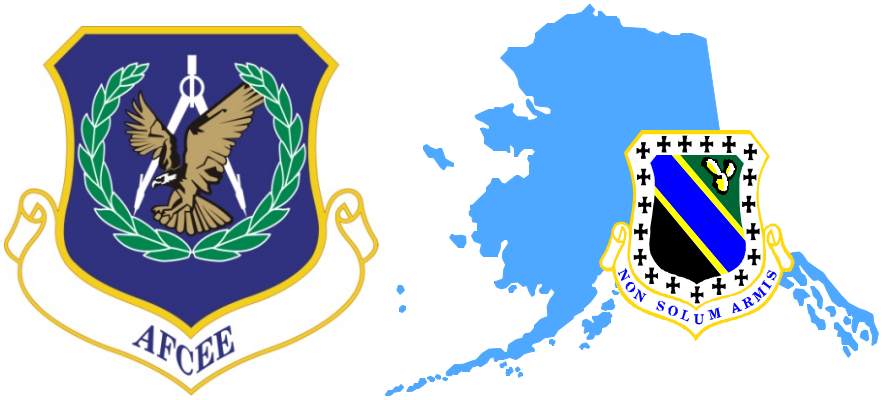
TECHNOLOGY DEMONSTRATION REPORT

FOR

BIOGEOCHEMICAL TRANSFORMATION OF CHLORINATED SOLVENTS AT THE DP98 SITE, JOINT BASE ELMENDORF-RICHARDSON, ALASKA



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and the

AIR FORCE CENTER FOR ENGINEERING AND THE ENVIRONMENT
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EXECUTIVE SUMMARY

A technology demonstration of biogeochemical transformation of chlorinated solvents in groundwater was conducted by Parsons Infrastructure and Technology Group, Inc. for the Air Force Center for Engineering and the Environment and Joint Base Elmendorf-Richardson, Alaska under Contract No. FA8903-08-D-8778, Task Order 0068. This and similar demonstrations are being conducted at multiple Air Force sites to independently evaluate the applicability, cost, and performance of enhanced biogeochemical transformation of chlorinated solvents under a wide variety of site conditions.

E.1 BIOGEOCHEMICAL TRANSFORMATION OF CHLORINATED ALIPHATIC HYDROCARBONS

There are three primary reactions that may degrade chlorinated aliphatic hydrocarbons (CAHs, commonly referred to as chlorinated solvents) under anaerobic conditions, including 1) direct biotic reductive dechlorination (halorespiration), 2) cometabolic reductive dechlorination, and 3) abiotic reductive dechlorination. Application of enhanced anaerobic bioremediation of chlorinated solvents has historically focused on biotic dechlorination processes. The ability to stimulate abiotic dechlorination of CAHs was the focus of the demonstration at the DP98 Site.

Abiotic reductive dechlorination is a chemical reaction where a CAH compound is reduced by a reactive mineral. For example, abiotic transformation of carbon tetrachloride, trichloroethane, tetrachloroethene (PCE), trichloroethene (TCE), and *cis*-1,2-dichloroethene (*cis*-DCE) has been investigated by numerous researchers using reduced iron minerals such as pyrite, troilite, mackinawite, and magnetite. This demonstration attempted to stimulate the abiotic reduction of TCE and DCE by reaction with reduced iron monosulfides (FeS) and/or iron disulfides (FeS_2). Formation of these minerals was enhanced by the addition of iron and sulfate amendments. In this case the overall degradation pathway is referred to as ***biogeochemical transformation*** because the reactive mineral is formed by both biological and chemical processes.

E.2 DEMONSTRATION OBJECTIVES

The overall objective for the DP98 technology demonstration was to evaluate the extent to which biogeochemical transformation or other *in situ* chemical reduction (ISCR) techniques may be used to reduce concentrations of CAHs within test cell treatment zones to levels protective of human health and the environment. Performance metrics developed for the demonstration included the following:

- Stimulate the production of reduced iron sulfides (measured as acid volatile sulfide [AVS]) to concentrations equal to or greater than 2,000 milligrams per kilogram (mg/kg) within two *in situ* treatment zones (test cells);
- Enhance the rates of *in situ* anaerobic degradation of PCE and TCE by one order of magnitude or more relative to rates of natural attenuation at the site;
- Reduce concentrations of PCE and TCE in the treatment zones to less than site-specific cleanup goals, and limit increases in DCE and VC to concentrations measured during base-line monitoring or to concentrations measured in upgradient monitoring locations; and

- Reduce total molar concentrations of chloroethenes within the treatment zones by 90 percent or more to demonstrate that complete transformation is occurring, and not just transformation of highly-chlorinated ethenes (PCE and TCE) to less-chlorinated ethenes (DCE and VC).

E.3 BIOGEOCHEMICAL TRANSFORMATION DESIGN

The demonstration objectives were accomplished by injecting iron, sulfate, and organic amendments into two *in situ* treatment zones (Test Cells No. 1 and No. 2). A commercial ISCR product was injected into a third treatment zone (Test Cell No. 3) for comparison. Amendments injected into the three test cells in May 2010 included the following products:

- **Test Cell No. 1:** EHC®, a controlled-release, integrated organic carbon and zero valent iron (ZVI) commercial product.
- **Test Cell No. 2:** Emulsified vegetable oil (EVO), sulfate in the form of powdered gypsum (calcium sulfate dihydrate), and iron in the form of powdered hematite (ferric iron oxide).
- **Test Cell No. 3:** EVO with iron and sulfate in the form of ferrous sulfate heptahydrate.

Quantities and concentrations of the iron and sulfate amendments were based on stoichiometric calculations intended to generate up to 2,000 mg/kg of iron sulfide minerals within the subsurface sediments.

E.4 GROUNDWATER BIOGEOCHEMISTRY

The injection of organic substrates increased concentrations of dissolved organic carbon (DOC), but differences in the magnitude of DOC between the three test cells were observed (**Figure E.1**). DOC concentrations were the highest in Test Cell No. 1 amended with EHC®, and lowest in Test Cell No. 2 amended with hematite, gypsum, and EVO. Approximately 3,750 pounds of EHC® product was injected into Test Cell No. 1, while approximately 900 pounds of vegetable oil (net weight) was injected into Test Cell No. 2 and Test Cell No. 3. While the reducing equivalents of the organic materials may differ, a greater quantity of organic material was injected into Test Cell No. 1 relative to the other two test cells.

The EHC® product injected into Test Cell No. 1 is comprised of organic carbon and ZVI. Concentrations of native sulfate up to 24.9 milligrams per liter (mg/L) were measured in September 2010, but were reduced to below detection by September 2011. Concentrations of sulfide as high as 3.09 mg/L were measured at DP98MP03 in September 2010, produced by reduction of native sulfate. Concentrations of ferrous iron increased substantially within Test Cell No. 1, to greater than 66 mg/L in September 2010. This is likely due to reduction of native ferric iron. Oxidation of the ZVI in the EHC® product may also produce ferrous iron.

The injection of calcium sulfate (gypsum) into Test Cell No. 2 was anticipated to increase the concentrations of sulfate in groundwater. Sulfate increased after injection to as high has 2,530 mg/L at DP98MP07 in September 2010. Concentrations of sulfate subsequently decreased to 895 mg/L at DP98MP07 and to 15.4 mg/L at DP98MP06 in September 2011, indicating sulfate reduction was occurring. Concentrations of sulfide were measured as high as 8.8 mg/L at DP98MP07, and a strong hydrogen sulfide odor was observed in the field. Concentrations of ferrous iron were anticipated to increase due to reduction of both native iron and the iron oxide (hematite) that was injected. In contrast to Test Cell No. 1, the maximum detected concentration of ferrous iron was 33 mg/L at DP98MP06 in May 2011. This suggests that much of the ferrous iron that was produced precipitated with sulfide to form iron-sulfide minerals.

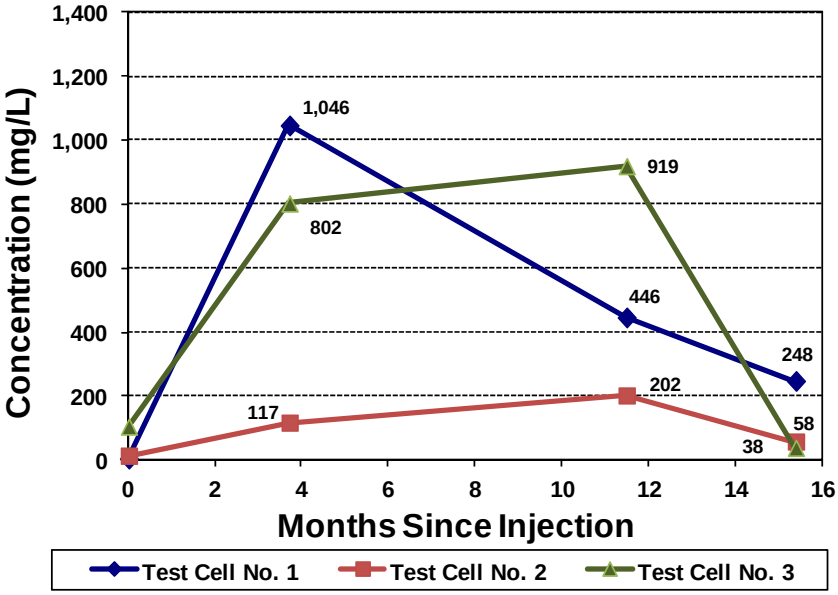

Figure E.1 Average Concentrations of DOC over Time within the Test Cells

The injection of soluble ferrous sulfate into Test Cell No. 3 was anticipated to immediately increase the concentrations of sulfate and ferrous iron in groundwater. The concentration of sulfate increased to as high as 1,160 mg/L at DP98INJ-02 in September 2010, and subsequently decreased to 27.6 mg/L in September 2011 at this location. Reductions in the concentration of sulfate may be due to biological sulfate reduction and/or migration of sulfate out of the reaction zone with groundwater flow. Concentrations of sulfide at DP98INJ-02 were 5.30 mg/L (estimated concentration) in September 2010 and 22.4 mg/L (estimated concentration) in September 2011. The sulfide concentration measured in September 2011 was the highest concentration of this constituent measured during the demonstration, providing a strong indication that sulfate reduction was stimulated in Test Cell No. 3. Concentrations of ferrous iron remained very high at Test Cell No. 3, with concentrations greater than 66 mg/L at all three injection wells in September 2011. This suggests that an excess of ferrous iron was present over the course of the demonstration.

The observed changes in groundwater biogeochemistry indicate favorable conditions for the formation of reduced iron sulfide minerals. In addition, the presence of low concentrations of DO, low oxidation-reduction potential (ORP), neutral pH, and elevated concentrations of dissolved methane in all three test cells indicated that redox conditions in the test cells were conducive to both biotic reductive dechlorination and biogeochemical transformation of CAHs.

E.5 REDUCTIONS IN CHLORINATED ALIPHATIC HYDROCARBONS

To illustrate the changes and trends in concentrations of CAHs, the average concentrations detected at monitoring locations within the test cell reaction zones from May 2010 (pre-injection baseline sampling event) to September 2011 (final performance monitoring event) were plotted over time. The following paragraphs describe the reduction in concentrations of CAHs that were achieved for each test cell.

Test Cell No. 1

Average concentrations of chlorinated ethenes and total molar CAHs within Test Cell No. 1 are shown on **Figure E.2.** Concentrations of TCE steadily decreased to 1.36 µg/L at DP98MP02 and 1.77 µg/L at DP98MP03 by September 2011, less than the performance objective of 5.0 µg/L. The average concentration of total DCE (sum of the three isomers) initially increased from 2,015 µg/L in May 2010 to 2,899 µg/L in May 2011, but then decreased to 270 µg/L in September 2011. This last concentration is substantially lower than the average pre-injection concentration.

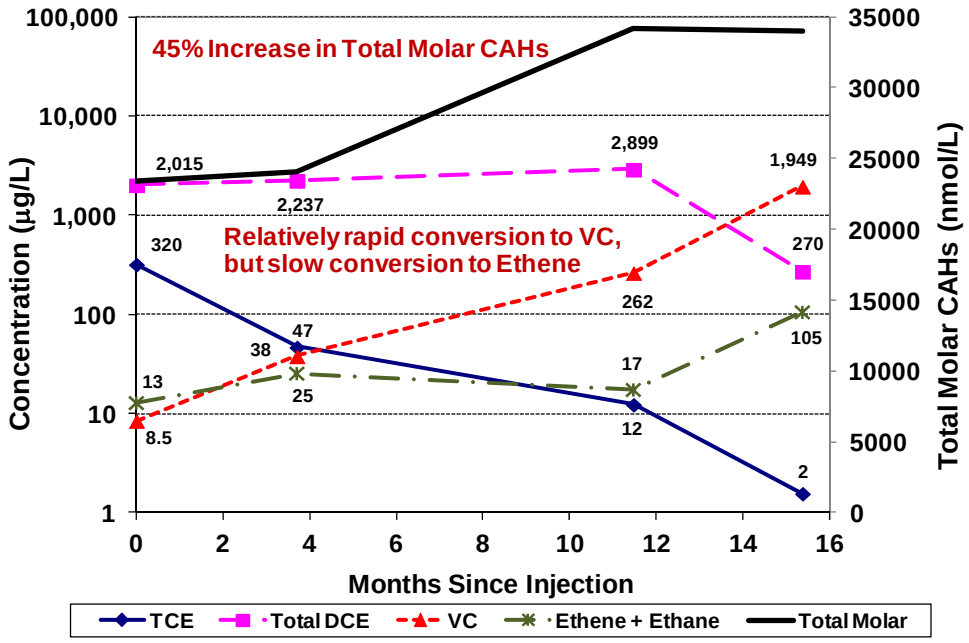

Figure E.2 Concentrations of Chlorinated Ethenes in Test Cell No. 1
(EHC®**:** Average of DP98MP02 and DP98MP03)

The average concentration of VC consistently increased from 8.5 µg/L in May 2010 to 1,949 µg/L in September 2011, indicating that TCE and DCE were transformed primarily by sequential biotic dechlorination. Concentrations of ethene also increased to an average of 105 µg/L in September 2011. The ethene data indicate that transformation of VC to ethene occurred, but not at a rate sufficient to prevent the accumulation of VC within the test cell.

A 45% increase in the total molar concentration of CAHs within Test Cell No. 1 during the performance monitoring period (measured as nanomoles per liter [nmol/L]) reflects incomplete transformation of TCE and DCE to VC. A significant portion of this increase is likely due to the lower sorption potentials for DCE and VC. As TCE is transformed to DCE and VC, a progressively greater percentage of the compound will be soluble in groundwater relative to that sorbed to the soil matrix.

Test Cell No. 2

Average concentrations of chlorinated ethenes and total molar CAHs within Test Cell No. 2 are shown on **Figure E.3**. Similar to Test Cell No. 1, concentrations of TCE steadily decreased to 1.18 µg/L at DP98MP06 and to 5.01 µg/L at DP98MP07 by September 2011; less than or very

close to the performance objective of 5.0 µg/L. The average concentration of DCE exhibited a 61% decrease from May 2010 to September 2011. The average VC concentration increased over the same period, but only to 20 µg/L, and was relatively stable compared to the other two test cells. The average ethene concentration was also relatively stable, and decreased from May 2010 to September 2011. These data suggest that the transformation of TCE and DCE in this test cell was primarily via an abiotic pathway that did not produce significant amounts of VC or ethene.

