
SUMMARY OF ENRICHMENT TREATMENTS ON MATRICES FROM ALAMAC AMERICAN KNITS, LUMBERTON, NC

Treatment Descriptions	Soil (2.00%)	MnO_2 (25 mM)	Humic Acids (5 ppm)	Acetate (500 ppm)	Ethene Added to Headspace	*c*DCE (5 ppm)	Formaldehyde (1.5%)	O_2 Added to Headspace
Sterile Control With MnO_2	X	X				X	X	
Sterile Control Without MnO_2	X					X	X	
Unamended	X							
Background Control	X					X		
Synthesized MnO_2	X	X				X		
Commercial MnO_2	X	X				X		
Humic Acid Amendment	X	X	X			X		
*c*DCE and Ethene	X	X			X	X		
*c*DCE and Acetate	X	X		X		X		
Aerobic	X	X				X		X
Acetate	X	X		X				
Ethene	X	X			X			

Aqueous samples were collected over the course of five months and analyzed for VOCs (EPA Method 8260). Bottles were sampled at 0 weeks, 1 month, 2 months, and 5 months for dissolved manganese via EPA Method SW-846 6010.

The analytical results for the Lumberton enrichment study are included in Appendix C11 and C12. In Figure 7-4, *c*DCE is represented as the percentage remaining relative to the sterile controls that did not contain MnO_2 (i.e., the single value for each treatment was divided by the single value for the sterile control treatment that did not contain MnO_2). Some treatments were re-spiked with *c*DCE when the *c*DCE was depleted. See Appendix C11 for additional details. Re-spiked values were not graphed for the purpose of comparing when complete loss of *c*DCE was observed across treatments. In Figure 7-5, the dissolved manganese values are single measurements for each treatment at each timepoint.

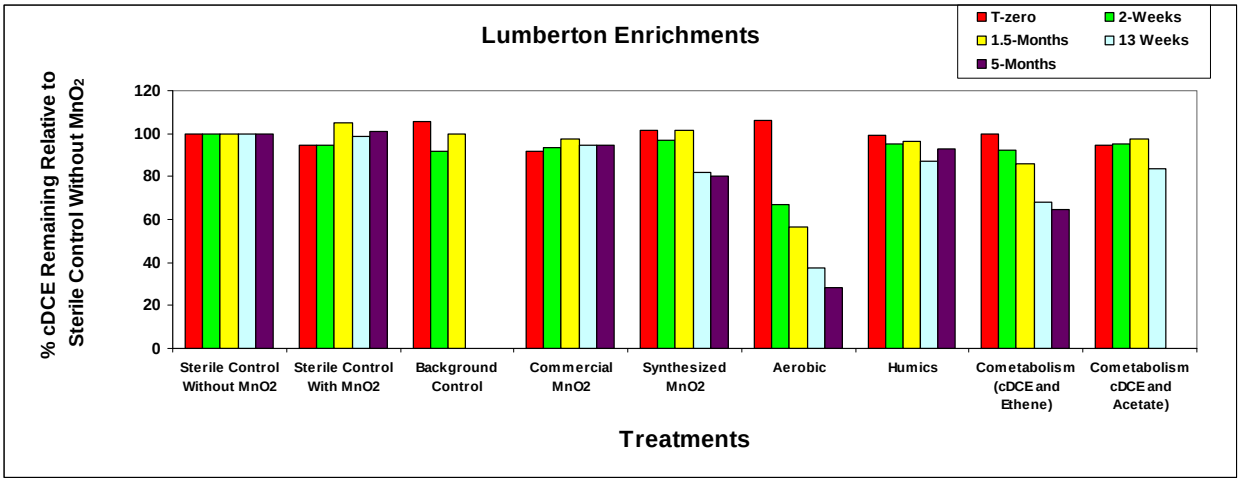

Figure 7-4. Lumberton Enrichment Results for *c*DCE Measurements

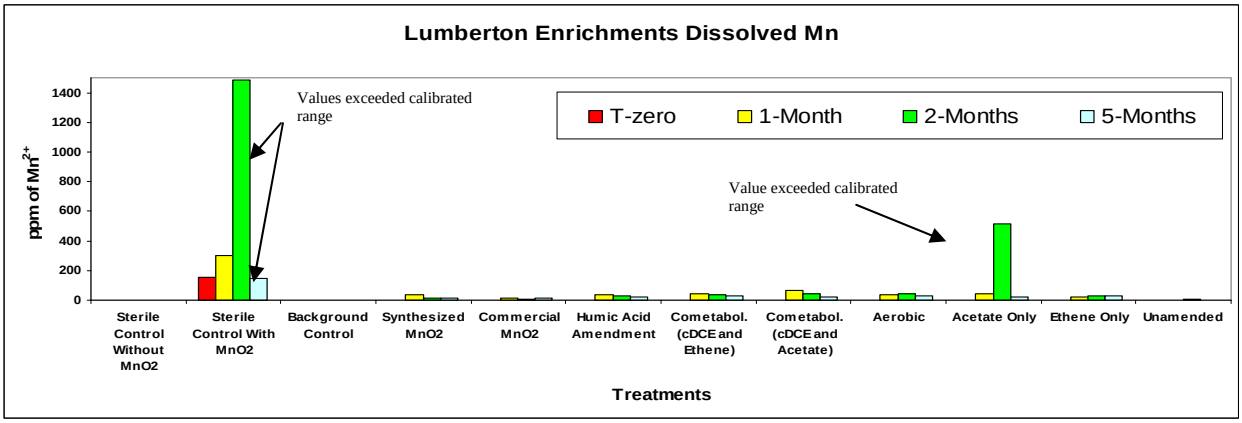

Figure 7-5. Lumberton Enrichment Results for Dissolved Manganese Measurements

7.4 Summary of Results

After 9 weeks, *c*DCE was completely depleted in the background control, and by four months it was completely removed from the cometabolism treatment amended with acetate. Significant *c*DCE degradation was observed in the aerobic treatment (72%). VC was detected in the background control, as well as the cometabolism treatment amended with acetate (data not included). The addition of humic acids did not enhance *c*DCE degradation. Although there was a lag, the addition of acetate did appear to enhance *c*DCE degradation after several months. Given the assumption that reductive dechlorination is the dominant process removing *c*DCE in site material, the acetate probably served as an additional electron donor. This is consistent with observations during the remediation efforts at the site that suggests the presence of a viable indigenous population of dehalorespiring microorganisms that can be enhanced by the addition of hydrogen donor. The addition of MnO_2 appears to have inhibited reductive dechlorination based on the lag period associated with treatments receiving MnO_2 compared to the background control treatment.

The results of the metals analysis showed a significant increase in soluble manganese in the sterile controls amended with MnO_2. Commercial formaldehyde contains low concentrations of formic acid, which can reduce MnO_2. Significant manganese reduction was also demonstrated in the treatment that was amended with only acetate as a carbon source. This finding suggests that site material from Alamac supports manganese reducers, and that the lag period associated with *c*DCE loss in the cometabolic treatment may have been attributed to consumption of the electron donor (acetate) during manganese reduction.