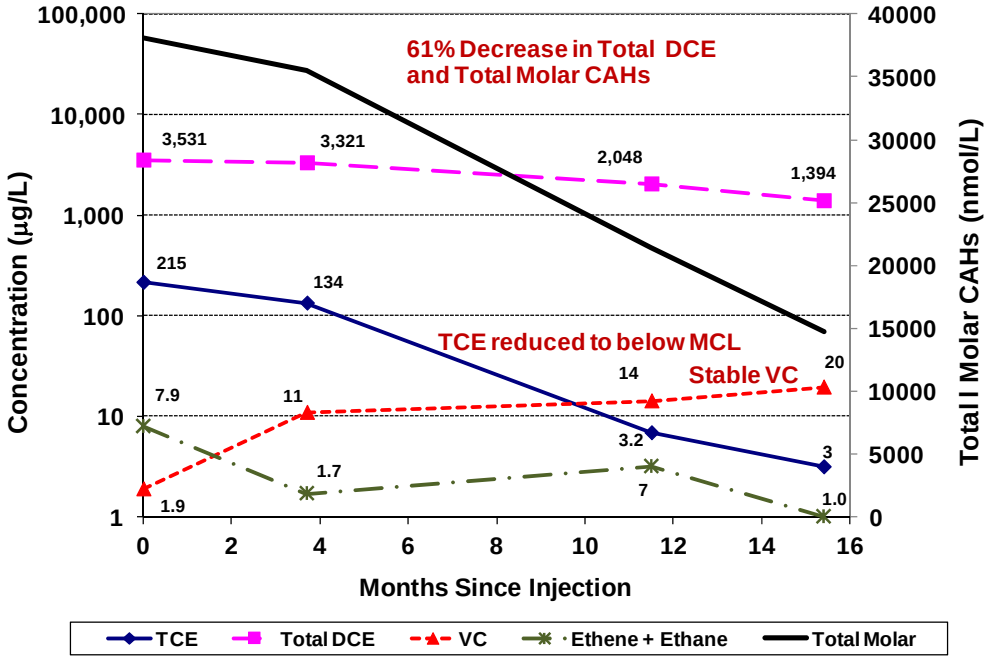

Figure E.3 Concentrations of Chlorinated Ethenes in Test Cell No. 2
(Hematite + Gypsum + EVO: Average of DP98MP06 and DP98MP07)

The total molar concentration of CAHs within Test Cell No. 2 also decreased by 61% during the performance monitoring period, which is a further indication that abiotic dechlorination was stimulated by biogeochemical processes without significant accumulation of DCE or VC. The decreasing trends in concentrations of TCE, DCE, and total molar CAHs shows promise for remediation of chlorinated ethenes in groundwater at the DP98 site by biogeochemical processes.

Fitting a first-order (exponential) trend line to the TCE and total DCE data in **Figure E.3** yields degradation rates of 0.01 percent per day (day^{-1}) for TCE and 0.002 day^{-1} for total DCE. Extrapolation of the regression trend for total DCE to a cleanup level of 70 µg/L for *cis*-DCE yields a timeframe of approximately 5 years to achieve the target concentration. This is only an estimate. Several conditions would have to be fulfilled for this to become a reality, including sustaining the appropriate biogeochemical conditions in the reaction zone.

Test Cell No. 3

Average concentrations of chlorinated ethenes and total molar CAHs within Test Cell No. 3 are shown on **Figure E.4**. Concentrations of TCE were already below 5.0 µg/L within the reaction zone at Test Cell No. 3 due to a prior bioremediation treatability study. The intent of injecting into Test Cell No. 3 was to see if further degradation of DCE and VC could be promoted.

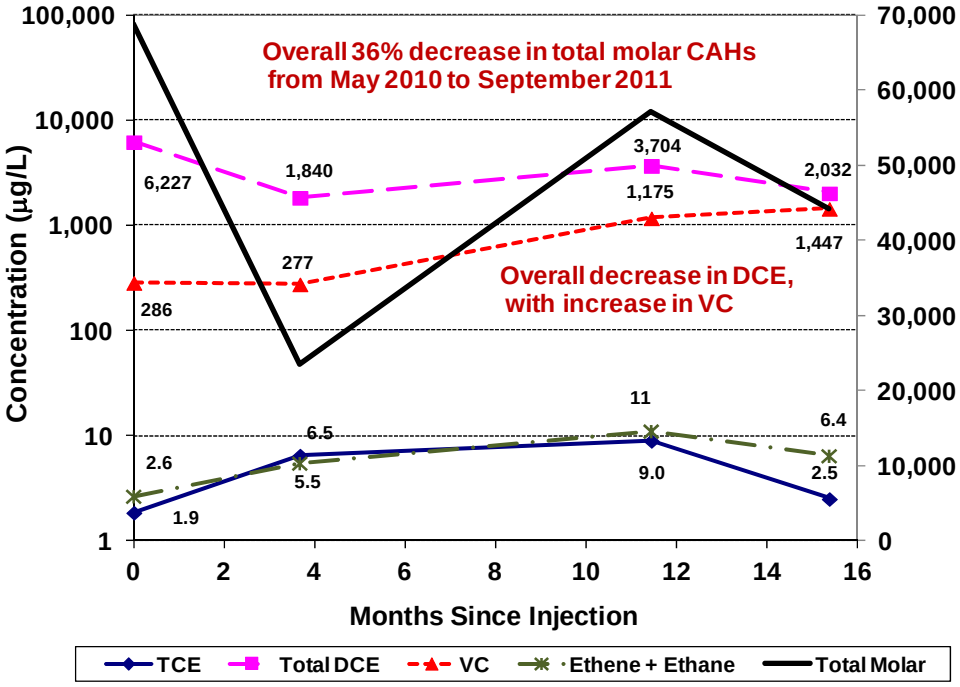

Figure E.4 Concentrations of Chlorinated Ethenes at Test Cell No. 3
(Ferrous Sulfate + EVO: Average of DP98INJ-01 through DP98INJ-03)

The average concentration of total DCE was variable during the performance monitoring period, but overall it decreased by 67% from 6,227 µg/L in May 2010 to 2,032 µg/L in September 2011. The average concentration of VC within Test Cell No. 3 increased from 286 µg/L in May 2010 to 1,447 µg/L in September 2011. These data suggest that DCE was transformed to VC by a primarily biotic pathway. The average concentration of ethene only increased from 3 µg/L to a maximum of 11 µg/L, indicating that biotic dechlorination of VC was limited.

The average total molar concentration of CAHs within Test Cell No. 3 over time exhibited a similar pattern to that observed for total DCE, with an overall reduction of 36% from May 2010 to September 2011. The persistence of VC in Test Cell No. 3 prevented a greater decrease in total molar CAH concentrations.

Degradation patterns for TCE, DCE, and VC at the three test cells indicate that both biotic sequential dechlorination and abiotic biogeochemical transformation processes occurred. The following summarizes the degradation processes evident at each test cell location:

- **Test Cell No. 1:** A substantial increase in VC indicates that biotic dechlorination of TCE and DCE to VC was the primary transformation process that was stimulated. The production of ethene towards the end of the monitoring period indicates that dechlorination of VC to ethene occurred, but not at a rate sufficient to prevent the accumulation and persistence of VC.
- **Test Cell No. 2:** Concentrations of TCE and DCE consistently decreased in Test Cell No. 2, with only a slight increase in VC and no production of ethene. These trends suggest an abiotic degradation pathway for TCE and DCE that produced little VC or ethene.

- **Test Cell No. 3:** Concentrations of DCE in Test Cell No. 3 were variable, but an overall decrease of approximately 67% from May 2011 to September 2011 was observed. A substantial increase in VC occurred, indicating that biotic dechlorination of DCE to VC was a primary degradation pathway. Little ethene was produced, suggesting that biotic dechlorination stalled at VC. However, an overall decrease in the total molar CAH concentration of 36% suggests that some abiotic dechlorination of DCE occurred. Therefore, both biotic and abiotic degradation were likely enhanced in Test Cell No. 3.

E.6 FORMATION OF REACTIVE IRON SULFIDE MINERALS

In theory, sufficient iron and sulfate amendments were added to Test Cell No. 2 and Test Cell No. 3 in May 2010 to produce approximately 2,000 mg/kg of FeS. The actual amount of FeS produced was estimated by analyzing soil samples for AVS. Following the AVS extraction, the soil samples were analyzed for chromium reducible sulfur (CRS) to estimate the amount of FeS_2 and elemental sulfur (S^o) in the samples. The target concentration of AVS (2,000 mg/kg) was not achieved in any of the post-injection soil samples. The highest concentration of AVS measured in soil samples was 841 mg/kg in Test Cell No. 3. Increases in concentrations of AVS relative to baseline conditions were only observed in Test Cell No. 1 and Test Cell No. 3.

The average combined concentration of AVS and CRS in baseline soil samples was 986 mg/kg, ranging from 880 to 1,080 mg/kg. The average combined concentration of AVS and CRS in the post-injection samples was 1,293 mg/kg in Test Cell No. 1 (31% increase), 911 mg/kg in Test Cell No. 2 (no increase), and 1,455 mg/kg in Test Cell No. 3 (48% increase). Therefore, only a modest increase in total iron sulfides was observed for Test Cell No. 1 and Test Cell No. 3.

Soil samples were also analyzed using a scanning electron microprobe (SEM). The SEM evaluation found hematite, magnetite, and pyrite to be present. Interpretation of the results suggests that any reduced FeS minerals that were produced were subsequently oxidized to the more stable, less reactive forms of pyrite (FeS_2). FeS minerals may be oxidized by reduction of CAHs, or by dissolved oxygen or nitrate that may migrate into the treatment zones. Pure hematite grains were observed in the samples from Test Cell No. 2. The presence of hematite (which was injected) indicates that reduction of iron and the subsequent formation of reduced iron sulfide minerals had not substantially progressed within the 3.5 months between the injection and soil sample collection. This observation is consistent with the lack of an increase in the average concentration of AVS in Test Cell No. 2 relative to the baseline concentration.

E.7 CONCLUSIONS

Engineered biogeochemical transformation shows promise for remediation of chlorinated solvents in groundwater, particularly for sites with chlorinated ethenes where sequential biotic dechlorination stalls at DCE or VC. The degree to which the performance metrics described in **Section E.2** were met at the three test cells is summarized in **Table E.2**.

The most promising results were observed at Test Cell No. 2, where a combination of natural hematite iron powder, calcium sulfate, and a buffered EVO product were injected. While an increase in concentrations of iron sulfides in soil were not observed, the degradation pattern for Test Cell No. 2 shows a strong abiotic signature. The greatest reductions in concentrations of chlorinated ethenes in Test Cell No. 2 occurred after the 3.5-month soil sampling event. Therefore, it is possible that the post-injection soil measurements are not representative of the extent to which biogeochemical transformation of TCE and DCE occurred over the duration of the demonstration.

Table E.2 Comparison of Demonstration Results to Performance Metrics

Performance Metric	Test Cell No. 1 (EHC®)	Test Cell No. 2 (Hematite + Gypsum + EVO)	Test Cell No. 3 (Ferrous Sulfate + EVO)
Generate at least 2,000 mg/kg of AVS within the treatment zone	Not applicable – Used EHC® for comparison	Not achieved (average AVS concentration = 308 mg/kg)	Not achieved (average AVS concentration = 731 mg/kg)
Enhance the rates of *in situ* anaerobic degradation of TCE and *cis*-DCE by at least 1 order of magnitude relative to rates of natural attenuation at the site	Achieved	Achieved	Achieved
Reduce concentrations of TCE in the reaction zone to less than 5 µg/L, and limit increases in DCE and VC	Achieved for TCE and *cis*-DCE but not for VC	Achieved	TCE < 5 µg/L prior to injection; achieved for *cis*-DCE but not for VC
Reduce total molar concentrations of CAHs within the reaction zone by at least 90%	Not achieved (increased by 45%)	Not achieved (decreased by 61%)	Not achieved (decreased by 36%)

Results for Test Cell No. 1 (EHC®) and Test Cell No. 3 (soluble ferrous sulfate and buffered EVO) indicated that sequential biotic dechlorination occurred, with a significant accumulation of VC. This may be due to the much higher concentrations of DOC in these two test cells, which may have preferentially stimulated biotic dechlorination relative to abiotic dechlorination by biogeochemical transformation. Ethene was produced, indicating the potential for sequential biotic dechlorination to go to completion. However, the relatively slow rate of VC transformation to ethene raises concern whether biotic processes alone can be an effective remedy at DP98.

The results of the SEM evaluation and mineral speciation analyses suggest that any reduced iron sulfide minerals that were produced were oxidized to more stable, less reactive forms of pyrite. The rate at which biogeochemical processes produce iron sulfide minerals from the amendments used is not well understood. The presence of hematite grains in Test Cell No. 2 at 3.5 months post-injection suggests the process was ongoing, with the potential for greater concentrations of iron sulfide to be produced over time. The rate of dechlorination of TCE and DCE at Test Cell No. 2 increased after the 3.5-month post-injection soil sampling event. Therefore, the concentrations of AVS and CRS measured may not be representative of the degree to which the formation of iron sulfide minerals was ultimately achieved.

Based on the observations from this demonstration, future applications of engineered biogeochemical transformation should consider the following:

- Over-stimulation of biological processes (e.g., resulting from concentrations of DOC over 100 to 200 mg/L) may favor biotic dechlorination processes over abiotic biogeochemical processes.
- Additional research is needed to understand the rates at which sulfate and iron reduction occur, and the rates at which iron sulfide minerals are formed. Engineered designs should consider the bioavailability of differing iron and sulfate products, and the impact of

groundwater flow, mixing, and temperature on the rates of the individual biogeochemical processes that lead to formation of reduced iron sulfide minerals.

- Soluble forms of iron and sulfate may migrate out of the treatment zone before they are utilized. Groundwater flow should be evaluated to determine if multiple injections of iron and sulfate amendments are necessary; for example, at sites where the rate of groundwater flow exceeds 0.2 to 0.5 foot per day.
- Iron or sulfate may become a limiting factor depending on the rate at which the amendments are utilized and the quantities of native iron and sulfate present. Groundwater monitoring may be useful to determine appropriate modifications to the ratio of iron and sulfate amendments for sites where multiple injections are used.
- Uniform distribution of iron and sulfate amendments is a challenge at low permeability or highly heterogeneous sites. Alternative distribution methods such as those employing groundwater re-circulation may provide better distribution.
- The ability to differentiate between abiotic and biotic dechlorination processes is difficult given conventional monitoring tools. Better tools are needed to fully understand the complex biological and chemical processes that occur in the subsurface when attempting to engineer the production of reactive iron sulfide minerals.

It is anticipated that future research and field experience with biogeochemical transformation processes will lead to a more robust understanding of how to engineer and implement the technology.