8.0 CONCLUSIONS

An apparent stall in *c*DCE biodegradation is observed at many natural attenuation sites where *c*DCE accumulates and is not further degraded. The lack of further breakdown of *c*DCE is often attributed to a lack of available hydrogen donor and/or absence of a suitable microbial community to further degrade the contaminant.

Bradley et al. (1998) reported that addition of Mn(IV) could enhance microbial oxidation of *c*DCE under anaerobic conditions. However, the extent to which this process occurs in groundwater and whether it can be enhanced is unknown. This study examined the effect of MnO_2 and other amendments in promoting biological oxidation of *c*DCE under anaerobic, aerobic or cometabolic conditions. Efforts were also made to find and enrich naturally-occurring microbial populations that could degrade *c*DCE using MnO_2 as an electron acceptor.

Groundwater and/or saturated soil from water bearing subsurface zones contaminated with chlorinated ethenes were collected from five locations at DoD facilities and one privately owned textile manufacturing facility. At each of these sites, there was evidence of a *c*DCE stall. The sample collection sites were located in Utah, Washington, South Carolina, Florida and North Carolina. Laboratory microcosm and/or enrichment cultures were constructed using the matrices collected from each location to evaluate the rate and extent of contaminant biodegradation under ambient conditions and with added manganese and organic substrates. Two indicators were used to measure the effectiveness of the treatments: 1) changes in the *c*DCE and VC concentrations and 2) changes in the concentration of soluble Mn(II).

The changes in the CVOC concentrations (specifically *c*DCE and VC) were recorded over the prescribed incubation period. Concentrations of dissolved Mn(II) were analyzed in solution. An increase in the rate and/or extent of *c*DCE loss in incubations amended with MnO_2 coupled with an increase in dissolved Mn was considered evidence that MnO_2 addition stimulated *c*DCE degradation. Conversely, the disappearance of *c*DCE with concurrent production of VC or ethene was considered evidence that anaerobic reductive dechlorination was the operational biodegradation pathway.

The different microcosm and enrichment studies were incubated and monitored from 2 months (LC-34) to 9 months (Keyport). All treatments contained added *c*DCE. The responses to each treatment by the site matrices tested are summarized below:

- *Treatment 1: (Sterile Control - without MnO_2, with formaldehyde)*. Changes in *c*DCE concentrations in all other treatments were measured against changes in this treatment. Some reduction of Mn(IV) to Mn(II) was observed in four of the five sites; the presence of low concentrations of formic acid in the formaldehyde was assumed to promote abiotic reduction of MnO_2 in this treatment.
- *Treatment 2: (Sterile Control - with MnO_2, with formaldehyde)*. Microcosms from all six sites showed dramatic and substantial increases in Mn(II) concentrations presumably due to low concentrations of formic acid contained in the formaldehyde. There was limited, if any, decrease in *c*DCE in five of six sites; a 20 to 40% decrease in *c*DCE in the

microcosms constructed from Myrtle Beach matrices suggested that the formaldehyde did not effectively inhibit the microbial population.

- *Treatment 3: (Unamended - No added cDCE or MnO_2)*. Unamended controls were created to monitor background, natural changes in three sites: Hill, Myrtle Beach and Keyport. Starting *c*DCE concentrations varied from BDL in microcosms from Keyport, 60 µg/L from Hill, and 270 µg/L from Myrtle Beach. Changes to *c*DCE concentrations were not measured. Mn(IV) concentrations changed only slightly suggesting little native biological or abiotic activity.
- *Treatment 4: (Background Control - No added MnO_2)*. A background control for each site was created from site-specific matrices. At most locations, 2 mg/L *c*DCE were added to the incubations without any supplemental MnO_2. However, 5 mg/L *c*DCE were added to the Lumberton enrichments. In the Keyport microcosms and Lumberton enrichments, *c*DCE was reduced to below detection within 4 and 1.5 months, respectively. However, there was no evidence for increased soluble Mn and some VC was noted in the Lumberton study, indicating reductive dechlorination. In the microcosms/enrichments from Myrtle Beach, Hill AFB, LC-34 Plume and LC-34 ESB, the *c*DCE concentrations fluctuated, but none consistently trended downward indicating biodegradation. There was very little change in Mn(II) concentrations.
- *Treatment 5 and 6: (Commercial and Synthesized MnO_2)*. There was no difference in response between the commercial and synthesized MnO_2. In four of the sites, the addition of MnO_2 did not appear to enhance the degradation of *c*DCE relative to the background control or result in an increase of soluble Mn. The greatest change occurred in the Keyport microcosms where, by 7 months, *c*DCE was completely depleted in the synthesized MnO_2 treatment. However, this lagged behind the background control by approximately 5 months. There was no appreciable change in soluble Mn that would indicate *c*DCE biodegradation was coupled to manganese reduction. The Keyport groundwater contained 8.9 mg/L TOC so it is assumed that the decrease in *c*DCE was due to reductive dechlorination. The observed lag implies that MnO_2 addition inhibited reductive dechlorination when compared to the background control treatments. Similar inhibition was suggested in the Alamac enrichments.
- *Treatment 7: (Humic Acid with MnO_2)*. These treatments were prepared to determine whether humic acids could facilitate electron shuttling between MnO_2 and *c*DCE as described by Cervantes *et al*. (2001). At Keyport, the addition of humic acid appeared to enhance reductive dechlorination by providing an additional electron donor. Humic acid addition did not facilitate the reduction of *c*DCE concentrations at the other five sites.
- *Treatment 8: (Cometabolism with Acetate and MnO_2)*. A treatment amended with acetate was prepared with matrices from five sites. Minimal changes to *c*DCE concentrations were observed at Myrtle Beach and either LC-34 location. However, there was about a 50% and 30% decrease in *c*DCE in the Hill and Lumberton incubations, respectively, over 5 months of incubation. Acetate appears to have served as an additional electron donor.
- *Treatment 9: (Aerobic with MnO_2)*. With an aerobic headspace and added MnO_2, *c*DCE decreased by greater than 60% in five of the six sites. The aerobic respiration of *c*DCE is not unexpected. However, the increase in soluble Mn(II) in the Keyport and Myrtle Beach microcosms was not expected as this would suggest reducing conditions in the

microcosms. Keyport microcosms were larger and deeper providing that anaerobic conditions may have occurred in the bottom of the incubations away from the aerobic headspace.

- *Additional Enrichments on LC34 ESB and Alamac matrices: (Ethene, NTA and Oxalic Acid).* The addition of ethene as an alternate carbon source had no affect on increasing the biodegradation of *c*DCE. The addition of the chelating agents, NTA and oxalic acid, did not enhance *c*DCE biodegradation.

In summary, there was some indication that the background conditions at several sites lead to VC formation by reductive dechlorination. This was more apparent at sites with residual TOC. The addition of acetate and/or humic acids may have furthered this reaction. The presence of an aerobic headspace appeared to promote the best biodegradation of *c*DCE, apparently through aerobic oxidation. The addition of MnO_2 appeared to have inhibited *c*DCE biodegradation at two sites. There was little evidence that increases in the concentration of soluble Mn(II) from the biological oxidation of *c*DCE occurred.

Results from all four of the microcosm studies (Hill, Keyport, Myrtle Beach and LC-34 Plume) showed that the dissolved Mn(II) concentrations were greater than expected based on the observed loss of *c*DCE. This indicates some manganese reduction was likely due to oxidation of indigenous carbon sources.

Multiple treatments were prepared to promote the anaerobic biological oxidation of *c*DCE. None of these treatments were effective in enhancing the anaerobic oxidation of *c*DCE using MnO_2 as an electron acceptor. Based upon these results, there is no evidence that addition of MnO_2 to aquifers will enhance *c*DCE biodegradation. Further pilot testing of MnO_2 addition as a technology to enhance *c*DCE biodegradation is NOT recommended at this time.

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10.0 POINTS OF CONTACT

POINT OF CONTACT	ORGANIZATION	ROLE IN PROJECT
M. Tony Lieberman	Solutions-IES, Inc. 1101 Nowell Rd. Raleigh, NC 27607 919-873-1060 (phone) 919-873-1074 (fax) tlieberman@solutions-ies.com	Principal Investigator
Dr. Robert C. Borden, P.E.	Solutions-IES, Inc. 1101 Nowell Rd. Raleigh, NC 27607 919-873-1060 (phone) 919-873-1074 (fax) rcborden@solutions-ies.com	Co-Principal Investigator
Dr. Nancy Ruiz	Naval Facilities Engineering Service Center1100 23rd Ave. Code 411 Port Hueneme, CA 93043 805-982-1155 (phone) 805-982-4304 (fax) nancy.ruiz@navy.mil	Contracting Officer Representative

Signature and Date:

_____ _____

M. Tony Lieberman Date
Solutions-IES, Inc.

APPENDIX A
SITE INFORMATION SPREADSHEET

Site Comparison Spreadsheet
ESTCP Project No.0625

Site Name & Location		Ideal site	Suggested MW	Suggested MW
			1	2
Site name				
Location				
Contact Person				
Affiliation				
Contact Phone				
Contact Fax				
Contact e-mail				
GW Plume Description				
	Plume Designation			
	Source of Release			
Aquifer Description (sand, silt, rock, etc.)		Need this to understand the potential that an injected material can be distributed around the injection point		
Aquifer Characteristics				
	Depth to Water	Shallow is easier to work with, but <100 ft is still workable		
	Hydraulic Conductivity	> 5 ft/d		
	Groundwater Flow Velocity	prefer 50 to 150 ft/yr		
Describe Extent of Natural Attenuation of TCE to DCE.				
	Is TCE essentially gone throughout the plume?	Not critical that TCE be entirely gone, but definitely should be a lot less than DCE		
	Is there a substantial DCE plume?	This is very important. Concentration of DCE would be preferred in the 300 to 2000 ppb range.		
	Is DCE stall at this site a significant regulatory issue?	If DCE stall is significant regulatory issue, then adding MnO2 to stimulate degradation may be worthwhile.		

Assuming TCE is degrading, what is the source of organic carbon driving reductive dechlorination?		High levels of BTEX or other TOC will increase MnO2 demand.		
Is there any evidence that DCE is degrading? If so, describe evidence.		Vinyl chloride or ethene concentrations are low or not detected.		
Is there any evidence/reason to believe manganese (Mn) concentrations in soil or groundwater would be low or high at this site? If so, what evidence.		Some manganese (<20 ppm) would be preferred since it increases the chance of an adapted microbial population that could be enriched. Non-detect manganese is also OK. High manganese probably means it would have happened already and hasn't.		
	pH	Optimal 6 to 8; 5 to 8 OK		
	Dissolved Oxygen	low DO is preferred		
	ORP	low (<+50 mV)		
	Nitrate	low		
	Sulfate	not applicable		
	TOC	low		
	Dissolved Iron	low to moderate		
	Methane	low to moderate		
	TCE	prefer <100 ppb		
	DCE	prefer 300 to 2000 ppb		
	VC	VC>BDL preferred, but not required		
	ethene	not applicable		
	co-contaminants	prefer none		
Soil Collection Methods	HAS, Hand Auger, Geoprobe, air rotary?	Shallower is less expensive.		
Qualitative Evaluation of Site Accessibility				

APPENDIX B
MANGANESE DIOXIDE SYNTHESIS AND MEDIA COMPONENTS

Manganese Dioxide (MnO_2) Synthesis

Manganese dioxide (MnO_2) was synthesized by a method modified from Lovley and Phillips (1988), in which a solution of manganese chloride ($MnCl_2$) is added to a solution of permanganate ($KMnO_4$). However, this method results in an excess of unreacted $KMnO_4$. Therefore, the process was reversed. A stock solution of permanganate (20 mM $KMnO_4$/40 mM NaOH) was slowly added to a stock solution of $MnCl_2$ (30 mM). The resulting MnO_2, which formed as a brown, amorphous precipitate, was slowly filtered through Whatman Qualitative filter paper. The precipitated MnO_2 was washed with one liter of distilled, deionized water to remove residual chloride. The MnO_2 was air-dried for several days prior to use.

Lumberton Microcosm Medium Components

A modified medium for Lumberton enrichments was prepared according to Lovley and Phillips (1988) and Balch et al. (1979). The medium components are found in the table below.

Basal Salts (1X)	**grams/L**
$NaHCO_3$	2.5
$CaCl_2 \cdot 2H_2O$	0.1
KCl	0.1
NH_4Cl	1.5
$NaH_2PO_4 \cdot H_2O$	0.6
$NaCH_3COO$	6.8
Yeast extract	0.2
Trace Minerals (0.1X)	**grams/L**
Nitrolotriacetic acid	1.5
Na_2MoO_4	0.025
$NiCl_2 \cdot 6H_2O$	0.024
$MgSO_4$ $7H_2O$	3
$MnSO_4 \cdot 2H_2O$	0.5
NaCl	1
$FeSO_4 \cdot 7H_2O$	0.1
$CoSO_4$ or $CoCl_2$	0.1
$CaCl_2 \cdot 2H_2O$	0.1
$ZnSO_4$	0.1
$CuSO_4 \cdot 5H_2O$	0.01
$ALK(SO_4)_2$	0.01
H_3BO_3	0.01