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ACRONYMS AND ABBREVIATIONS

%	percent
‰	parts per thousand or parts per mil
δC^{13}	isotope ratio of carbon 13 to carbon 12
µg/L	microgram(s) per liter
µm	micron(s)
AFB	Air Force Base
AFCEE	Air Force Center for Engineering and the Environment (formerly the Air Force Center for Environmental Excellence)
APPL	Agriculture and Priority Pollutants Laboratories, Inc.
ARARs	Applicable or Relevant and Appropriate Requirements
AVS	acid volatile sulfide
bgs	below ground surface
CAH	chlorinated aliphatic hydrocarbon
CDM	Camp Dresser & McKee
cells/ml	cells per milliliter
CFR	Code of Federal Regulations
CRS	chromium reducible sulfur
CSIA	compound-specific isotope analysis
CT	carbon tetrachloride
day^{-1}	percent per day
DCE	dichloroethene
DO	dissolved oxygen
DOC	dissolved organic carbon
DNT	dinitrotoluene
DPT	direct-push technology
DRO	diesel-range organics
EE/CA	Engineering Evaluation/Cost Analysis
Eh	reduction-oxidation potential relative to a standard hydrogen electrode
ESTCP	Environmental Security Technology Certification Program
EVO	emulsified vegetable oil
Fe^{2+}	ferrous iron
Fe^{3+}	ferric iron
$FeCO_3$	siderite
Fe_2O_3	hematite
Fe_3O_4	magnetite
FeS	iron monosulfide (e.g., mackinawite)
FeS_2	iron disulfide (e.g., pyrite)
Fe_3S_4	greigite
ft^2	square feet
ft^3	cubic feet
ft/day	feet per day
ft/ft	foot per foot
ft/yr	feet per year

ACRONYMS AND ABBREVIATIONS (CONTINUED)

GRO	gasoline-range organics
gpm	gallons per minute
H_2S/HS^-	hydrogen sulfide
IDW	investigation-derived waste
ISCR	*in situ* chemical reduction
JBER	Joint Base Elmendorf Richardson
kg	kilogram(s)
lb	pound(s)
MCL	maximum contaminant level
mg/kg	milligram(s) per kilogram
mg/L	milligram(s) per liter
Mn^{4+}	manganese (IV)
MNA	monitored natural attenuation
mV	millivolt(s)
NFESC	Naval Facilities Engineering Service Center
nmol/L	nanomole(s) per liter
NRC	National Research Council
ORP	oxidation-reduction potential
Parsons	Parsons Infrastructure and Technology Group, Inc.
PCE	tetrachloroethene or perchloroethene
PPE	personal protective equipment
PVC	polyvinyl chloride
qPCR	quantitative polymerase chain reaction
RAO	remedial action objective
RC	response complete
ROD	Record of Decision
RI/FS	Remedial Investigation/Feasibility Study
RIP	remedy-in-place
S^0	elemental sulfur
SAE	strong acid extraction
SEM	scanning electron microprobe
SO_4^{2-}	sulfate
TCA	trichloroethane
TCE	trichloroethene
TO	Task Order
USAF	United States Air Force
USEPA	United States Environmental Protection Agency
UST	Underground Storage Tank
VFA	volatile fatty acid
VC	vinyl chloride
VOC	volatile organic compound
ZVI	zero-valent iron

1.0 INTRODUCTION

A technology demonstration of biogeochemical transformation of chlorinated solvents in groundwater was conducted by Parsons Infrastructure and Technology Group, Inc. (Parsons) for the Air Force Center for Engineering and the Environment (AFCEE) and Joint Base Elmendorf-Richardson (JBER), Alaska under Contract No. FA8903-08-D-8778, Task Order (TO) 0068. The demonstration was conducted at the DP98 site from May 2010 to September 2011. The DP98 site is located in the northwestern portion of JBER (**Figure 1.1**). This report describes 1) the technical approach that was implemented to stimulate the biogeochemical transformation of chlorinated aliphatic hydrocarbons (CAHs, commonly referred to as chlorinated solvents) in groundwater; 2) results obtained and an interpretation of their meaning, significance, and implications; and 3) summary and conclusions.

The AFCEE Technology Transfer Program includes an initiative to demonstrate *in situ* biogeochemical transformation of chlorinated solvents in groundwater. The objectives of this initiative are to:

1) Identify approaches for stimulating biogeochemical transformation processes that will reduce concentrations of trichloroethene (TCE) in soil and groundwater with limited, if any, production of cis-1,2-dichloroethene (cis-DCE) or vinyl chloride (VC);
2) Compare the cost of commercial remediation products to the use of readily available, low-cost, bulk iron and sulfate amendments to stimulate biogeochemical transformation of CAHs; and
3) Develop low-cost, alternative *in situ* biogeochemical transformation techniques that the Air Force can use to reduce the cost of implementing remedy-in-place (RIP) and achieving response complete (RC).

This and similar projects are being conducted at several Air Force sites to independently evaluate the applicability, cost, and performance of stimulating biogeochemical transformation of chlorinated solvents under a wide variety of site conditions. Results of these demonstrations will ultimately be incorporated into an AFCEE guidance document.

1.1 DEMONSTRATION OBJECTIVES

In addition to the objectives of the AFCEE biogeochemical transformation initiative described above, the site-specific objectives for the DP98 site were to demonstrate the degree to which biogeochemical transformation or other *in situ* chemical reduction (ISCR) techniques may be used to reduce concentrations of CAHs within the test cell treatment zones to levels protective of human health and the environment (**Section 1.1.1**). Performance metrics were developed (**Section 1.1.2**) to measure and evaluate the ability of biogeochemical transformation to create geochemical conditions optimal for abiotic dechlorination processes to occur and to reduce concentrations of CAHs in groundwater.

The technology demonstration at DP98 was accomplished by injecting various organic substrates and iron/sulfate amendments into three test cells using direct-push technology (DPT). After the amendments were injected, groundwater and soil in the test cells were monitored for a period of approximately 15 months. The following sections describe the regulatory requirements and performance objectives associated with this demonstration at the DP98 site.

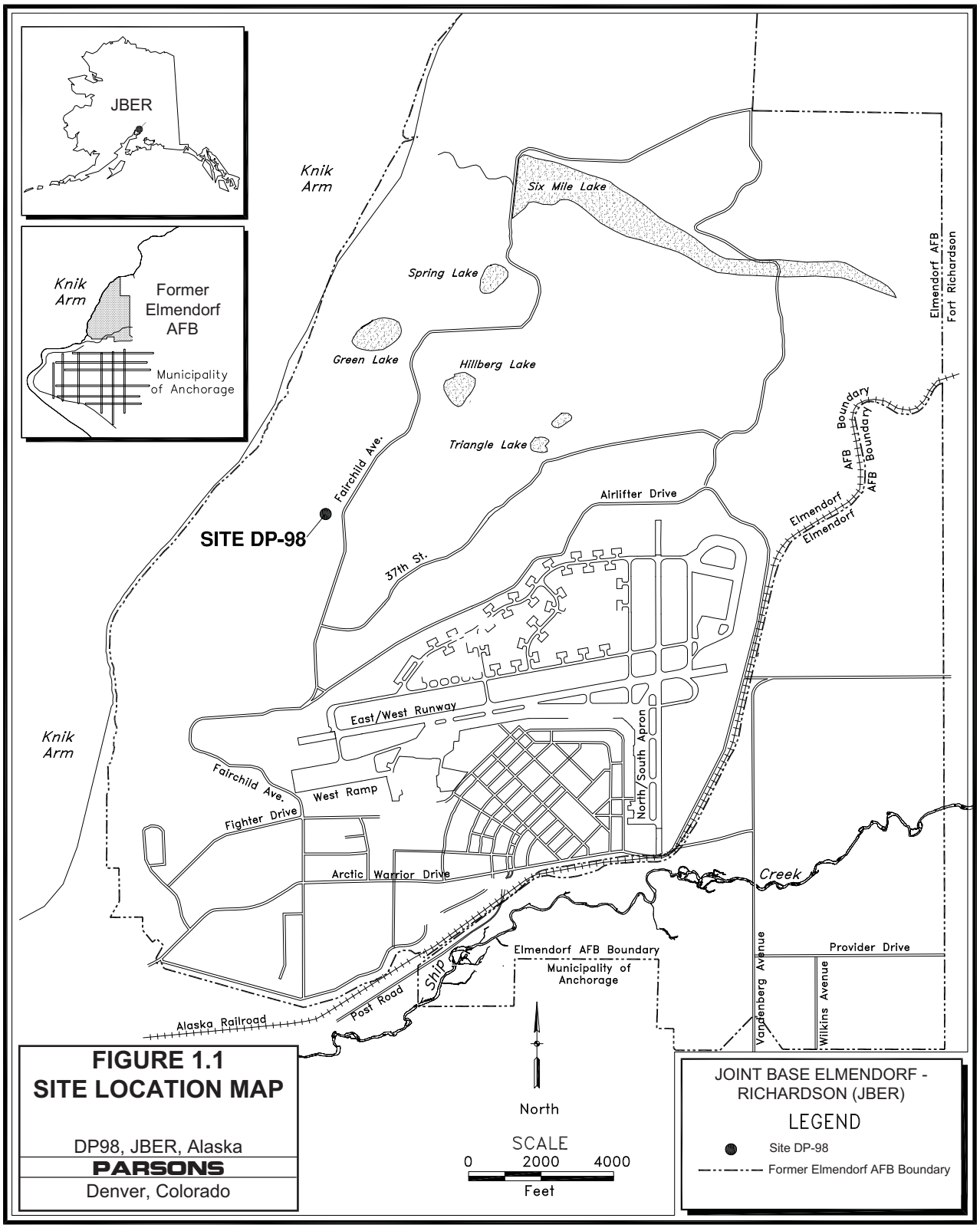

FIGURE 1.1
SITE LOCATION MAP

DP98, JBER, Alaska

PARSONS

Denver, Colorado

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1.1.1 DP98 Regulatory Requirements

Remedial action objectives (RAOs) for DP98 were established in the 2004 Record of Decision (ROD) for DP98 (United States Air Force [USAF], 2004). Chemical-specific Applicable or Relevant and Appropriate Requirements (ARARs) for CAHs in groundwater from the ROD are listed in **Table 1.1** for reference. Concentrations of CAHs in groundwater currently exceed the applicable groundwater compliance standards. One of the long-term objectives of environmental restoration at the DP98 site is to reduce concentrations of CAHs in groundwater to below the compliance standards listed in **Table 1.1**.

Table 1.1 Compliance Levels for Groundwater at the DP98 Site

Chemical of Concern	Unit	Compliance Level	Basis for Compliance Level
1,1-Dichloroethene	µg/L	7.0	MCL, 40 CFR § 141.61
cis-1,2-Dichloroethene	µg/L	70	MCL, 40 CFR § 141.61
Tetrachloroethene	µg/L	5.0	MCL, 40 CFR § 141.61
Trichloroethene	µg/L	5.0	MCL, 40 CFR § 141.61
Vinyl Chloride	µg/L	2.0	MCL, 40 CFR § 141.61

Notes:
µg/L = micrograms per liter
MCL = drinking water maximum contaminant level
CFR = Code of Federal Regulations

The 2004 ROD describes the use of monitored natural attenuation (MNA) to meet these groundwater compliance levels, and the ROD estimated that the timeframe to meet groundwater compliance levels by MNA alone would be 35 to 75 years. The 2004 ROD also specifies that a treatability study of enhanced MNA (enhanced bioremediation) be conducted as a potential contingency measure in the event MNA alone cannot meet compliance requirements within this period of time. Results of an enhanced bioremediation treatability study indicate that bioremediation alone may not a suitable technology to reduce the overall time-frame for remediation at the DP98 site (USAF, 2007). The biogeochemical transformation demonstration that is the subject of this report tested alternative *in situ* technologies to evaluate whether the limitations of stimulating complete dechlorination of CAHs can be overcome.

1.1.2 Performance Objectives

The primary objective of the demonstration is to determine the feasibility of stimulating the formation of reduced iron sulfide minerals that will degrade tetrachloroethene (PCE), TCE, and *cis*-DCE in groundwater at the DP98 site. Performance metrics were developed to evaluate the effectiveness of the demonstration, which included the following:

- Stimulate the production of reduced iron sulfides (measured as acid volatile sulfide [AVS]) to concentrations equal to or greater than 2,000 milligrams per kilogram (mg/kg) within the treatment zones for Test Cells No. 2 and No. 3;
- Enhance the rates of *in situ* anaerobic degradation of PCE and TCE by one order of magnitude or more relative to rates of natural attenuation at the site;
- Reduce concentrations of PCE and TCE in the reaction zone to less than site-specific cleanup goals, and limit increases in DCE and VC to concentrations measured during

base-line monitoring or to concentrations measured in upgradient monitoring locations; and

- Reduce total molar concentrations of chloroethenes within the reaction zone by 90 percent or more to demonstrate that complete transformation is occurring, and not just transformation of highly-chlorinated ethenes (PCE and TCE) to less-chlorinated ethenes (DCE and VC).

The system design, injection protocols, and monitoring requirements developed and implemented to meet these performance objectives are described in Section 2. Results of this demonstration are described in Section 3.

1.2 PROJECT SCOPE

Activities associated with this demonstration included the following:

- Preparation of a work plan describing the field methods to be employed, and the performance objectives by which the demonstration will be measured.
- Installation of monitoring points using DPT to evaluate two test cells. Each test cell contains four monitoring points installed to a depth of approximately 30 to 32 feet below ground surface (bgs). A third test cell was evaluated using existing wells installed for a prior bioremediation pilot test (**Figure 1.2**).
- Baseline (initial condition) sampling of soil and groundwater immediately preceding injection of amendments.
- Injection of organic substrates and inorganic biogeochemical amendments into three test cells. Two test cells received a combination of emulsified vegetable oil (EVO) and iron/sulfate amendments to stimulate production of reduced iron-sulfide minerals by biogeochemical processes. The third test cell received an injection of a commercial product (EHC®) to stimulate ISCR.
- Performance monitoring at approximately 3, 11, and 15 months following injection. Monitoring consisted of groundwater and soil sampling during the 3-month event, and groundwater sampling during the 11- and 15-month sampling events.
- Preparation of this demonstration report describing the system installation and results of performance monitoring.

The materials and methodologies that were used to accomplish the field activities are described in Section 2.

1.3 REPORT ORGANIZATION

This technology demonstration report is organized into five sections and two attachments, including this introductory section. **Section 2** describes the methods and materials used for the demonstration, and **Section 3** describes the performance monitoring results. A summary and conclusions are provided in **Section 4**, and **Section 5** contains citations for the references used in preparing this report. Attachments to this report include design calculations (**Attachment A**) and plots of chlorinated ethene concentrations and molar ratios for individual wells (**Attachment B**).

INJECTION WELL
MONITORING POINT
MONITORING WELL
AREA OF INJECTION
SANITARY SEWER
ELECTRICAL (BELOW GROUND)
NOTE: UTILITY LOCATIONS ARE APPROXIMATE

41755–WL–14
41755–WL–23
41755–WL–17
41755–WL–08
DEMONSTRATION STUDY AREA
DP98MP10
41755–WL–09
41755–WL–13
41755–WL–04
DP98MP08
DP98MP04
TEST CELL NO. 2
TEST CELL NO. 1
DP98MP06
DP98MW–06
DP98MP07
41755–WL–22A
DP98MW–05
DP98MP05
DP98INJ–02
DP98MP02
DP98MP03
41755–WL–05
DP98MP01
TEST CELL NO. 3
DP98INJ–03
DP98INJ–01
DP98MW–04
BUILDING 18224
41755–WL–03
41755–WL–21
41755–WL–02
41755–PZ–03
41755–PZ–02
FAIRCHILD AVENUE

N
0 25 50 100
SCALE 1" = 50'

FIGURE 1.2

DP98 SITE LAYOUT

DP98, JBER, Alaska

PARSONS
Denver, Colorado

S:\ES\Remed\747093 TO 0068\02000 Elmendorf FS\Reporting\1-DP98 Draft Demonstration Report\Figures\11DN0069.DWG 01/03/2012 1:24PM SEH

A supporting data package has been provided to the Air Force under separate cover. The data package includes copies of field sampling forms, a report describing the results of scanning electron microscope (SEM) analysis of soil samples, results received from fixed-base analytical laboratories, data quality assessment reports, site photos, and report files in their original electronic format.

1.4 TECHNOLOGY DESCRIPTION

1.4.1 Anaerobic Degradation Processes

There are three primary reactions may degrade CAHs under anaerobic conditions. ***Direct biotic reductive dechlorination*** is a biologically-mediated reaction where microorganisms gain energy as one or more chlorine atoms on a CAH molecule are replaced with hydrogen atoms in an anaerobic environment. Biotic reductive dechlorination is the degradation process most often targeted by enhanced anaerobic bioremediation. In general, biotic anaerobic reductive dechlorination occurs by sequential removal of chlorine ions. For example, the chlorinated ethenes are transformed sequentially from tetrachloroethene (PCE) to TCE to the DCE isomers (*cis*-DCE or *trans*-DCE) to VC to ethene as illustrated in Pathway 1 on **Figure 1.3**. This reaction has also been referred to as halorespiration or dehalorespiration (United States Environmental Protection Agency [USEPA], 2000).