APPENDIX C
MICROCOSM DATA

APPENDIX C1

*c*DCE Analyses in Microcosms Established with Site Material from Hill AFB

Treatment Description	Bottle #	T-zero (ppm)	T-zero AVG	T-zero % Relat. to ST	2-Weeks (ppm)	2-Weeks AVG	2-Weeks % Relat. to ST	2-Months (ppm)	2-Months AVG	2-Months % Relat. to ST
Sterile Control Without MnO_2	19	1.558	1.50	100.00	1.41	1.57	100.00	1.63	1.60	100.00
	20	1.495			1.54			1.58		
	21	1.502			1.75			1.59		
Sterile Control With MnO_2	4	1.767	1.66	111.08	2.16	1.95	124.25	1.52	1.53	95.40
	5	1.688			1.88			1.53		
	6	1.641			1.80			1.54		
Background Control	1	1.391	1.58	105.44	1.32	1.42	90.92	1.36	1.50	93.41
	2	1.387			1.56			1.49		
	3	1.773			1.40			1.64		
Commercial MnO_2	7	1.637	1.59	106.14	1.48	1.34	85.82	1.57	1.52	94.84
	8	1.426			1.24			1.46		
	9	1.755			1.31			1.53		
Synthesized MnO_2 (CLAY)	10	1.585	1.51	100.93	1.18	1.16	73.89	1.51	1.40	87.74
	11	1.27			1.01			1.22		
	12	1.755			1.28			1.49		
Synthesized MnO_2 (SAND)	28	1.393	1.40	93.13	1.23	1.24	79.09	1.48	1.40	87.53
	29	1.503			1.25			1.38		
	30	1.288			1.24			1.35		
Aerobic	13	1.556	1.46	97.10	1.22	1.18	75.62	1.07	1.06	66.28
	14	1.525			1.33			1.05		
	15	1.385			1.01			1.06		
Humic Acid Amendment	16	1.871	1.44	96.10	1.44	1.35	86.09	1.53	1.48	92.29
	17	1.551			1.41			1.53		
	18	1.329			1.19			1.37		
Cometabolism (*c*DCE & Acetate)	22	1.539	1.89	125.93	1.44	1.42	90.59	1.45	1.51	94.37
	23	1.712			1.48			1.57		
	24	2.062			1.34			1.52		
Unamended	25	0	0	0	NT	NT	NT	NT	NT	NT
	26	0			NT			NT		
	27	0			NT			NT		

NT= Not tested

APPENDIX C1 (Continued)
*c*DCE Analyses in Microcosms Established with Site Material from Hill AFB

Treatment Description	Bottle #	11-Weeks (ppm)	11-Weeks AVG	11-Weeks % Relat. to ST	15-Weeks (ppm)	15-Weeks AVG	15-Weeks % Relat. to ST	5-Months (ppm)	5-Months AVG	5-Months % Relat. to ST
Sterile Control Without MnO_2	19	1.28	1.16	100.00	1.31	1.35	100.00	1.22	1.21	100.00
	20	1.23			1.39			1.19		
	21	0.96			1.36			1.23		
Sterile Control With MnO_2	4	1.40	1.29	111.67	1.15	1.15	85.03	1.11	1.14	93.83
	5	1.41			1.07			1.18		
	6	1.07			1.24			1.13		
Background Control	1	0.69	1.14	98.08	0.00	0.66	48.74	0.95	1.04	85.30
	2	1.29			0.96			1.04		
	3	1.43			1.02			1.11		
Commercial MnO_2	7	1.08	0.99	85.78	1.19	1.04	77.04	1.02	1.05	86.89
	8	0.78			1.05			1.04		
	9	1.11			0.89			1.10		
Synthesized MnO_2 (CLAY)	10	1.08	0.99	85.70	1.09	1.07	78.92	1.11	1.01	83.49
	11	0.80			1.11			0.87		
	12	1.10			1.00			1.06		
Synthesized MnO_2 (SAND)	28	0.90	0.85	73.78	1.22	1.18	87.33	0.81	0.73	60.15
	29	0.86			1.15			0.77		
	30	0.80			1.18			0.61		
Aerobic	13	0.55	0.60	51.62	1.14	0.66	48.61	0.33	0.38	31.13
	14	0.64			0.37			0.50		
	15	0.60			0.47			0.30		
Humic Acid Amendment	16	1.19	1.11	95.80	1.31	1.15	84.95	1.16	1.07	88.42
	17	1.06			1.06			1.06		
	18	1.08			1.08			1.01		
Cometabolism (*c*DCE & Acetate)	22	0.89	0.84	72.27	0.31	0.33	24.48	0.49	0.74	61.29
	23	0.76			0.25			0.85		
	24	0.86			0.43			0.89		
Unamended	25	NT	NT	NT	NT	NT	NT	NT	NT	NT
	26	NT			NT			NT		
	27	NT			NT			NT		

NT= Not tested

Appendix C2
Dissolved Manganese in Microcosms Established with Site Material from Hill AFB

Treatment Description	Bottle #	T-zero Mn(II) (ug/L)	T-zero Average Mn(II) (mg/L)	2-Months Mn(II) (ug/L)	2-Month Average Mn(II) (mg/L)
Background Control	1	338	468	315	0.8
	2	527		959	
	3	539		982	
Sterile Control With MnO_2	4	3540	4433.333	10700	6.6
	5	3940		5760	
	6	5820		3480	
Commercial MnO_2	7	671	701.333	2660	2.1
	8	915		2080	
	9	518		1480	
Synthesized MnO_2	10	389	374.333	1330	1.2
	11	219		1100	
	12	515		1140	
Aerobic	13	429	585	1.71	0.7
	14	516		2080	
	15	810		6.41	
Humic Acid Amendment	16	152	262.667	731	1.2
	17	306		1270	
	18	330		1520	
Sterile Control Without MnO_2	19	827	882	2810	1.6
	20	864		1140	
	21	955		972	
Cometabolism (*c*DCE and Acetate)	22	441	374	1520	1.4
	23	330		1320	
	24	351		1320	
Unamended	25	297	557.667	836	0.9
	26	788		885	
	27	588		892	
Synthesized MnO_2 (SAND)	28	155	113.1	1840	1.5
	29	106		1740	
	30	78.3		839	

J = The reported value was obtained from a reading that was less than the Contract Required Detection Limit, but greater than or equal to the Instrument Detection Limit

APPENDIX C3

*c*DCE Analyses in Microcosms Established with Site Material from Navy Base Kitsap

Treatment Description	Bottle #	T-Zero (ppm)	T-Zero Average	% Relative to ST. Control	2-Weeks (ppm)	2-Weeks Average	% Relative to ST. Control	1-Month (ppm)	1-Month Average	% Relative to ST. Control
Sterile Control Without MnO_2	19	1.81	1.81	100.00	1.51	1.68	100.00	2.02	1.98	100.00
	20	1.77			1.53			1.93		
	21	1.86			2.00			2.00		
Sterile Control With MnO_2	4	1.86	1.86	102.52	1.58	1.58	93.85	2.09	2.11	106.51
	5	1.88			1.58			2.16		
	6	1.83			1.57			2.08		
Background Control	1	1.56	1.70	93.73	1.35	1.45	86.44	1.81	1.83	92.20
	2	1.82			1.59			1.84		
	3	1.72			1.42			1.83		
Commercial MnO_2	7	1.83	1.76	96.89	1.51	1.53	90.88	1.86	1.97	99.56
	8	1.87			1.62			2.16		
	9	1.57			1.45			1.90		
Synthesized MnO_2	10	1.93	1.82	100.36	1.38	1.39	82.94	1.90	1.79	90.22
	11	1.84			1.49			1.89		
	12	1.69			1.31			1.58		
Aerobic	13	1.41	1.66	91.34	1.17	1.28	76.31	1.44	1.58	79.56
	14	1.76			1.32			1.59		
	15	1.80			1.35			1.71		
Humic Acid Amendment	16	1.62	1.75	96.68	1.46	1.51	90.17	1.70	1.82	91.99
	17	1.81			1.55			1.94		
	18	1.83			1.53			1.83		

APPENDIX C3 (Continued)
*c*DCE Analyses in Microcosms Established with Site Material from Navy Base Kitsap

Treatment Description	Bottle #	2-Months (ppm)	2-Months Average	% Relative to ST. Control	4-Months (ppm)	4-Months Average	% Relative to ST. Control	Respiked 4/26/2007	6-Months (ppm)	6-Months Average	% Relative to ST. Control
Sterile Control Without MnO_2	19	1.57	1.56	100.00	1.57	1.56	100.00		1.61	1.56	100.00
	20	1.38			1.52				1.47		
	21	1.72			1.59				1.59		
Sterile Control With MnO_2	4	1.62	1.63	105.00	1.57	1.59	102.02		1.60	1.62	103.85
	5	1.69			1.66				1.69		
	6	1.59			1.54				1.56		
Background Control	1	1.31	1.40	90.06	0.00	0.00	0.00	1.30	0	0.00	0.00
	2	1.44			0.00			1.27	0		
	3	1.46			0.00			1.21	0		
Commercial MnO_2	7	1.21	1.35	86.76	1.15	1.13	72.28		0.39	0.64	41.10
	8	1.48			1.29				1.16		
	9	1.37			0.93				0.37		
Synthesized MnO_2	10	1.40	1.29	82.68	1.15	1.01	65.15		0.24	0.12	8.01
	11	1.46			1.31				0.05		
	12	0.99			0.58				0.08		
Aerobic	13	0.96	0.98	62.93	0.57	0.66	42.42		0.37	0.47	30.30
	14	0.91			0.68				0.56		
	15	1.06			0.74				0.48		
Humic Acid Amendment	16	1.66	1.52	97.50	0.00	0.34	21.85		0.53	0.18	11.26
	17	1.49			0.44				0.00		
	18	1.41			0.58				0.00		

APPENDIX C3 (Continued)
*c*DCE Analyses in Microcosms Established with Site Material from Navy Base Kitsap

Treatment Description	Bottle #	Respiked 6/13/2007	7-Months (ppm)	7-Months Average	% Relative to ST. Control	Respiked 7/24/2007	8-Months (ppm)	8-Months Average	% Relative to ST. Control	9-Months (ppm)	9-Months Average	% Relative to ST. Control
Sterile Control Without MnO_2	19		2.31	2.25	100.00		1.44	1.44	100.00	1.37	1.31	100.00
	20		2.21				1.41			1.22		
	21		2.23				1.46			1.34		
Sterile Control With MnO_2	4		2.24	2.34	104.06		1.48	1.53	106.24	1.24	1.30	99.36
	5		2.41				1.55			1.37		
	6		2.37				1.55			1.29		
Background Control	1	1.45	1.50	0.50	22.22		0	0.00	0.00	0	0.00	0.00
	2	1.19	0.00			1.03	0			0		
	3	1.23	0.00			1.08	0			0		
Commercial MnO_2	7		0.52	0.73	32.52		0	0.34	24.01	0	0.29	21.80
	8		1.67				1.03			0.86		
	9		0				0			0		
Synthesized MnO_2	10		0.01	0.00	0.12	1.74	0	0.00	0.00	0.93	0.93	71.27
	11		0			1.87	0			1.08		
	12		0				0			0.79		
Aerobic	13		0.53	0.71	31.53		0.31	0.40	27.89	0.20	0.28	21.61
	14		0.75				0.43			0.32		
	15		0.85				0.46			0.33		
Humic Acid Amendment	16		0	0.00	0.00	1.67	0	0.00	0.00	0.95	0.86	65.67
	17		0			1.73	0			1.06		
	18		0			1.73	0			0.57		

Appendix C4
Dissolved Manganese in Microcosms Established with Site Material from Navy Base Kitsap

Treatment Description	Bottle #	2-Months Mn(II) (ug/L)	2-Months Mn(II) (mg/L)	8-Months Mn(II) (mg/L)	8-Months Mn(II) Average
Sterile Control Without MnO_2	19	1070	1.07	1.74	2.077
	20			2.49	
	21			2	
Sterile Control With MnO_2	4	15500	15.5	40.3	30.867
	5			24.6	
	6			27.7	
Unamended	22	893	0.921	1.28	1.31
	23	875		1.34	
	24	994		1.31	
Background Control	1	901	0.901	5.74	2.64
	2			1.05	
	3			1.13	
Commercial MnO_2	7	7440	7.44	9.56	11.06
	8			9.41	
	9			14.2	
Synthesized MnO_2	10	8960	8.96	15.2	14.5
	11			13.1	
	12			15.2	
Aerobic	13	8630	8.63	45.7	39.8
	14			33.1	
	15			40.6	
Humic Acid Amendment	16	6730	6.73	12.4	12.87
	17			15.7	
	18			10.5	

APPENDIX C5

*c*DCE Analyses in Microcosms Established with Site Material from Myrtle Beach AFB

Treatment Description	Bottle #	T-zero (ppm)	T-Zero Avg	% Relative to ST. Control	2-Weeks (ppm)	2-Weeks Avg	% Relative to ST. Control	1-Month (ppm)	1-Month Avg	% Relative to ST. Control
Sterile Control Without MnO_2	19	1.79	1.93	100.00	1.85	1.75	100.0	1.32	1.33	100.0
	20	2.04			1.53			1.35		
	21	1.96			1.87			1.34		
Sterile Control With MnO_2	4	2.14	2.07	107.21	1.65	1.49	85.0	1.25	1.29	96.7
	5	1.96			1.37			1.38		
	6	2.11			1.45			1.24		
Background Control	1	2.13	1.93	100.07	1.11	1.18	67.1	1.11	1.06	79.5
	2	1.87			1.21			1.04		
	3	1.81			1.21			1.03		
Commercial MnO_2	7	2.22	2.01	103.97	1.53	1.34	76.3	1.19	1.10	82.2
	8	1.86			1.26			1.05		
	9	1.94			1.22			1.04		
Synthesized MnO_2	10	1.93	1.80	93.19	1.56	1.43	81.3	1.18	1.13	84.4
	11	1.79			1.50			1.13		
	12	1.67			1.22			1.07		
Aerobic	13	1.90	1.94	100.42	1.05	1.19	68.2	0.94	0.93	69.8
	14	2.02			1.26			0.87		
	15	1.90			1.27			0.99		
Humic Acid Amendment	16	1.92	1.83	94.90	1.41	1.40	79.8	1.53	1.31	98.5
	17	1.77			1.35			1.23		
	18	1.81			1.44			1.19		
Cometabolism (*c*DCE & Acetate)	22	1.74	1.95	100.71	1.35	1.70	96.9	1.30	1.36	102.3
	23	1.84			1.85			1.33		
	24	2.254			1.89			1.46		
Unamended	25	0.2015	0.20	10.24	NT	NT	NT	NT	NT	NT
	26	0.1795			NT			NT		
	27	0.2125			NT			NT		

NT = Not tested

APPENDIX C5 (Continued): Myrtle Beach
*c*DCE Analyses in Microcosms Established with Site Material from Myrtle Beach AFB