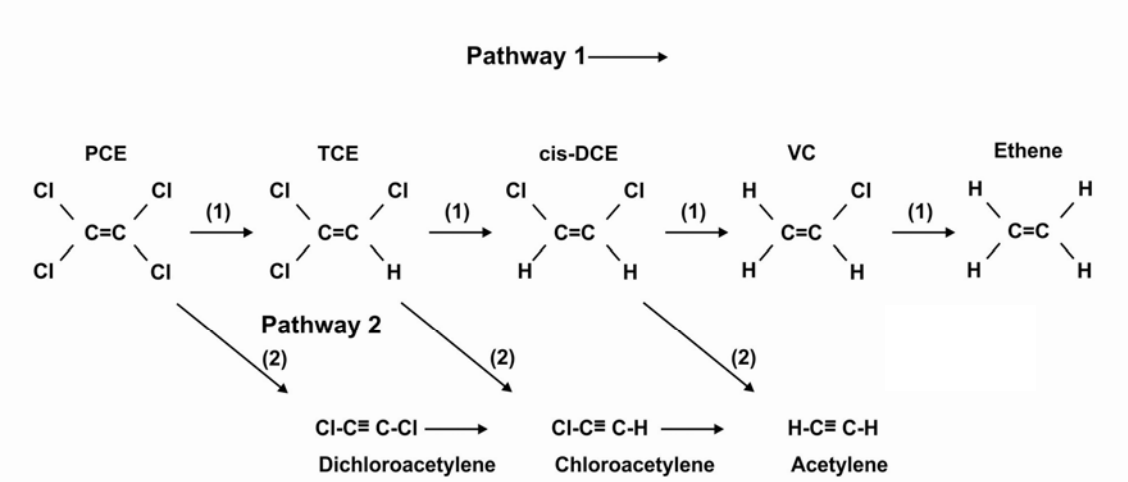


Figure 1.3 Pathways for (1) Biotic Transformation of Chlorinated Ethenes and (2) Abiotic Transformation by Iron Monosulfide (modified from Butler and Hayes, 2001)

A second anaerobic degradation process, termed ***cometabolic anaerobic reductive dechlorination,*** is a reaction in which a chlorinated compound is reduced by a non-specific enzyme or co-factor produced during microbial metabolism of another compound (i.e., the primary substrate) in an anaerobic environment. By definition, cometabolism of the chlorinated compound does not yield any energy or growth benefit for the microbe mediating the reaction (USEPA, 2000).

A third anaerobic degradation process is ***abiotic reductive dechlorination,*** a chemical reaction where a CAH compound is reduced by a reactive mineral. For example, abiotic transformation of carbon tetrachloride (CT), trichloroethane (TCA), PCE, TCE, and *cis*-DCE by metal sulfides has been investigated using pyrite (Weerasooriya and Dharmasena, 2001; Kriegman-King and Reinhard, 1994), troilite (Sivavec and Horney, 1997), mackinawite (Butler and Hayes, 1999 and 2000; Jeong and Hayes, 2007), and magnetite (Ferrey *et al.*, 2004). Pathway 2 on **Figure 1.3**

illustrates the abiotic reduction of chlorinated ethenes by reaction with iron monosulfide (FeS). In this case the overall degradation pathway is referred to as ***biogeochemical transformation*** because the reactive mineral may be formed by the operation of both biological and chemical processes.

As defined in Becvar *et al*. (2008), biogeochemical transformation refers to processes where contaminants are degraded by abiotic reactions with minerals that are either naturally occurring or are biogenically produced in the subsurface. These reactive minerals are thought to include reduced sulfide minerals such as FeS (e.g., Butler and Hayes, 1999 and 2000), green rusts which are layered structures composed of mixed divalent and trivalent iron oxides interspersed with water and anions including sulfate, chloride, and carbonate (Christianson and Stipp, 2003; Lee and Batchelor, 2002), or magnetite which is a ferromagnetic mineral composed of mixed divalent and trivalent iron with the formula Fe_3O_4 (e.g., Ferrey *et al*., 2004).

In many cases these minerals are formed at least in part by, or indirectly from, anaerobic biological processes. For example, chlorinated solvents such as PCE and TCE may be reduced in an abiotic reaction with FeS that is formed in the subsurface under iron- and sulfate-reducing conditions. Alternatively, *cis*-DCE may be oxidized by reaction with magnetite, which could be a product of anaerobic biological ferric iron reduction. An advantage of these transformation reactions is that, in general, regulated intermediate dechlorination products are not produced.

A fourth process that may occur under apparently anaerobic conditions is oxygen-linked mineralization of less chlorinated compounds such as DCE and VC under low dissolved oxygen (DO) or hypoxic conditions. Bradley and Chapelle (2011) define hypoxic conditions as being characterized by DO concentrations of about 0.1 milligram per liter (mg/L), and they found significant VC and DCE mineralization under hypoxic conditions relative to nominally anoxic conditions (DO at or less than a detection limit of 0.01 mg/L). Groundwater systems typically exhibit a moderate degree of geochemical heterogeneity, in which electron acceptor and oxidation reduction potential (ORP) measurements may indicate that a range of terminal electron accepting processes are occurring. Therefore, oxidation of DCE and VC may occur under hypoxic conditions, even when other anaerobic reduction processes (such as nitrate, manganese, and iron reduction) are evident.

1.4.2 Evaluating Anaerobic Degradation Processes

Adding organic substrate to the subsurface stimulates anaerobic conditions that may directly or indirectly stimulate one or more of the degradation reactions described above. It is often difficult to differentiate the presence and/or magnitude of one anaerobic process from another at the field-scale. The USEPA (1998) and the National Research Council (NRC, 2000) both recommend that a multiple lines of converging evidence approach be used to evaluate *in-situ* degradation of CAHs.

As described in the *Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents* (AFCEE *et al*., 2004), the lines-of-evidence approach emphasizes that the primary line of evidence for evaluation of contaminant degradation is the observation of changes in contaminant concentrations (or mass) over time and space. Biogeochemical data are then used as a secondary/confirmatory line of evidence that helps explain why the observed contaminant concentration trends are occurring.

Abiotic and biotic degradation mechanisms can be differentiated by analyzing the patterns of reductions in CAHs over time. Biotic reductive dechlorination of CAHs is a sequential process where PCE and TCE are sequentially dechlorinated to *cis*-DCE, VC, and ethene (**Figure 1.3**). Ethene may be further reduced to ethane. This sequential dechlorination pattern is evident as

sequential peaks in the concentration of each dechlorination product over time, for example as depicted on **Figure 1.4**. Thus, the formation of intermediate dechlorination products is indicative of sequential biotic reductive dechlorination.

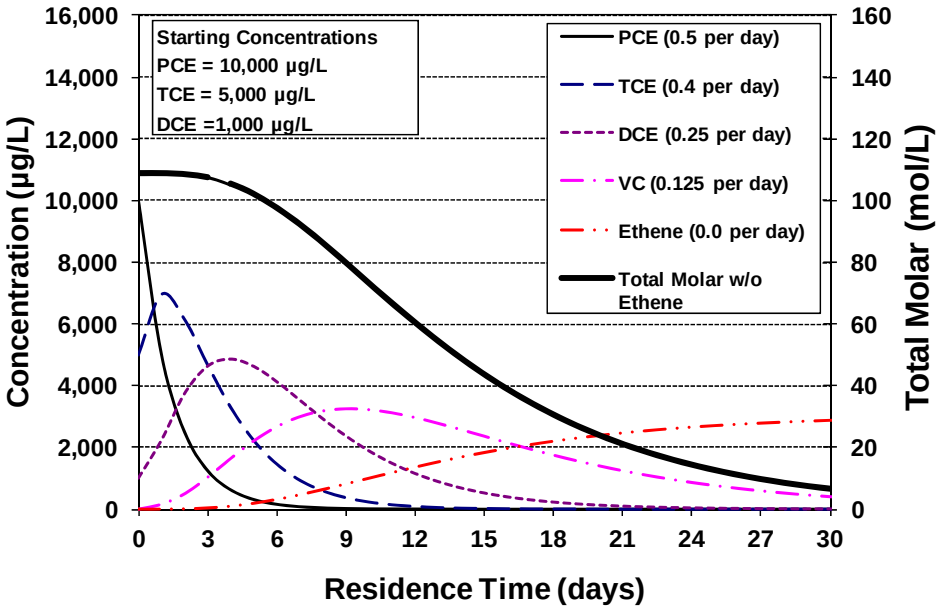


Figure 1.4 Changes in Molar Concentrations of Chloroethenes over Time with Sequential Dechlorination at Specified Degradation Rates

Abiotic dechlorination by reactive iron-sulfide minerals (e.g., FeS) may also be a primary degradation pathway for CAHs. The biological reduction of sulfate (SO_4^{2-}) coupled with the oxidation of organic material by sulfate-reducing bacteria produces hydrogen sulfide (H_2S or HS^-), for example in the following reactions (from AFCEE, 2002):

$$CH_3COOH\ (organic) + SO_4^{2-} + 2H_2O \rightarrow 2CO_2 + H_2S + 2H_2O + 2OH^- \qquad (1\text{-}1)$$

$$2CH_2O\ (organic) + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S \qquad (1\text{-}2)$$

Using these reactions, the reduction of one mole of sulfate produces one mole of hydrogen sulfide.

Ferric iron (Fe^{3+}) in the subsurface soil may be reduced to ferrous iron (Fe^{2+}) by either biological or chemical processes. The biological reduction of ferric iron to ferrous iron may proceed as follows (from AFCEE, 2002):

$$CH_2O\ (organic) + 4Fe^{3+}(s) \rightarrow 4Fe^{2+}(aq) + HCO_3^- + 5H^+ \qquad (1\text{-}3)$$

Most ferrous iron will precipitate in mineral form, for example with sulfides to form FeS or iron disulfide (FeS_2), with carbonate to form siderite ($FeCO_3$), or with other iron oxides/hydroxides to form magnetite (Fe_3O_4).

Iron oxide or iron hydroxide minerals provide a strong chemical sink for H_2S, forming various iron sulfide minerals. Hydrogen sulfide may chemically reduce Fe^{3+} present in iron oxides or iron hydroxides to form FeS, for example with goethite according to the following reaction (from AFCEE, 2002):

$$2FeOOH\ (s)\ (goethite) + 3H_2S\ (aq) \rightarrow 2FeS(s) + S^o + 4H_2O \qquad (1\text{-}4)$$

Using this equation, two moles of goethite (iron hydroxide) reduced by three moles of hydrogen sulfide produces two moles of FeS. Precipitated iron sulfide mineral forms include amorphous iron sulfide (FeS), mackinawite (FeS), pyrrhotite (FeS), greigite (Fe_3S_4), and others (AFCEE, 2002).

FeS minerals, which exist in a reduced state, may react rapidly with oxidized compounds such as TCE to form acetylene (Butler and Hayes, 1999). The suggested chemical expression for TCE dechlorination via FeS oxidation is (from Kennedy and Everett, 2003):

$$4FeS + 9C_2HCl_3\ \textit{(TCE)} + 28H_2O \rightarrow 4Fe(OH)_3 + 4SO_4^{2-} + 9C_2H_2\ \textit{(acetylene)} + 27Cl^- + 35H^+ \quad (1\text{-}5)$$

Using this equation, four moles of FeS is sufficient to degrade nine moles of TCE. Based on the molar mass of FeS (87.91) and TCE (131.39), it takes approximately 0.30 milligram of FeS to degrade 1.0 milligram of TCE. However, the degree to which FeS is actually oxidized by reduction of TCE is uncertain (Kennedy and Everett, 2003). Therefore, an excess of FeS will be required under field conditions to optimize contact with TCE and to facilitate other oxidation reactions with FeS.

Because intermediate dechlorination products are typically not produced by the dechlorination of PCE and TCE with FeS (**Figure 1.3**), abiotic dechlorination over time would be expected to produce a concentration profile as depicted on **Figure 1.5**, where the concentration of each of the CAH compounds would be expected to decrease over time at rates specific to each. Abiotic degradation may result in the attainment of regulatory goals more rapidly than biotic reductive dechlorination if the rates of abiotic degradation are similar to biotic reductive dechlorination, because regulated dechlorination products are not produced (e.g., *cis*-DCE and VC).

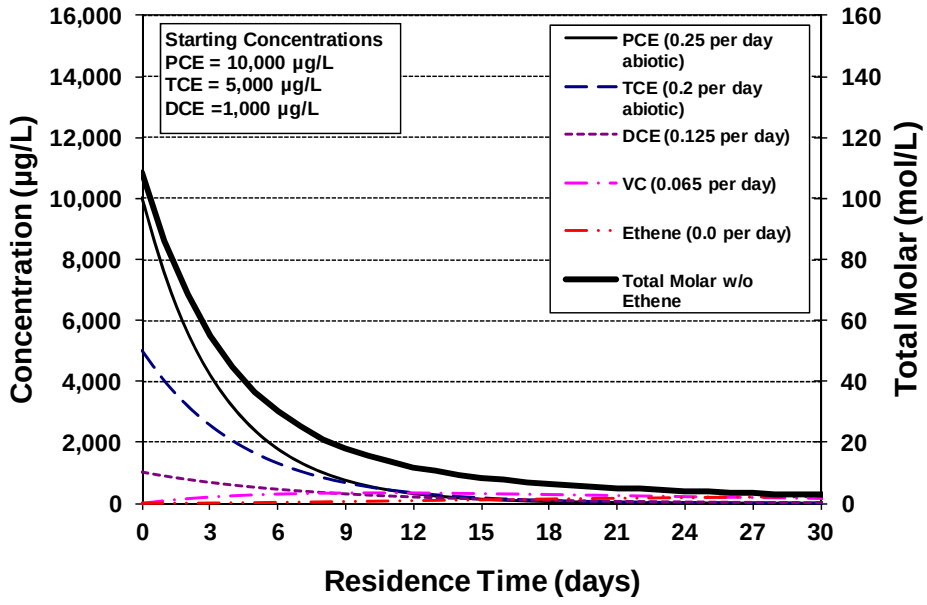


Figure 1.5 Changes in Molar Concentrations of Chloroethenes over Time With Biogeochemical Transformation at Specified Degradation Rates

1.4.3 Stimulating Biogeochemical Transformation Processes

Attempts have been made to engineer the *in situ* biogeochemical transformation of CAHs by addition of iron- or sulfate-bearing amendments to biowall backfill materials (e.g., Parsons, 2006

and 2010a), and by direct injection of dissolved sulfate and sodium lactate (Kennedy *et al*., 2006).

Stimulating the production of reduced iron sulfides requires 1) a source of sulfate that can be reduced to form hydrogen sulfide, 2) a source of reducible iron for the sulfide to react with to precipitate FeS, and 3) a source of organic substrate to stimulate anaerobic iron- and sulfate-reduction processes. The organic substrate must also sustain reducing conditions to prevent oxidation of the reduced iron sulfide minerals that are formed. Iron and sulfate are present naturally in the subsurface, but typically not at concentrations sufficient for effective stimulation of biogeochemical transformation. Therefore, supplemental forms of sulfate and iron that can be injected into the subsurface are needed.

Common sources of iron and sulfate that can be injected as fluids into the subsurface include, but are not limited to, the following:

- Sulfate from gypsum (calcium sulfate) or Epsom salts (magnesium sulfate),
- Iron and sulfate from ferrous iron sulfate (a common soil amendment), and
- Iron from natural or synthetic forms of iron oxides or iron hydroxides, for example hematite (Fe_2O_3).

Gypsum and Epsom salts are available in powdered forms that may be dissolved in water for injection into the subsurface. Ferrous iron sulfate is available in powder or granular forms that are soluble in water. Solid forms of iron may be injected as suspended solids in slurries. For this demonstration powdered hematite was obtained from a supplier of purified minerals.

Any fluid organic substrate may be considered for stimulating the anaerobic processes of iron- and sulfate-reduction required for biogeochemical transformation. Because it is desirable to sustain anaerobic conditions long enough for the reduced iron sulfides to form (weeks to months) and to prevent oxidation of the reduced iron sulfides (months to years), a long-lasting organic substrate such as EVO is a suitable product.

For this demonstration, two scenarios using common sources of iron and sulfate (ferrous sulfate, calcium sulfate, hematite powder), and EVO were tested. A third commercial product (EHC®) was also tested for comparison. Descriptions of the materials and the assumptions and calculations used to determine the amounts of product that were used are included in **Section 2** and in **Attachment A**.

1.5 DP98 SITE DESCRIPTION

JBER is located in south-central Alaska, along the Knik Arm of Cook Inlet and adjacent to the City of Anchorage. The DP98 site is located in the western portion of the former Elmendorf Air Force Base (AFB), on the west side of Fairchild Avenue between Hillberg Lake and 37th Street (**Figure 1.1**). The site includes a secured facility, with undeveloped land north of the secured facility being the location of this demonstration.

1.5.1 Environmental History

Two underground storage tanks (USTs) were used to store diesel fuel near the southwest corner of Building 18224 (see **Figure 1.2** for building location). The USTs were removed or abandoned in place in 1995, with fuel hydrocarbons discovered during replacement. During subsequent field investigations from 1997 to 1999, chlorinated solvents and their degradation products also were detected in soil and groundwater. Release of chlorinated solvents is attributed to historic maintenance and cleaning operations in Building 18244

In 2000, an Engineering Evaluation/Cost Analysis (EE/CA) (USAF, 2001) was conducted to determine the nature and extent of contamination, and a Remedial Investigation/Feasibility Study (RI/FS) was completed in 2003 (USAF, 2003). CAHs detected in groundwater included 6,400 µg/L of PCE; 5,000 µg/L of TCE; 5,700 µg/L of *cis*-DCE; 19 µg/L of 1,1-DCE; and 16 µg/L of VC. Maximum concentrations of diesel-range organics (DRO) and gasoline-range organics (GRO) detected in groundwater were 1,300 mg/L and 4.4 mg/L, respectively. Cleanup criteria for DP98 are specified in ARARs listed in the DP98 ROD. For groundwater these include state and federal drinking water MCLs for PCE, TCE, cis-DCE, 1,1-DCE, and VC.

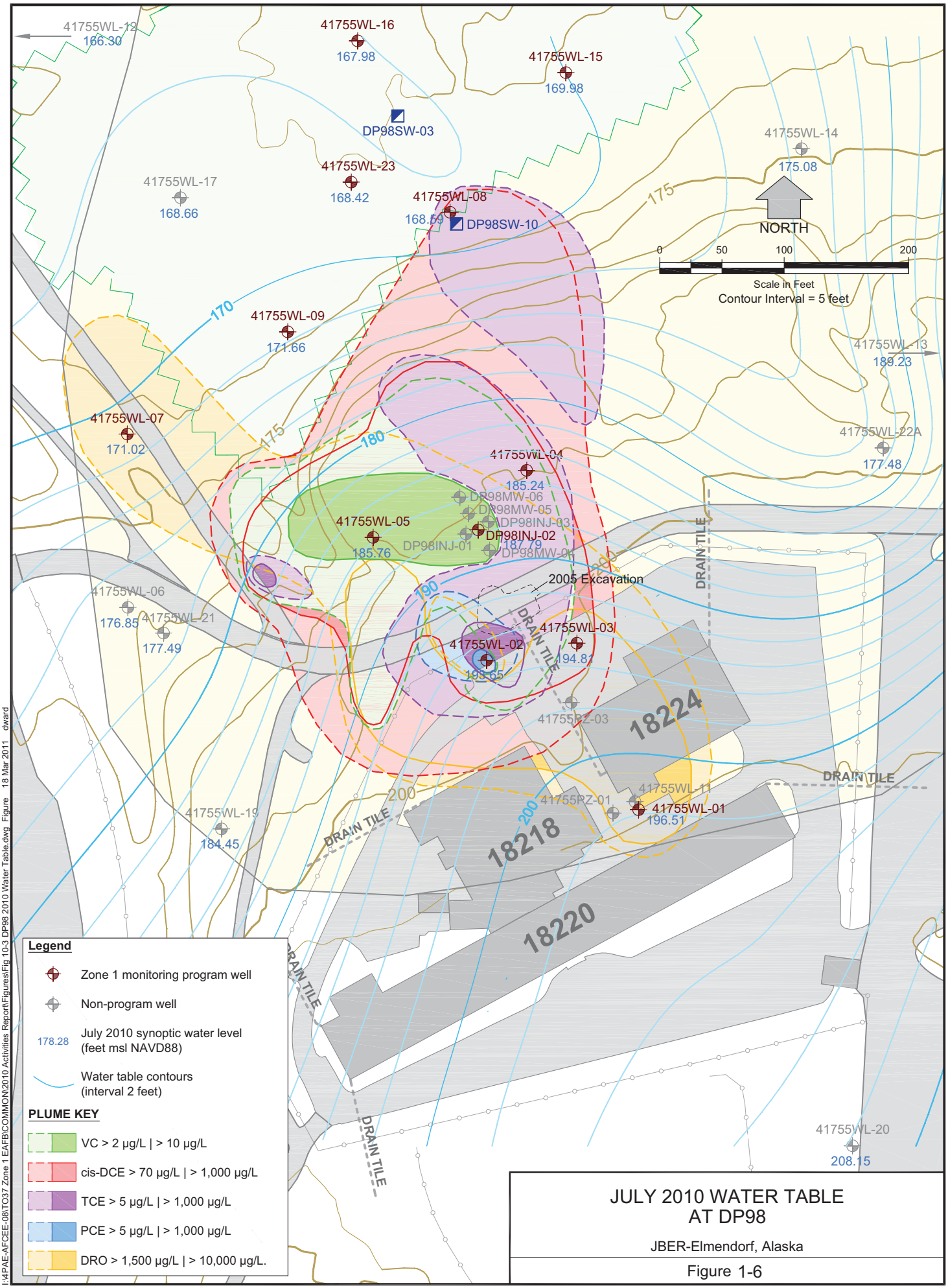
CAHs are the primary risk drivers at DP98, with fuel contaminants present but posing less risk to human health. The presence of fuel compounds has also resulted in the partial anaerobic degradation of CAHs. Therefore, remedial alternatives were developed to address CAHs in groundwater. The 2004 ROD specifies MNA as the remedy for CAHs in groundwater. As a contingency measure, the ROD specifies that a treatability study to demonstrate enhanced MNA (or enhanced bioremediation) be conducted. A treatability study was conducted from 2005 to 2006 as a field pilot test of enhanced *in situ* anaerobic bioremediation. Results of the treatability study (USAF, 2007) indicated that biotic transformation of TCE was incomplete and apparently "stalled" at cis-DCE and VC. Further evaluation in June 2008 (Parsons, 2009) indicated that *cis*-DCE and VC were persisting at elevated concentrations, and that the growth of dechlorinating *Dehalococcoides* species was not stimulated in the low-temperature environment of the site.

1.5.2 Hydrogeology

The major geological and geomorphological feature on JBER-Elmendorf is the Elmendorf End Moraine that makes up southwest-trending ridges north of the Base runways. DP98 sits on a local topographic rise on the end moraine, and the ground surface slopes downward to the north into a wetland area about 400 feet from Building 18224.

The predominant geological units in this area are the pre-Wisconsin age Knik and Wisconsin age Naptowne glacial sequences. The Bootlegger Cove Formation, a blue silty clay, underlies the site and is a lower confining layer to shallow groundwater in the area. Surface soils at the DP98 site are dominated by fill material that is well-drained and characterized as gravelly sand or sandy loam. A sloped embankment north of the site consists mostly of poorly drained silt, sand, and gravel mixtures. An undeveloped wetland exists at the base of the slope north of the site. Subsurface soil layers are predominantly glacial deposits, and range from gravelly clay loam to gravelly sand.

An unconfined aquifer underlies DP98 with a total saturated thickness ranging up to approximately 75 feet. The bottom of the unconfined aquifer is defined by the Bootlegger Cove Formation, encountered at 45 to 90 feet bgs across the site. The shallow hydraulic gradient reflects ground surface topography, and groundwater generally flows toward the north/northwest (**Figure 1.6**, from USAF, 2011). The depth to groundwater near Building 18224 is approximately 5 to 15 feet bgs. Toward the north, groundwater surfaces as intermittent seeps along the edge of the wetlands at the bottom of the slope. The wetland extends from the base of the slope about 500 feet in a northerly direction, where surface water is impounded in a small kettle pond.



JULY 2010 WATER TABLE AT DP98

JBER-Elmendorf, Alaska

Figure 1-6

Source: USAF, 2011

The horizontal hydraulic gradient in the shallow aquifer at DP98 ranges from approximately 0.01 to 0.1 foot/foot (ft/ft), and tends to be steepest near the sloped embankment. Estimates of hydraulic conductivity from the DP98 Treatability Study (USAF, 2007) range from 0.09 to 1.72 feet per day (ft/day), and the average hydraulic gradient in the treatability study test area was 0.042 ft/ft. Using this range of hydraulic conductivity, the average hydraulic gradient, and an assumed effective porosity of 22%, the horizontal groundwater velocity in the treatability study area was calculated to be on the order of 6.3 to 120 feet per year (ft/yr).

1.5.3 Nature and Extent of Contamination

The nature and extent of contamination at DP98 was most recently described in the *2010 Zone 1 Field Activities Report* (USAF, 2011). CAHs exceeding groundwater standards specified in the 2004 ROD include PCE, TCE, *cis*-DCE, 1,1-DCE, and VC. Concentrations of these compounds measured in 2010 are shown on **Figure 1.7** (from USAF, 2011). The DP98 CAH plume extends from an apparent source area located near well 41755-WL02 for approximately 350 feet to downgradient well 41755-WL08.

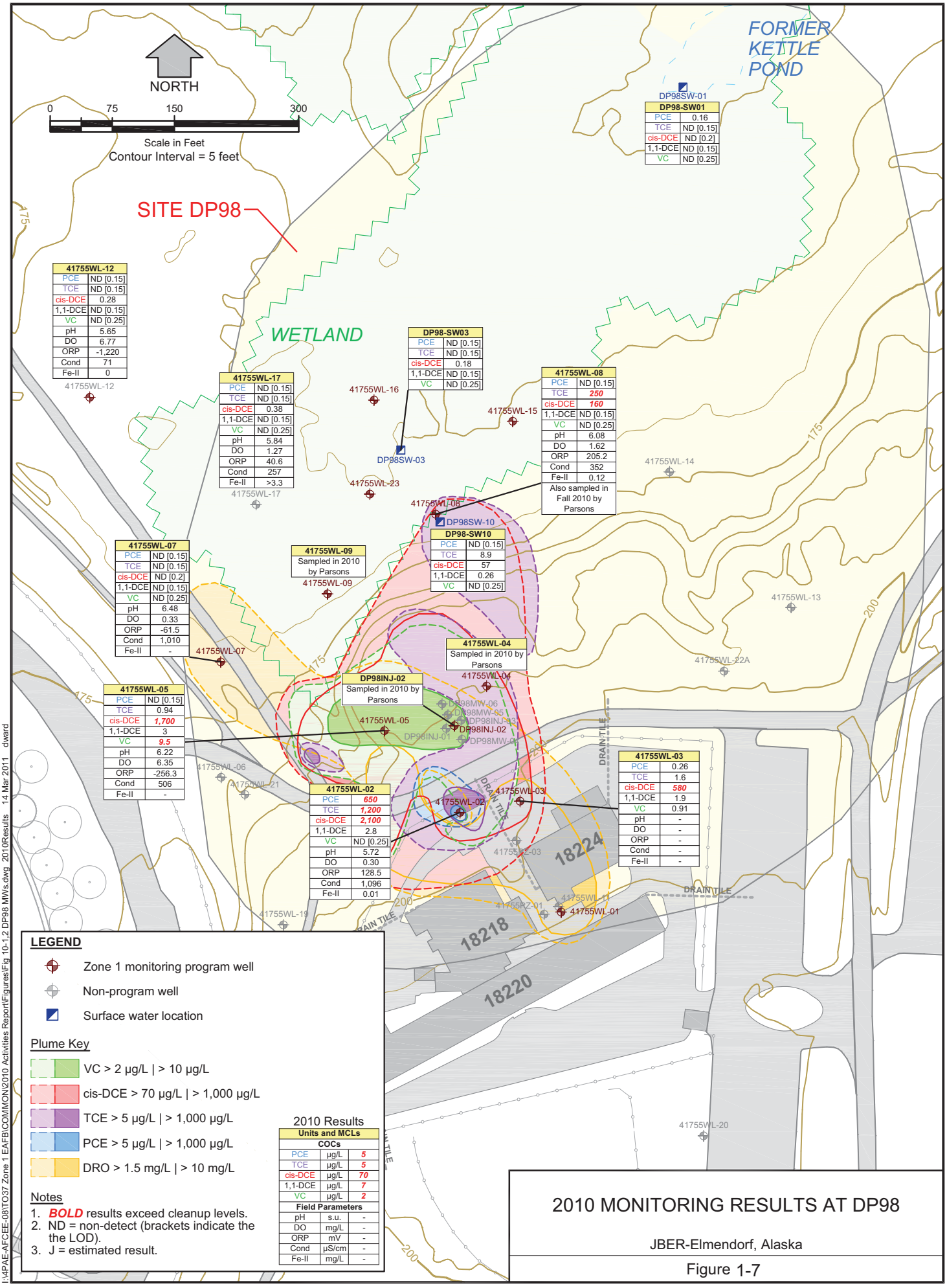
Concentrations of PCE, TCE, and *cis*-DCE at source area well 41755-WL02 in 2010 were 650 µg/L, 1,200 µg/L, and 2,100 µg/L respectively. Concentrations of *cis*-DCE measured after the 2005 treatability study were as high as 18,000 µg/L at location DP98-MW05 in June 2008, and VC was as high as 200 µg/L at location DP98-INJ02 in June 2008 (Parsons, 2009). Near the downgradient toe of the plume at location 41755WL-08, concentrations of TCE and *cis*-DCE in 2010 were 250 µg/L and 160 µg/L, respectively. PCE is limited to the untreated source area near well 41755-WL02, while TCE and cis-DCE persist throughout the DP98 CAH plume.

1.6 DP98 SITE SELECTION

Results of a treatability study of enhanced *in situ* bioremediation suggested that the native microbial population at the DP98 site is not capable of complete transformation of PCE, TCE and *cis*-DCE (USAF, 2007; Parsons, 2009). Biogeochemical transformation provides an alternative *in situ* technology to potentially mitigate this limitation.

Hydraulic and geochemical conditions at the DP98 site are suitable for a demonstration of biogeochemical transformation of chlorinated solvents. The rate of groundwater flow at the site is estimated to range from 6 to 120 ft/yr (**Section 1.5.2**). At the upper end of this range of groundwater flow rates, the residence time of groundwater in a reaction zone extending 12 feet along the direction of flow would be approximately 36 days. This should be sufficient to meet the demonstration performance objectives (**Section 1.1.2**).

The DP98 site is mildly anaerobic with DO generally less than 1.0 mg/L throughout most of the CAH groundwater plume. Anaerobic conditions should be readily sustained, and the low DO concentrations should limit the oxidation of reduced iron sulfides within the test cells. Sulfate levels are typically less than 10 mg/L; therefore, the biogeochemical amendment must contain a sufficient amount of sulfate to form the desired concentration of FeS. The aquifer sediments likely have a moderate amount of reducible iron (perhaps 2,000 to 3,000 mg/kg); however, the biogeochemical amendment should also contain a sufficient amount of iron to form the desired concentration of FeS.



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Source: USAF, 2011

2.0 MATERIALS AND METHODS

2.1 TECHNICAL APPROACH

Three injection scenarios were tested during the demonstration of biogeochemical transformation of chlorinated solvents in groundwater at the DP98 site. Two scenarios were intended to stimulate biogeochemical transformation processes through the formation of reduced iron sulfides. A third scenario used a commercial product (EHC®) to stimulate ISCR for comparison.