Treatment Description	Bottle #	2-Months (ppm)	2-Months Avg	% Relative to ST. Control	3-Months (ppm)	3-Months Avg	% Relative to ST. Control	4-Months (ppm)	4-Months Avg	% Relative to ST. Control
Sterile Control Without MnO_2	19	1.36	1.37	100.0	0.77	0.99	100.0	1.35	1.44	100.0
	20	1.42			1.19			1.53		
	21	1.33			0.99			1.45		
Sterile Control With MnO_2	4	1.14	1.14	83.2	0.92	0.93	94.0	0.81	0.78	54.2
	5	1.19			1.00			0.86		
	6	1.08			0.87			0.68		
Background Control	1	1.18	1.12	81.8	0.99	0.88	88.9	0.90	0.86	59.9
	2	1.05			0.76			0.73		
	3	1.13			0.88			0.96		
Commercial MnO_2	7	1.29	1.21	88.1	1.22	1.14	115.1	1.12	0.97	67.4
	8	1.21			1.14			0.85		
	9	1.12			1.05			0.95		
Synthesized MnO_2	10	1.33	1.19	86.9	1.04	1.01	102.3	1.20	1.15	79.4
	11	1.25			1.09			1.23		
	12	0.99			0.90			1.01		
Aerobic	13	0.97	0.99	72.4	0.68	0.71	71.8	0.54	0.62	43.0
	14	0.96			0.67			0.59		
	15	1.03			0.77			0.74		
Humic Acid Amendment	16	1.42	1.34	97.8	0.69	0.87	88.7	1.64	1.61	111.4
	17	1.35			1.21			1.77		
	18	1.24			0.73			1.41		
Cometabolism (*c*DCE & Acetate)	22	1.20	1.45	106.0	0.88	1.01	102.2	1.01	1.27	88.2
	23	1.62			1.14			1.65		
	24	1.53			1.00			1.16		
Unamended	25	NT	NT	NT	NT	NT	NT	NT	NT	NT
	26	NT			NT			NT		
	27	NT			NT			NT		

NT = Not tested

APPENDIX C5 (Continued)
*c*DCE Analyses in Microcosms Established with Site Material from Myrtle Beach AFB

Treatment Description	Bottle #	5-Months (ppm)	5-Months Avg	% Relative to ST. Control	7-Months (ppm)	7-Months Avg	% Relative to ST. Control
Sterile Control Without MnO_2	19	0.81	0.90	100.0	0.68	0.58	100
	20	0.96			0.39		
	21	0.93			0.67		
Sterile Control With MnO_2	4	0.68	0.65	72.4	0.47	0.42	72.16
	5	0.70			0.45		
	6	0.57			0.33		
Background Control	1	0.76	0.78	86.6	0.51	0.54	93.69
	2	0.67			0.45		
	3	0.91			0.67		
Commercial MnO_2	7	0.92	0.86	96.0	0.40	0.53	90.72
	8	0.78			0.57		
	9	0.89			0.61		
Synthesized MnO_2	10	0.91	0.83	91.9	0.66	0.62	106.89
	11	0.85			0.66		
	12	0.73			0.53		
Aerobic	13	0.39	0.42	46.4	0.10	0.23	39.56
	14	0.37			0.22		
	15	0.49			0.37		
Humic Acid Amendment	16	1.08	0.93	103.6	0.74	0.71	123.05
	17	0.87			0.75		
	18	0.85			0.64		
Cometabolism (*c*DCE & Acetate)	22	0.54	0.71	78.4	0.32	0.45	77.72
	23	0.86			0.54		
	24	0.71			0.49		
Unamended	25	NT	NT	NT	NT	NT	NT
	26	NT			NT		
	27	NT			NT		

NT = Not tested

Appendix C6
Dissolved Manganese in Microcosms Established with Site Material from Myrtle Beach AFB

Treatment Description	Bottle #	T-zero Mn(II) (ug/L)	T-zero Mn(II) (ug/L)	T-zero Mn(II) (mg/L)	2-Months Mn(II) (ug/L)	2-Months Mn(II) (mg/L)
Sterile Control Without MnO_2	19	20400	20266.7	20.27	63700.64[OR]	70.7
	20	19900			80800	
	21	20500			67600	
Sterile Control With MnO_2	4	20500	25666.7	25.67	183000	175.8
	5	23600			206000	
	6	32900			138469.1[OR]	
Unamended	25	12500	11700.0	11.7	5600	5.7
	26	11800			6110	
	27	10800			5360	
Background Control	1	9390	9476.7	9.48	4280	4.1
	2	9590			3910	
	3	9450			4250	
Commercial MnO_2	7	8530	9876.7	9.88	3100	3.3
	8	10300			3440	
	9	10800			3280	
Synthesized MnO_2	10	7890	7470.0	7.47	5260	4.4
	11	7380			3570	
	12	7140			4250	
Aerobic	13	6790	6473.3	6.47	80900	85.7
	14	6880			92600	
	15	5750			83500	
Humic Acid Amendment	16	8340	7670.0	7.67	1330	4.5
	17	8610			4410	
	18	6060			7890	
Cometabolism (*c*DCE & Acetate)	22	9770	8936.7	8.94	777	0.7
	23	7820			409	
	24	9220			934	

[OR] Indicates the analyte's concentration exceeds the calibrated range of the instrument for that specific analysis

APPENDIX C7
cDCE Analyses in Microcosms Established with Site Material from Launch Complex IW-51 / ESB-SB-2

Treatment Description	Bottle #	T-zero (ppm)	T-Zero Average	% Relative to ST Control	2-Weeks (ppm)	2-Weeks Average	% Relative to ST Control
Sterile Control Without MnO_2	4-6	4.12	4.11	100.00	3.60	3.58	100.00
		4.03			3.58		
		4.17			3.55		
Sterile Control With MnO_2	7-9	3.62	3.72	90.69	3.48	3.40	95.12
		3.80			3.27		
		3.76			3.46		
Background Control	1-3	3.70	3.89	94.67	3.27	3.46	96.66
		3.86			3.56		
		4.10			3.54		
Commercial MnO_2	10-12	3.78	3.68	89.66	3.51	3.48	97.19
		3.58			3.43		
		3.69			3.48		
Synthesized MnO_2	13-15	3.90	3.80	92.48	3.56	3.54	98.84
		3.70			3.50		
		3.79			3.54		
Low Humic Acid Amendment	16-18	3.65	3.52	85.80	3.41	3.54	98.85
		3.47			3.65		
		3.45			3.56		
High Humic Acid Amendment	19-21	3.18	3.21	78.07	3.37	3.44	96.19
		3.44			3.48		
		3.00			3.48		
NTA Amendment	22-24	3.20	3.45	84.11	3.49	3.40	94.97
		3.34			3.22		
		3.83			3.48		
Oxalic Acid Amendment	25-27	3.70	3.55	86.56	3.44	3.44	96.13
		3.39			3.36		
		3.57			3.52		
Cometabolism (*c*DCE & Ethene)	28-30	3.69	3.69	89.98	3.30	3.41	95.26
		3.83			3.41		
		3.57			3.52		
Cometabolism (*c*DCE & Acetate)	31-33	3.48	3.56	86.64	3.46	3.42	95.55
		3.75			3.45		
		3.45			3.35		
Aerobic	43-45	4.57	4.57	111.40	3.66	3.68	102.72
		4.68			3.75		
		4.47			3.62		
Ethene	34-36	2.02	2.26	55.10	1.95	1.99	55.67
		2.13			2.00		
		2.63			2.03		
Acetate	37-39	2.58	2.56	62.27	1.92	2.01	56.29
		2.47			1.96		
		2.62			2.16		
Unamended	46-48	2.70	2.76	67.20	2.20	2.20	61.41
		2.86			2.27		
		2.71			2.12		