2.1.1 Test Cell Layout

The locations of the three test cells are shown on **Figure 1.2**. Four monitoring points were installed for Test Cells No. 1 and No. 2 to allow monitoring of groundwater quality upgradient, within, and immediately downgradient of the reaction zone. Based on initial results of monitoring point installation, changes to the work plan were required to achieve the technical objective of the third test cell. Drilling and injection at the DP98 Site was a challenge based on unanticipated changes in soil lithology and permeability between the area of a prior bioremediation pilot test and the locations of the proposed test cells. Therefore, the work plan was amended to substitute the former bioremediation pilot test wells for the previously proposed location of Test Cell No. 3, where monitoring point installation and injection proved to be impractical (Parsons, 2010b).

2.1.2 Amendment Selection

Amendments injected into three test cells consisted of the following products:

- **Test Cell No. 1:** EHC® from Adventus Americas, Inc. EHC® is a controlled-release, integrated organic carbon and zero-valent iron (ZVI) product.
- **Test Cell No. 2:** Organic substrate in the form of EVO (AquaBu*pH*® from EOS Remediation, Inc.). Sulfate and iron in the form of powdered gypsum (calcium sulfate dihydrate) from Advanced Scientific & Chemical, Inc. and powdered hematite (ferric iron oxide) from Reade Metals and Minerals Corporation.
- **Test Cell No. 3:** Organic substrate in the form of EVO (AquaBu*pH*® from EOS Remediation, Inc.), and iron and sulfate in the form of ferrous sulfate heptahydrate from Advanced Scientific & Chemical, Inc.

The amendment design and injection strategy are described in **Section 2.3**, and calculations used to determine suitable quantities of substrate, iron/sulfate amendments, and EHC® are included in **Attachment A**.

EVO was selected as the organic substrate for Test Cells 2 and 3 because it would sustain anaerobic conditions over the duration of the demonstration. The concentration of EVO used in this demonstration was anticipated to last approximately 12 to 18 months. Because the formation and reactivity of iron monosulfides is pH sensitive, an EVO product (AquaBu*pH*®) with a buffering agent (magnesium hydroxide) was selected to maintain a pH of at least 7.0. The EVO product also contained approximately 4% by weight sodium lactate, which was anticipated to rapidly deplete native electron acceptors (e.g., DO) and quickly induce anaerobic conditions.

2.2 MONITORING SYSTEM INSTALLATION

To supplement the existing monitoring well network at the site, eleven (11) groundwater monitoring points were installed using DPT. Modifications to the proposed locations of the test cells and monitoring point locations were required, as described below.

2.2.1 Test Cell and Groundwater Monitoring Locations

The locations of the three test cells are shown on **Figure 1.2**, and monitoring point construction details are summarized in **Table 2.1**. The locations of Test Cells No. 1 and No. 2 were selected to be in open areas that had not been impacted by the prior enhanced bioremediation treatability study. These locations also allow for a sufficiently long groundwater migration pathway to facilitate downgradient monitoring before the transition zone to the wetlands is reached.

Based on observations that permeability decreases towards the east and north, a decision was made to inject EHC® in Test Cell No. 1. EHC® was considered to have the largest particle size of the different amendments, and it was beneficial to inject it into the most permeable test cell.

Because of the inability to install well points at the proposed location for Test Cell No. 3, and the questionable ability to inject there, Parsons proposed injecting the ferrous sulfate/EVO solution in the former bioremediation pilot test injection wells. Concentrations of TCE in the pilot test area were beginning to rebound in 2008 (up to 120 µg/L), and high concentrations of *cis*-DCE were present. Therefore, use of the pilot test area for Test Cell No. 3 would provide information on the ability to degrade TCE and *cis*-DCE by biogeochemical transformation processes, and would also permit assessment of whether the technology is a suitable optimization technique for sites that have stalled at DCE.

2.2.2 Monitoring Point Construction

Temporary groundwater monitoring points were installed using DPT, and constructed of 1.5-inch nominal diameter, flush-threaded, Schedule 40 polyvinyl chloride (PVC) screen and riser. The screens were factory slotted with 0.010-inch openings. The screen interval for each of the groundwater monitoring points is provided in **Table 2.1**. The bottom of the screen was fitted with a bottom cap (an expendable drive point).

A number 10-20 sand pack was placed around the screen from the bottom of the borehole to approximately 2 feet above the top of the screened interval. A 2-foot-thick granular bentonite seal was installed immediately above the sand pack in 0.5-foot lifts. A neat cement/bentonite grout was installed to fill the space extending from the top of the bentonite seal to approximately 1.0 foot bgs. The grout was overlain by concrete that secured the surface completion. Each well point was completed with a flush mount well box protective casing. The PVC well casing was installed so that the top of the casing was 2 to 4 inches bgs, and the protective well box was anchored in an 18-inch-diameter concrete surface pad.

All monitoring points were abandoned in October 2011 at the conclusion of the field demonstration. Surface completions were removed and the well casings were pulled to the extent possible. Each boring (and any remaining screen and riser pipe) was grouted from the bottom up using a cement/bentonite grout. The ground surface was then leveled and well construction materials (casing and surface completions) were removed from the site.

2.2.3 Datum Survey

The locations and elevations of the newly installed monitoring points were surveyed by Lounsbury & Associates, a surveyor registered in the State of Alaska (**Table 2.1**). Horizontal locations were measured relative to the World Geodetic System of 1984, Universal Transverse Mercator Zone 6N coordinate system in units of meters. Horizontal locations were also converted to the Alaska State Plane, North American Datum of 1983, Zone 4 in units of feet.

Table 2.1 Summary of Monitoring Point and Monitoring Well Construction

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Well/Borehole Identification	Monitoring Location	Completion Date	Well Diameter (inches)	Screened Interval (feet bgs)[a/]	Ground Elevation (feet amsl)[b/]	Elevation Top of Casing[c/] (feet amsl)	Survey Northing[d/] (feet)	Survey Easting[d/] (feet)	Survey Northing[e/] (meters)	Survey Easting[e/] (meters)
Test Cell No. 1										
DP98MP01	Upgradient	19-May-10	1.5	21.5 - 31.5	196.16	195.97	2654507.73	1667654.33	6795687.36	347432.02
DP98MP02	Treatment Zone	19-May-10	1.5	22.0 - 32.0	195.75	195.36	2654531.44	1667640.62	6795694.77	347428.17
DP98MP03	Treatment Zone	19-May-10	1.5	21.0 -31.0	195.71	195.29	2654527.02	1667637.80	6795693.46	347427.25
DP98MP04	Downgradient	19-May-10	1.5	20.7 - 30.7	194.86	194.52	2654545.45	1667630.59	6795699.17	347425.32
Test Cell No. 2										
DP98MP05	Upgradient	18-May-10	1.5	20.5 - 30.5	195.89	195.36	2654521.72	1667678.87	6795691.27	347439.68
DP98MP06	Treatment Zone	18-May-10	1.5	21.0 - 31.0	195.09	194.86	2654551.33	1667670.64	6795700.40	347437.59
DP98MP07	Treatment Zone	18-May-10	1.5	21.0 - 31.0	195.24	194.82	2654548.71	1667666.03	6795699.67	347436.15
DP98MP08	Downgradient	18-May-10	1.5	21.5 - 31.5	194.65	194.31	2654564.42	1667663.29	6795704.49	347435.54
Test Cell No. 3										
DP98INJ-01	Injection Well	29-Sep-11	2.0	21.5 - 31.5	195.89	198.54	2654539.90	1667579.88	6795685.55	347417.24
DP98INJ-02	Injection Well	29-Sep-11	2.0	21.0 - 31.0	196.10	199.03	2654540.61	1667593.80	6795687.37	347420.14
DP98INJ-03	Injection Well	29-Sep-11	2.0	21.0 - 31.0	196.14	199.02	2654541.19	1667605.61	6795688.85	347422.60
DP98MW-04	Upgradient	29-Sep-11	2.0	20.5 - 30.5	196.46	199.28	2654538.35	1667607.48	6795681.59	347422.99
DP98MW-05	Downgradient	29-Sep-11	2.0	21.0 - 31.0	195.49	197.95	2654542.07	1667582.81	6795691.12	347417.85
DP98MW-06	Downgradient	29-Sep-11	2.0	21.0 - 31.0	194.73	197.32	2654543.64	1667572.34	6795695.13	347415.67
Other Monitoring Wells and Points										
DP98MP10	Crossgradient	19-May-10	1.5	17.0 - 27.0	186.41	186.01	2654653.24	1667706.24	6795730.94	347449.86
41755-WL04	Downgradient	29-Sep-11	2.0	20.1 - 30.1	195.20	198.07	2654546.19	1667650.77	6795701.67	347432.01
41755-WL05	Crossgradient	NA [f/]	2.0	13.3 - 23.3	193.60	196.79	2654488.55	1667509.86	6795683.54	347387.76

[a/] feet bgs indicates depth in feet below ground surface.

[b/] feet amsl indicates elevation in feet above mean sea level.

[c/] Elevation of top of casing (vertical datum) in feet relative to North American Vertical Datum of 1988 (NAVD88).

[d/] Horizontal coordinates in feet relative to Alaskan State Plane, North American Datum of 1983, Zone 4 (ASP-NAD83-Zone 4).

[e/] Horizontal coordinates in meters relative to World Geodetic System of 1984, Universal Transverse Mercator Zone 6N (WGS84-UTM-6N).

[f/] NA indicates data not available.

The elevations of the ground surface adjacent to each monitoring point and the measurement datum (top of the PVC casing), were measured relative to existing monitoring well 41755-WL04; a surveyors benchmark was not present near the site. Elevations were measured to the nearest 0.01 foot with respect to the North American Vertical Datum of 1988.

2.3 AMENDMENT DESIGN AND INJECTION

The following sections describe the amendment content and preparation for each test cell. The designs for Test Cells No. 1 and No. 2 were based on generating a target concentration of FeS within the treatment zone, while the design for Test Cell No. 3 was based on the vendor's recommendation. Calculations and assumptions for the quantities of products to use for Test Cells No. 1 and No. 2 are included in **Attachment A**.

The target concentrations of FeS were based on achieving a reduction in TCE concentrations of 99% (two orders of magnitude) based on rates from a column study conducted by the USEPA (Shen and Wilson, 2007). These rates are based on the moles of TCE removed per day when in contact with 1 mole FeS in one liter of groundwater. The lower rate of the range reported by Shen and Wilson (2007) was used to determine a target concentration of 2,000 mg/kg of FeS. In practice, the concentration of FeS in soil is estimated by measuring the concentration of AVS.

The site is naturally low in dissolved sulfate (less than 30 mg/L); therefore, the amendment mixtures used for Test Cells No. 1 and No. 2 incorporated sufficient sulfate to generate the desired quantity of FeS. Five soil samples were collected within the former treatability study test area by a prior contractor in 2009 and analyzed for ferric and ferrous iron. While iron in this area has likely been reduced by anaerobic degradation, these data provided an approximation of the amount of iron in soil at the DP98 site. Concentrations of ferric iron ranged from 99 to 870 mg/kg, and averaged 314 mg/kg. Concentrations of ferrous iron ranged from 440 to 2,500 mg/kg, and averaged 1,670 mg/kg. It can be assumed that the sediments at the DP98 site contain approximately 2,000 mg/kg of total iron. In theory, this is sufficient to produce 2,000 mg/kg FeS. However, since not all of the iron may be bioavailable or may already be reduced, the amendments for Test Cells No. 1 and No. 2 included ferric or ferrous iron.

Injections were performed from 21 May to 01 June 2010, as described in the following sections. In general, the amendments were mixed in batch mode and the volumes injected into each point were metered to achieve the target volumes. The amendment mixture was injected into two to three injection points at any given time, and the injection points pulled as the target quantities were achieved. Injections points were abandoned by grouting from the bottom of the borehole to the ground surface with a cement/bentonite grout.

2.3.1 Test Cell No. 1

EHC® is a controlled-release, integrated organic carbon and ZVI product that the vendor (Adventus Group, Inc.) claims will yield an ORP in the range of -500 to -650 millivolts (mV) relative to a standard hydrogen electrode (Eh). This Eh is significantly lower than that achieved when using either organic materials (e.g., lactate, sugars, or vegetable oil) or ZVI alone. ORPs in this range can potentially facilitate degradation of PCE and TCE without the formation of intermediates such as DCE and VC.

The test cell design called for 11 temporary injection points to be spaced 5 feet apart, potentially creating a reaction zone approximately 20 feet wide in the cross-gradient direction and 13 feet long perpendicular to groundwater flow. The injection interval was designed to be 10 feet thick.

Adventus Group, Inc. recommended that the product be applied on a mass basis relative to the mass of soil in the treatment zone. EHC® mass requirements for chlorinated solvent sites typically range from 0.5 to 1.0% for grid applications, and up to 2.0% for applications in a permeable reactive barrier configuration. For this application, the intent was to inject EHC® in a grid pattern at a rate of approximately 350 pounds per injection point, corresponding to an EHC® mass to soil mass ratio of 1.4%. This application rate was considered to be sufficient given the relatively slow rate of groundwater flow at the site (less than 0.33 ft/day) and a residence time of approximately 40 days in the reaction zone.

The actual quantities injected are listed in **Table 2.2**. In practice, a total of 3,750 pounds (lb) of EHC® product was mixed with approximately 3,490 gallons of makeup water (**Section 2.3.4**) and injected into 14 injection points at depths ranging from 22 to 35 feet bgs. The target substrate quantity could not be achieved in all injection points due to the low permeability of sediments in the test cell. Therefore, three additional injection points were located on the downgradient side of the test cell to permit injection of the total target quantity (**Figure 2.1**). Because the injection was spread over a larger area, the resulting mass of EHC® to mass of soil was 1.1%.

2.3.2 Test Cell No. 2

A mixture of hematite (iron oxide) powder, calcium sulfate, and EVO was injected into Test Cell No. 2. A pre-mixed soybean oil emulsion product (AquaBu*pH*®) was used, consisting of approximately 40% soybean oil by weight, 7% food-grade emulsifiers by weight, 4% sodium lactate by weight, and 15% magnesium hydroxide (buffer) by weight. The vendor prepared the emulsion product prior to shipment to Alaska. The product is reported to have an oil droplet diameter of 2 to 4 microns. The injected EVO was designed to occupy approximately 3% (by volume) of the effective porosity (interstitial void space) of the aquifer matrix after the post-injection water push.

Sulfate was added in the form of calcium sulfate dihydrate (gypsum), shipped as a dry powder. Iron was added in the form of powdered iron oxide (natural hematite). Approximately 1,600 pounds of calcium sulfate dihydrate and 500 pounds of powdered iron oxide were mixed with approximately 3,360 gallons of makeup water (**Section 2.3.4**) and injected into 11 temporary direct-push injection points over a vertical interval of 10 feet (**Table 2.3** and **Figure 2.2**). Based on the actual concentrations of sulfate and iron in the products, this resulted in the addition of approximately 893 lb of sulfate and 340 lb of ferric iron.

Injection points for Test Cell No. 2 were located in three rows oriented perpendicular to groundwater flow and spaced 5 feet apart (**Figure 2.2**). Given an estimated radius of influence of approximately 2.8 feet per injection point, this created a reaction zone approximately 20 feet wide in the cross-gradient direction and 13 feet long perpendicular to groundwater flow, resulting in a treatment zone area of 260 square feet (ft^2). The injection interval was approximately 10 feet thick, resulting in a treatment zone volume of 2,600 cubic feet (ft^3).

2.3.3 Test Cell No. 3

The ferrous sulfate product is soluble and the EVO product has a very fine oil droplet size. Therefore, it was the best formulation to inject into existing injection/monitoring wells at the former pilot test area. To account for the difference between injecting into the three existing injection wells versus the proposed 11 direct-push points, the injection scenario was revised to re-distribute the amendment between injection wells DP98INJ-01 through DP98INJ-03 (**Figure 1.2**).

Table 2.2 Test Cell No. 1 As-Built Injection Scenario

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Injection Point ID	Injection Points		EHC® [a/] Injection Mixture			Estimated Effective Porosity (percent)	Estimated Radius of Influence (feet)
	Injection Interval (feet)	Injection Spacing (feet)	Product Quantity (pounds)	Makeup Water (gallons)	Pounds per Gallon		
DPT-EHC-01	22-32	5	350	326	1.07	22%	2.5
DPT-EHC-02	22-32	5	200	186	1.08	22%	1.9
DPT-EHC-03	22-32	5	200	186	1.08	22%	1.9
DPT-EHC-04	27-32	5	125	116	1.08	22%	2.1
DPT-EHC-05	22-32	5	300	279	1.08	22%	2.3
DPT-EHC-06	22-32	5	350	326	1.07	22%	2.5
DPT-EHC-07	27-32	5	400	372	1.08	22%	3.8
DPT-EHC-08	22-32	5	425	395	1.08	22%	2.8
DPT-EHC-09	22-32	5	350	326	1.07	22%	2.5
DPT-EHC-10	22-32	5	350	326	1.07	22%	2.5
DPT-EHC-11	22-32	5	350	326	1.07	22%	2.5
DPT-EHC-12	27-32	5	150	140	1.07	22%	2.3
DPT-EHC-13	27-32	5	150	140	1.07	22%	2.3
DPT-EHC-14	32-35	5	50	47	1.06	22%	1.3
TOTALS:			**3,750**	**3,491**			

Product Calculations

Volume of Treatment Zone =	3,398	cubic feet
Volume of Treatment Zone =	96	cubic meters
Bulk Density =	1.68	grams per cubic meter
Mass of Soil =	161,622	kilograms
Mass of Soil =	356,312	pounds
Mass EHC® to Mass Soil =	1.1%	percent

[a/] EHC® = controlled release, integrated carbon and zero valent ion source that reduces redox potential.

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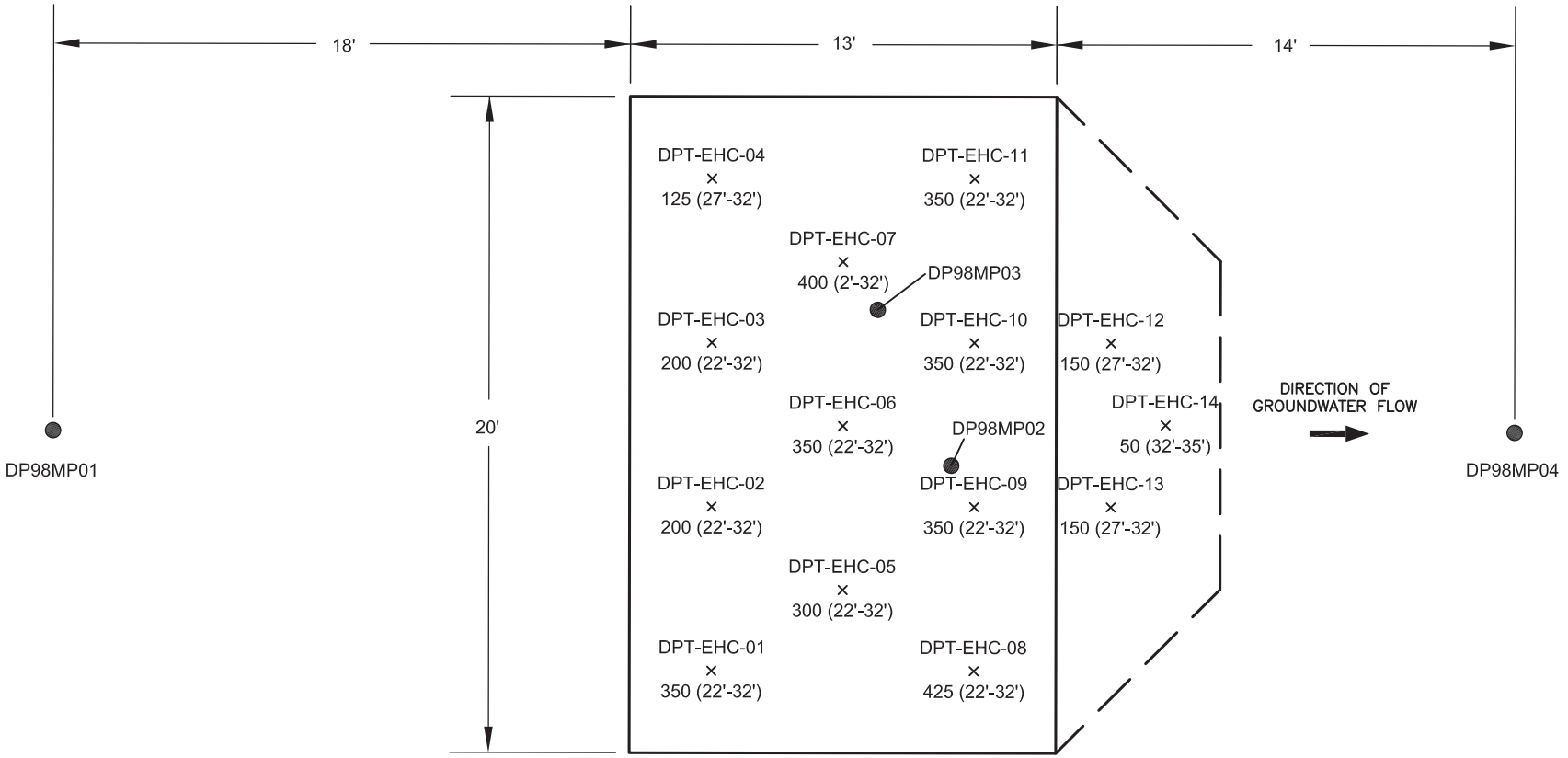

LEGEND

Well ID × INJECTION POINT

● MONITORING POINT

350 (22'-32') TOTAL PRODUCT QUANTITY IN POUNDS (INJECTION INTERVAL, IN FEET BELOW GROUND SURFACE)

FIGURE 2.1

TEST CELL NO. 1 MONITORING AND INJECTION POINT LAYOUT AS-BUILT

DP98, JBER, Alaska

PARSONS

Denver, Colorado

Table 2.3 Test Cell No. 2 As-Built Injection Scenario

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Injection Point ID	Injection Points		Emulsion Injection Mixture								Total Water/ Substrate (gallons)	Estimated Effective Porosity (percent)	Estimated Radius of Influence (feet)
	Injection Interval (feet)	Injection Spacing (feet)	EVO[a/] Volume (gallons)	Soybean Oil Component (gallons)	Soybean Oil Component (pounds)	Calcium Sulfate (pounds)	Sulfate Content (pounds)	Powdered Hematite (pounds)	Iron Content (pounds)	Makeup Water (gallons)			
DPT-2-01	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-02	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-03	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-04	NA[b/]	5	0.0	0	0	0	0	0.0	0	0	0	20%	0.0
DPT-2-05	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-06	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-07	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-08	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-09	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-10	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
DPT-2-11	22 - 32	5	25.0	12	91	160	89	50.0	34	336	361	20%	2.8
TOTAL:			**250**	**116**	**905**	**1,600**	**893**	**500**	**340**	**3,360**	**3,610**		

AMENDMENT CONCENTRATIONS

Effective Oil Concentration: **3.22%** **percent by volume**

Effective Sulfate Concentration: **29,847** **mg/L**[c/]

Effective Iron Concentration: **11,366** **mg/L**

Notes: Vegetable Oil Emulsion Product

1. Assumes emulsion product is 47 percent soybean oil and food-grade emulsifiers by weight.
2. Weight of soybean oil/emulsifiers is 7.8 pounds per gallon.

Notes: Sulfate and Iron Products

3. Assumes anhydrous calcium sulfate product is 55.8 percent sulfate by weight.
4. Assumes powdered iron oxide (hematite) is 68 percent ferric iron by weight.

Acronyms:

[a/] EVO = emulsified vegetable oil.

[b/] NA = not applicable, no injection at this location.

[c/] mg/L = milligram(s) per liter.

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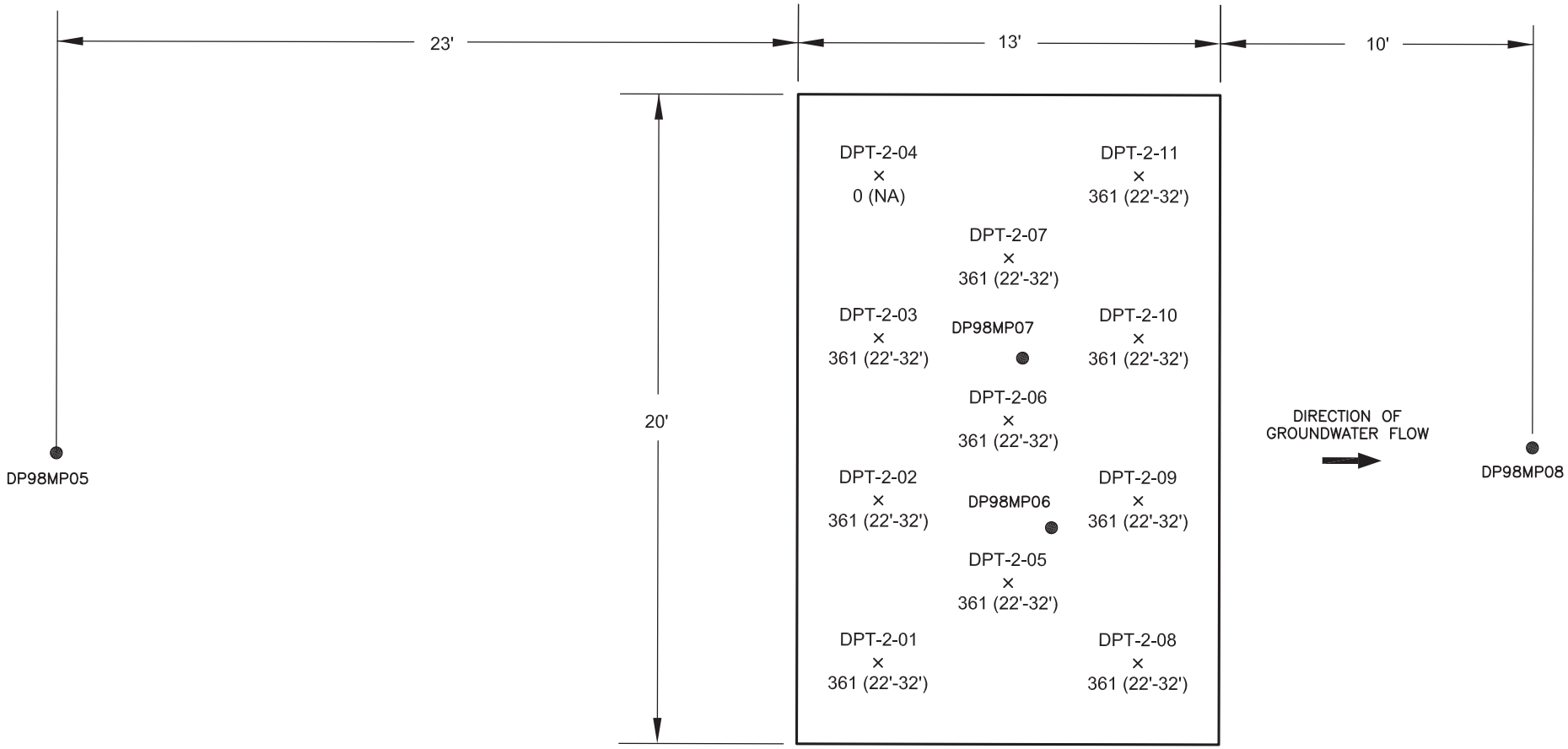

LEGEND

× INJECTION POINT

● MONITORING POINT

361 (22'–32') TOTAL GALLONS OF WATER/SUBSTRATE (INJECTION INTERVAL, IN FEET BELOW GROUND SURFACE)

FIGURE 2.2

TEST CELL NO. 2 MONITORING AND INJECTION POINT LAYOUT AS-BUILT

DP98, JBER, Alaska

PARSONS

Denver, Colorado

The target amount of amendments could not be injected into well DP98INJ-01 because some of the injected amendment migrated vertically upward and "daylighted" at the ground surface during injection. Therefore, additional amendment was injected into a new DPT point (DP98INJ-04) located 5 feet downgradient of DP98INJ-02. The as-built distribution of injected materials between the three existing injection wells and the DPT point is provided in **Table 2.4**.

The EVO product used for Test Cell No. 3 was identical to that used for Test Cell No. 2 (**Section 2.3.2**), and was applied at a similar concentration (approximately 3% of the interstitial pore volume). Iron and sulfate were added in the form of ferrous sulfate heptahydrate, shipped as a soluble granular material. Approximately 2,500 lb of the ferrous sulfate product were mixed with approximately 3,255 gallons of makeup water (**Section 2.3.4**) and injected over a vertical interval of 5 to 10 feet (**Table 2.4**). This resulted in the addition of approximately 865 lb of sulfate and 503 lb of ferrous iron.

2.3.4 Makeup Water

To the extent possible, makeup water for the substrate/amendment injections was obtained from development and purging of the newly installed monitoring points or from existing monitoring wells located within the immediate vicinity of the test cells at the DP98 site. However, due to the low water yield of the wells, most of the makeup water used for the injection was obtained from a City of Anchorage potable water supply, with only a limited quantity (approximately 300 gallons) of groundwater obtained from monitoring well development and purging.

2.3.5 Amendment Emplacement

Mixing of makeup water with the amendments was performed using a grout pump and central mixing tanks in batch mode (**Figure 2.3**). Mixtures were measured on a bulk volume or weight basis in the mixing tanks. The mixtures were injected directly through slotted Geoprobe® push rods over a 42-inch interval (**Figure 2.4**). In general, the rods were pushed to the bottom 5 feet of the injection interval and one-half of the target volume was injected. The rods were then raised 5 feet and one-half of the target volume was injected into the upper 5 feet of the target interval. The target injection rate for the substrate mixtures was approximately 3.0 gallons per minute (gpm), although this could not be achieved at all locations.

System pressures were monitored and flow rate adjustments made as needed to avoid excessive pressure which could constitute a health and safety hazard or result in daylighting of the amendment at the ground surface. A water push consisting of approximately 10 gallons of makeup water was injected at the end of each DPT point injection to clear the slotted Geoprobe® rod of sediment and amendment mixture.

2.4 MONITORING PROTOCOLS

Baseline (initial condition) soil sampling was conducted during well point installation in May 2010. Baseline groundwater sampling was conducted after well point installation and before injection of amendments. Baseline sampling was performed to characterize pre-injection, site-specific geochemical and contaminant conditions. To monitor system performance over time, groundwater was sampled at approximately 3, 11, and 15 months after injection of amendments (September 2010, May 2011, and September 2011). The analytical protocols that were used for the demonstration monitoring program are summarized in **Table 2.5**.

Table 2.4 Test Cell No. 3 As-Built Injection Scenario

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Injection Well ID	Injection Points		Emulsion Injection Mixture							Total Water/ Substrate (gallons)	Estimated Effective Porosity (percent)	Estimated Radius of Influence (feet)
	Injection Interval (feet)	Injection Spacing (feet)	EVO[a/] Volume (gallons)	Soybean Oil Component (gallons)	(pounds)	Ferrous Sulfate (pounds)	Sulfate Content (pounds)	Iron Content (pounds)	Makeup Water (gallons)			
DP98INJ-01	22 - 32	10	39	18	141	390	135	78	512	551	20%	3.4
DP98INJ-02	22 - 32	10	113	52	409	1110	384	223	1465	1,578	20%	5.8
DP98INJ-03	22 - 32	10	84	39	304	840	291	169	1093	1,177	20%	5.0
DP98INJ-04	27-32	10	14	7	51	160	55	32	186	200	20%	2.9
TOTAL:			**250**	**116**	**905**	**2,500**	**865**	**503**	**3,255**	**3,505**		

NOTE: DP98INJ-04 was a direct-push injection point located 5 feet downgradient (north) of injection well DP98INJ-02

AMENDMENT CONCENTRATIONS

Effective Oil Concentration	**3.31%**	**percent by volume**
Effective Sulfate Concentration	**29,783**	**mg/L**[b/]
Effective Iron Concentration	**17,302**	**mg/L**

Notes: Vegetable Oil Emulsion Product

1. Assumes emulsion product is 47 percent soybean oil and food-grade emulsifiers by weight.
2. weight of soybean oil/emulsifiers is 7.8 pounds per gallon.