APPENDIX C7 (Continued)
*c*DCE Analyses in Microcosms Established with Site Material from Launch Complex IW-51I / ESB-SB-2

Treatment Description	Bottle #	1-Month (ppm)	1-Month Average	% Relative to ST Control	2-Month (ppm)	2-Month Average	% Relative to ST Control
Sterile Control Without MnO_2	4-6	4.60	4.74	100.00	4.75	4.81	100.00
		4.77			4.72		
		4.86			4.96		
Sterile Control With MnO_2	7-9	4.93	4.67	98.41	4.46	4.32	89.77
		4.42			4.11		
		4.65			4.38		
Background Control	1-3	4.22	4.56	96.25	4.55	4.39	91.28
		4.67			4.45		
		4.81			4.18		
Commercial MnO_2	10-12	4.83	4.79	100.90	4.54	4.26	88.52
		4.84			4.19		
		4.68			4.05		
Synthesized MnO_2	13-15	4.94	4.98	105.06	3.98	4.12	85.68
		4.96			4.46		
		5.05			3.92		
Low Humic Acid Amendment	16-18	3.70	3.73	78.71	4.07	4.33	90.08
		3.83			4.17		
		3.66			4.75		
High Humic Acid Amendment	19-21	3.50	3.62	76.31	4.36	4.58	95.29
		3.70			4.87		
		3.66			4.51		
NTA Amendment	22-24	3.51	3.54	74.60	3.93	3.99	82.84
		3.49			4.06		
		3.61			3.97		
Oxalic Acid Amendment	25-27	3.52	3.53	74.45	4.23	3.80	78.97
		3.53			3.47		
		3.55			3.69		
Cometabolism (*c*DCE & Ethene)	28-30	3.44	3.36	70.92	3.44	3.41	70.82
		3.33			3.41		
		3.32			3.37		
Cometabolism (*c*DCE & Acetate)	31-33	3.45	3.39	71.46	3.34	3.41	70.98
		3.37			3.27		
		3.35			3.63		
Aerobic	43-45	3.48	3.53	74.48	4.33	4.02	83.61
		3.62			3.52		
		3.50			4.22		
Ethene	34-36	1.89	1.96	41.31	2.06	2.15	44.70
		2.05			2.25		
		1.94			2.14		
Acetate	37-39	1.86	1.94	40.82	2.39	2.13	44.21
		1.89			2.07		
		2.06			1.92		
Unamended	46-48	2.09	2.18	45.96	2.17	2.42	50.28
		2.19			2.50		
		2.27			2.59		

APPENDIX C8
***c*DCE Analyses in Microcosms Established with Site Material from Launch Complex ESB-SB-1**

Treatment Description	T-Zero (ppm)	% Relative to ST Control	2-Weeks (ppm)	% Relative to ST Control	1-Month (ppm)	% Relative to ST Control	2-Months (ppm)	% Relative to ST Control
Sterile Control Without MnO_2	1.67	100.00	1.98	100.00	2.75	100.00	2.47	100.00
Sterile Control With MnO2	2.13	127.46	2.02	102.23	2.81	102.32	2.28	92.35
Background Control	1.97	117.88	2.05	103.56	2.80	101.83	1.86	75.53
Commercial MnO_2	2.09	125.44	2.05	103.67	2.70	98.35	2.42	98.25
Synthesized MnO_2	2.05	122.92	1.91	96.81	2.65	96.46	2.10	85.03
Low Humic Acid Amendment	2.12	126.95	1.98	100.11	2.73	99.14	1.94	78.61
High Humic Acid Amendment	2.20	131.93	1.96	99.31	2.72	98.93	2.36	95.64
NTA Amendment	1.99	119.52	2.03	102.92	2.72	99.08	2.84	115.17
Oxalic Acid Amendment	2.23	133.75	1.93	97.71	2.68	97.62	1.92	77.88
Cometabolism (*c*DCE and Ethene)	1.96	117.44	1.95	98.78	2.63	95.54	2.13	86.36
Cometabolism (*c*DCE and Acetate)	1.92	114.99	1.94	98.46	2.61	94.75	2.12	86.02
Aerobic	1.89	113.35	1.85	93.89	2.37	86.19	2.35	95.35
Unamended	0	0	0	0	0.12	4.34	0.10	4.19

APPENDIX C9
Dissolved Manganese in Microcosms Established with Site Material from
Launch Complex IW-51I/ESB-SB-2

Treatment Description	Bottle #	T-zero Mn(II) (ug/L)	T-zero Avg. Mn(II) (mg/L)	2-Month Mn(II) (ug/L)	2-Month Avg Mn(II) (mg/L)
Background	1-3	24.3	0.025	4.67[J]	0.042
		24.9		35.6	
		26.4		47.5	
Sterile Control Without MnO_2	4-6	93	0.090	115	0.120
		87		113	
		89.9		131	
Sterile Control With MnO_2	7-9	56208.16[OR]	52.692	389646.1[OR]	343.330
		57168.87		389061.4[OR]	
		44700		251296.2[OR]	
Commercial MnO_2	10-12	646	0.546	5020	5.52
		541		6100	
		450		5440	
Synthesized MnO_2	13-15	124	0.105	288	0.356
		111		302	
		79.8		478	
Low Humic Acid Amendment	16-18	146	0.151	481	0.606
		141		561	
		167		777	
High Humic Acid Amendment	19-21	128	0.149	1500	1.023
		182		712	
		136		858	
NTA Amendment	22-24	4690	5.34	408505.1[OR]	449.060
		6130		534521.5[OR]	
		5200		404159.3[OR]	
Oxalic Acid Amendment	25-27	333	0.372	5960	6.36
		458		5920	
		325		7200	
Cometabolism (*c*DCE & Ethene)	28-30	96.6	0.1142	381	0.317
		108		290	
		138		281	
Cometabolism (*c*DCE & Acetate)	31-33	154	0.131	412	0.362
		112		351	
		127		324	
Ethene	34-36	169	0.157	382	0.321
		171		281	
		131		300	
Acetate	37-39	170	0.118	390	0.337
		94.2		382	
		89.7		239	
Aerobic	43-45	172	0.171	45.9	0.045
		173		41.5	
		168		47.4	
Unamended	46-48	52.6	0.037	26	0.028
		24.6		19.8	

	34.2	39.5

[J] Reported value was obtained from a reading that was less than the Contract Required Detection Limit, but is greater than or equal to the Instrument Detection Limit

[OR] = The analyte's concentration exceeds the calibrated range of the instrument; Not enough sample to dilute and reanalyze

APPENDIX C10
Dissolved Manganese in Microcosms Established with Site Material from
Launch Complex ESB-SB-1

Treatment Description	T-zero Mn(II) (ug/L)	T-zero Mn(II) (mg/L)	2-Months Mn(II) (ug/L)	2-Months Mn(II) (mg/L)
Sterile Control Without MnO_2	3200	3.20	10900	10.9
Sterile Control With MnO_2	7190	7.19	48200	48.2
Background Control	133	0.13	0.8*	0.0008
Commercial MnO_2	173	0.17	24.3	0.0243
Synthesized MnO_2	71.3	0.07	456	0.456
Low Humic Acid Amendment	60.9	0.06	2.77	0.00277
High Humic Acid Amendment	176	0.18	330	0.33
NTA Amendment	3330	3.33	24500	24.5
Oxalic Acid Amendment	8040	8.04	14000	14
Cometabolism (*c*DCE & Ethene)	91.8	0.09	33.3	0.0333
Cometabolism (*c*DCE & Acetate)	134	0.13	154	0.154
Ethene	117	0.12	5.43[J]	0.00543
Acetate	48.9	0.05	2280	2.28
Aerobic	151	0.15	0.8*	0.0008
Unamended	126	0.13	0.8*	0.0008

[J] Reported value was obtained from a reading that was less than the Contract Required Detection Limit but is greater than or equal to the Instrument Detection Limit

*** Undetected**

APPENDIX C11
*c*DCE Analyses in Microcosms Established with Site Material from Alamac American Knits, Lumberton, NC

Treatment Description	Bottle #	T-zero (ppm)	% Relative to ST Control	2-Weeks (ppm)	% Relative to ST Control	1-Month (ppm)	% Relative to ST Control	1.5-Months (ppm)	% Relative to ST Control
Sterile Control Without MnO_2	5	4.362	100.00	4.127	100.00	4.19	100.00	3.66	100.00
Sterile Control With MnO_2	4	4.126	94.59	3.9	94.50	4.33	103.51	3.85	105.10
Background Control	1	4.61	105.69	3.779	91.57	3.99	95.26	3.65	99.66
Commercial MnO_2	3	4.005	91.82	3.862	93.58	4.34	103.81	3.57	97.54
Synthesized MnO_2	2	4.422	101.38	4.003	97.00	4.10	97.97	3.72	101.60
Aerobic	9	4.626	106.05	2.751	66.66	2.72	65.08	2.07	56.39
Humic Acid Amendment	6	4.341	99.52	3.928	95.18	4.40	105.09	3.54	96.50
Cometabolism (*c*DCE & Ethene)	7	4.347	99.66	3.81	92.32	4.23	101.00	3.15	85.85
Cometabolism (*c*DCE & Acetate)	8	4.135	94.80	3.919	94.96	4.04	96.41	3.58	97.71
Acetate	10	0	0	0	0	NT	NT	0.00	0.00
Ethene	11	0	0	0	0	NT	NT	0.00	0.00
Unamended	12	0	0	NT	NT	NT	NT	NT	NT

NT = Not tested

APPENDIX C11 (Continued)
***c*DCE Analyses in Microcosms Established with Site Material from**
Alamac American Knits, Lumberton, NC

Treatment Description	Bottle #	2-Months (ppm)	% Relative to ST Control	9 weeks (ppm)	% Relative to ST Control	13 Weeks (ppm)	% Relative to ST Control	13-Jun-07 Respiked	4-Months (ppm)	% Relative to ST Control
Sterile Control Without MnO_2	5	3.26	100.00	3.30	100.00	3.71	100.00		3.56	100.00
Sterile Control With MnO_2	4	3.08	94.63	3.64	110.04	3.67	98.84		3.74	105.05
Background Control	1	2.99	91.81	0	0.00	0.00	0.00	0.3066	0.24	6.63
Commercial MnO_2	3	3.10	95.11	2.51	75.95	3.51	94.49		3.30	92.70
Synthesized MnO_2	2	2.97	91.21	3.08	93.12	3.04	81.90		2.78	78.05
Aerobic	9	1.67	51.34	1.67	50.68	1.40	37.73		1.30	36.47
Humic Acid Amendment	6	3.22	98.93	3.26	98.60	3.23	86.91		3.25	91.16
Cometabolism (*c*DCE & Ethene)	7	2.56	78.71	2.39	72.19	2.53	68.21		2.31	64.82
Cometabolism (*c*DCE & Acetate)	8	3.23	99.08	3.46	104.55	3.10	83.48		0	0.00
Acetate	10	NT	NT	NT	NT	NT	NT		NT	NT
Ethene	11	NT	NT	NT	NT	NT	NT		NT	NT
Unamended	12	NT	NT	NT	NT	NT	NT		NT	NT

NT = Not tested

_c_DCE Analyses in Microcosms Established with Site Material from Alamac American Knits, Lumberton, NC

Treatment Description	Bottle #	5-Months (ppm)	% Relative to ST Control	23-Jul-07 Respiked	25-Jul-07 Respiked
Sterile Control Without MnO_2	5	3.31	100		
Sterile Control With MnO_2	4	3.33	100.68		
Background Control	1	0	0	1.704	
Commercial MnO_2	3	3.13	94.40		
Synthesized MnO_2	2	2.65	79.99		
Aerobic	9	0.94	28.30		
Humic Acid Amendment	6	3.08	92.85		
Cometabolism (*c*DCE & Ethene)	7	2.14	64.75		
Cometabolism (*c*DCE & Acetate)	8	0	0		3.91
Acetate	10	NT	NT		
Ethene	11	NT	NT		
Unamended	12	NT	NT		

NT = Not tested

APPENDIX C12
Dissolved Manganese in Enrichments Established With Site Material from Alamac American Knits, Lumberton, NC

Treatment Description	Bottle #	T-zero Mn(II) (ppm)	1-Month Mn(II) (ppm)	2-Months Mn(II) (ppm)	5-Months Mn(II) (ppm)
Sterile Control Without MnO_2	5	1.32	1.36	1.41	1.59
Sterile Control With MnO_2	4	155	298	1485.409[OR]	146.9507[OR]
Background Control	1	0.641	0.642	0.831	0.67
Synthesized MnO_2	2	0.678	35.1	14.6	13.7
Commercial MnO_2	3	0.87	13.9	10.6	11.6
Humic Acid Amendment	6	0.642	39.5	25.8	20.8
Cometabolism (*c*DCE & Ethene)	7	0.735	47.4	39	29.1
Cometabolism (*c*DCE & Acetate)	8	0.733	68.4	46.7	23.6
Aerobic	9	0.745	40.4	41	32.5
Acetate Only	10	0.752	46.8	516.6104[OR]	22.9
Ethene Only	11	0.814	24.7	26.8	26.5
Unamended	12	0.782	0.736	7.69	0.782

[OR] Indicates the analyte's concentration exceeds the calibrated range of the instrument; not enough sample to reanalyze