Notes: Sulfate and Iron Products

3. Assumes ferrous sulfate product is 34.6 percent sulfate by weight.
4. Assumes ferrous sulfate product is 20.1 percent ferrous iron by weight.

Acronyms:

[a/] EVO = emulsified vegetable oil.

[b/] mg/L = milligram(s) per liter.

Figure 2.3 Grout Pump Used to Mix EHC® and Hematite Powder Slurries

Figure 2.4 Injection into DPT Points at Test Cell No. 1

Table 2.5 Analytical Protocols for Soil and Groundwater

Matrix/Analyte	Method	Field (F) or Lab (L)	Screening (S) or Definitive (D)
Soil			
Volatile Organic Compounds	SW8260B	L	D
Total Iron, Potassium, and Phosphorous	SW6010B	L	D
Bulk Iron and Sulfides	Microseeps, Inc. SOP [a/]	L	S
Water			
Dissolved Oxygen	Direct-reading meter	F	S
Oxidation-Reduction Potential	Direct-reading meter	F	S
pH	Direct-reading meter	F	S
Specific Conductance	Direct-reading meter	F	S
Temperature	Direct-reading meter	F	S
Ferrous Iron	Colorimetric, Hach Method 8146	F	S
Manganese	Colorimetric, Hach Method 8034	F	S
Sulfide	Colorimetric, Hach Method 8131	F	S
Alkalinity	Titrimetric, Hach Method 8203	F	S
Carbon Dioxide	Titrimetric, Hach Method 8205	F	S
Volatile Organic Compounds	SW8260B	L	D
Dissolved Organic Carbon	SW9060M	L	D
Methane, Ethane, Ethene, and Acetylene	AM-20GAX [b/]	L	S
Anion Suite [c/]	SW9056 (filtered samples)	L	D
Cation Suite [d/]	SW6010B (filtered samples)	L	D
Sulfate and Chloride	SW9056	L	D
Dissolved Hydrogen	AM-20GAX [b/]	L	S
Volatile Fatty Acids	APPL, Inc. SOP	L	S
Compound-Specific Isotope Analysis (CSIA)	Microseeps SOP	L	S
Dehalococcoides species by quantitative polymerase chain reaction	Microbial Insights SOP	L	S

[a/] Bulk iron and sulfides included bioavailable or weak acid extractable ferric and ferrous iron, strong acid extractable iron, acid volatile sulfide, and chromium reducible sulfide by Microseeps internal Standard Operating Procedure (SOP).

[b/] AM-20GAX is an in-house method developed by Microseeps.

[c/] Anion suite included chloride, sulfate, sulfide, phosphate, nitrate, nitrite, and fluoride.

[d/] Cation suite included sodium, potassium, calcium, iron, magnesium, and manganese.

2.4.1 Soil Analytical Protocol

During installation of monitoring points in May 2010, soil samples were collected from the injection interval of each test cell (see **Figure 2.5** for approximate locations) using DPT with clear acetate core liners. Upon retrieval and inspection, an approximately 6-inch-long section was removed from the middle of each core and processed for analysis. One set of core samples was capped, sealed, frozen, and sent to Microseeps, Inc. in Pittsburgh, Pennsylvania for analysis of bulk iron and sulfur content. Another set of samples were submitted to Agriculture and Priority Pollutants Laboratories, Inc. (APPL) in Clovis, California for analysis of volatile organic compounds (VOCs) and total iron, potassium, and phosphorous.

During the second monitoring event in September 2010, another set of soil samples was collected from the injection interval of each test cell using the same procedures. A set of frozen samples was submitted to Microseeps, Inc. for analysis of bulk iron and sulfur content. A second set of frozen samples was provided to Camp Dresser & McKee (CDM) for mineralogical analysis using a SEM at the University of Colorado in Boulder.

2.4.2 Groundwater Analytical Protocol

Groundwater samples were submitted to APPL for analysis of VOCs, dissolved organic carbon (DOC, filtered samples), dissolved anion and cation suites (first two sample events only), sulfate and chloride (last two sample events only), and volatile fatty acids (VFAs) (second sample event only). Additional samples were sent to Microseeps, Inc. for analysis of dissolved gases (methane, ethane, ethene, and acetylene) and dissolved hydrogen (second sampling event only). In addition, analytical results were previously obtained (as part of a separate AFCEE task order) for compound-specific isotope analysis (CSIA) by Microseeps, Inc. and for quantitative polymerase chain reaction (qPCR) analysis of *Dehalococcoides* species by Microbial Insights, Inc. in Nashville, Tennessee. The results of these additional analyses are not considered to represent definitive data, but are considered to be screening-level only.

2.4.3 Groundwater Field Analysis

Groundwater samples were analyzed in the field for ORP, DO, pH, specific conductance, temperature, ferrous iron, manganese, alkalinity, hydrogen sulfide, and carbon dioxide (**Table 2.5**). Some of the measurements were made with direct-reading meters, while others were made using a Hach® Company portable colorimeter or titration kit.

2.5 RESIDUALS MANAGEMENT

Investigation-derived waste (IDW) generated during the demonstration included water generated during development and sampling of groundwater monitoring points, equipment decontamination rinsate, expendable sampling supplies, and personal protective equipment (PPE). Well point installation and soil sampling used direct-push techniques that did not produce any soil cuttings requiring disposal.

Purge water generated during monitoring point development and initial (baseline) groundwater sampling was collected in a bulk storage tank and used as make-up water for the mixing and injection of amendments. All decontamination water and purge water generated during subsequent sampling events was containerized and transported to the Contractor's Staging Yard where it was placed in a bulk storage tank. This water was then disposed through the 673 CES/CEANR groundwater treatment system.

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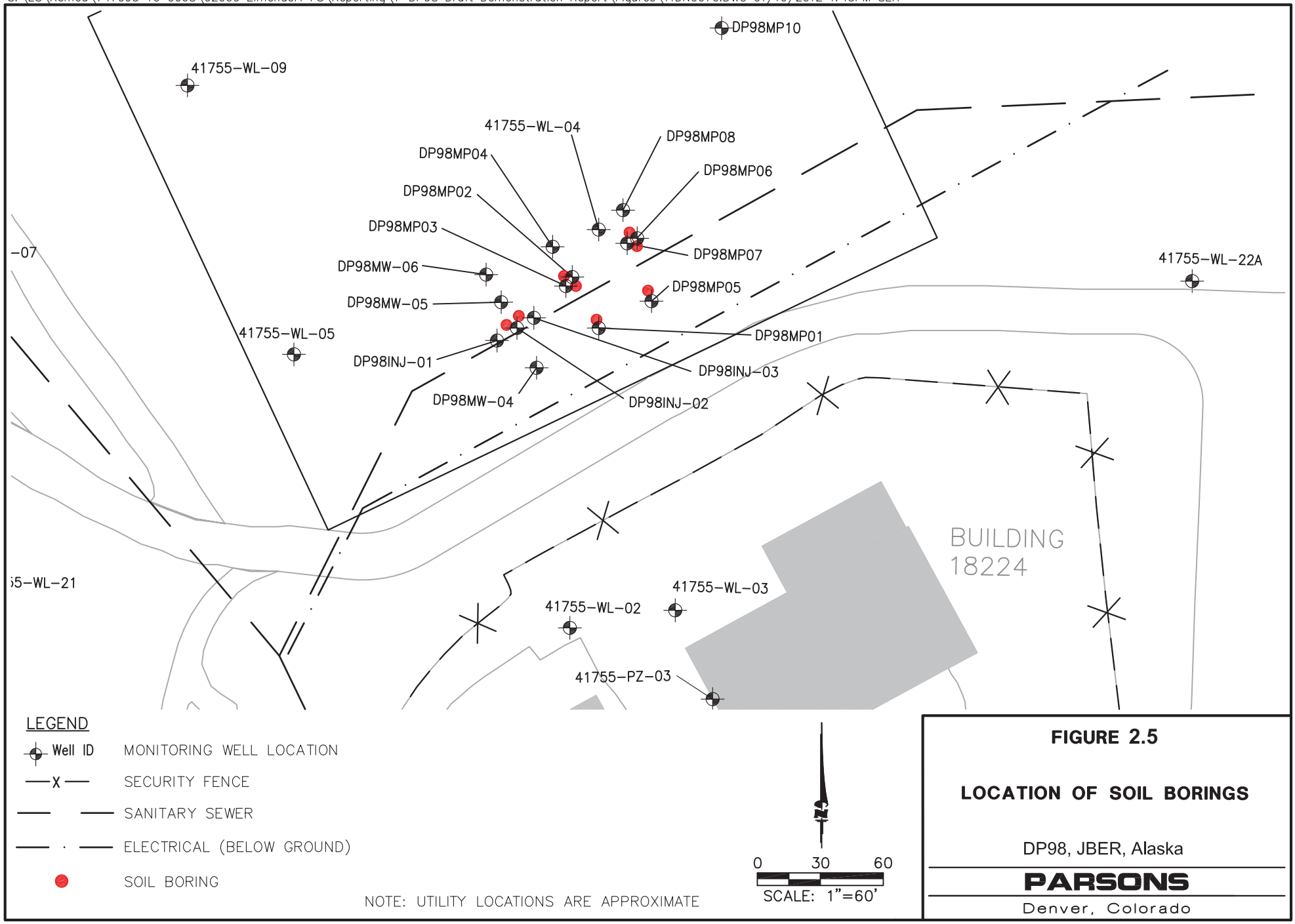

FIGURE 2.5

LOCATION OF SOIL BORINGS

DP98, JBER, Alaska

PARSONS

Denver, Colorado

PPE and expendable sampling equipment generated during field activities (e.g., sample tubing), was bagged and disposed of in a JBER trash dumpster located near the Staging Yard. Miscellaneous trash generated during field activities (i.e., empty sand bags and bentonite containers) was also placed in a dumpster.

2.6 DATA MANAGEMENT AND VALIDATION

All laboratory analytical data were loaded into a Microsoft Access® database that is maintained by a Parsons database administrator. Parsons performed a Level III validation of all laboratory analytical results for groundwater samples, and data were qualified as appropriate based on the validation results. Data validation reports are included in the Supporting Data Package. The results of the mineral speciation analyses performed on soil samples by Microseeps were not validated.

3.0 DEMONSTRATION RESULTS AND DISCUSSION

3.1 HYDROGEOLOGY

Groundwater levels measured during the demonstration are listed in **Table 3.1**. Depth to groundwater varied from approximately 11 to 18 feet bgs. In the wetlands area to the north of the demonstration area, groundwater is approximately 1.0 foot bgs (well 41755-WL09). The inferred potentiometric surface for September 2011 is shown on **Figure 3.1**. Some wells were slow to recharge after purging, and groundwater measurements made in these wells may not accurately reflect the unconfined water table elevation (i.e., water level data for DP98MP03 and DP98MP08 were not used for contouring the potentiometric surface shown on **Figure 3.1**). Groundwater flow is from the south toward the north with an average gradient of 0.08 ft/ft across the test cell area. Assuming an effective porosity of 22% and a hydraulic conductivity ranging from 0.09 ft/day to 1.72 ft/day (USAF, 2007), the average rate of groundwater flow across the test cells is estimated to range from 0.033 ft/day to 0.63 ft/day (12 to 228 ft/yr).

Visual observations made during collection of soil cores and observations of drawdown and recharge while purging groundwater monitoring points and wells indicates a moderate to high degree of sediment heterogeneity. One effect of this heterogeneity is the nearly two order-of-magnitude range in hydraulic conductivity reported in USAF (2007). This degree of heterogeneity suggests there are preferential groundwater flow pathways that likely resulted in uneven distribution of injected amendments. This scenario should be taken into consideration when interpreting contaminant and biogeochemical data for the demonstration site.

3.2 RESULTS OF GROUNDWATER BIOGEOCHEMISTRY

A number of biogeochemical parameters were measured during the baseline and performance monitoring events to determine whether the desired biogeochemical conditions were established and sustained. Most of the biogeochemical data collected at the DP98 site are summarized in **Table 3.2**. The following paragraphs discuss key biogeochemical indicator parameters, with emphasis on the pre-injection baseline (May 2010) data relative to post-injection monitoring events (September 2010 to September 2011).

3.2.1 Dissolved Organic Carbon

Concentrations of DOC in groundwater at most locations prior to the May-June 2010 injection were relatively low, ranging from 2.2 to 24 mg/L. The two exceptions were wells DP98INJ-02 (105 M mg/L) and DP98INJ-03 (33.4 mg/L) in Test Cell No. 3; these injection/monitoring wells were used for a prior enhanced bioremediation treatability study. The M data qualifier indicates an estimated concentration due to matrix interference. After the test cell injections, DOC ranged up to 1,560 mg/L at well DP98MP03 in Test Cell No. 1; up to 361 mg/L at well DP98MP07 in Test Cell No. 2; and up to 919 J mg/L (estimated concentration) in Test Cell No. 3 at well DP98INJ-02.

Differences in the magnitude of the concentrations of DOC between the three test cells were observed. **Figure 3.2** shows the average concentration of DOC for wells within Test Cell No. 1 (average of DP98MP02 and DP98MP03), within Test Cell No. 2 (average of DP98MP06 and DP98MP07), and within Test Cell No. 3 (average of DP98INJ-01, DP98INJ-02, and DP98INJ-01). The average DOC concentration was highest in Test Cell No. 1 amended with EHC®, and lowest in Test Cell No. 2 amended with hematite, gypsum, and EVO. Average concentrations of DOC in Test Cells No. 2 and 3 increased from September 2010 to May 2011, but decreased in all three test cells from May 2011 to September 2011 as the injected substrate was utilized by microbial populations and impacted by groundwater advection, dilution, and dispersion.

Table 3.1 Summary of Groundwater Elevations

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Well/Borehole Identification	Date	Screened Interval (feet bgs)[a/]	Ground Surface Elevation (feet amsl)[b/]	Elevation Top of Casing (feet amsl)	Depth to Water (feet btoc)[c/]	Groundwater Elevation (feet amsl)
Test Cell No. 1						
DP98MP01	2-Jun-10	21.5 - 31.5	196.2	195.97	12.35	183.62
	24-Sep-10				11.33	184.64
	20-May-11				17.41	178.56
	12-Sep-11				14.82	181.15
DP98MP02	2-Jun-10	22.0 - 32.0	195.8	195.36	13.04	182.32
	24-Sep-10				13.05	182.31
	20-May-11				18.35	177.01
	12-Sep-11				17.92	177.44
DP98MP03	2-Jun-10	21.0 -31.0	195.7	195.29	12.40	182.89
	24-Sep-10				14.54	180.75
	20-May-11				18.16	177.13
	12-Sep-11				19.40	175.89
DP98MP04	2-Jun-10	20.7 - 30.7	194.9	194.52	12.72	181.80
	24-Sep-10				12.92	181.60
	20-May-11				18.06	176.46
	12-Sep-11				17.72	176.80
Test Cell No. 2						
DP98MP05	2-Jun-10	20.5 - 30.5	195.9	195.36	11.52	183.84
	24-Sep-10				10.54	184.82
	20-May-11				18.19	177.17
	12-Sep-11				15.44	179.92
DP98MP06	2-Jun-10	21.0 - 31.0	195.1	194.86	12.75	182.11
	24-Sep-10				13.12	181.74
	20-May-11				18.20	176.66
	12-Sep-11				17.99	176.87
DP98MP07	2-Jun-10	21.0 - 31.0	195.2	194.82	12.66	182.16
	24-Sep-10				13.31	181.51
	20-May-11				18.12	176.70
	12-Sep-11				17.85	176.97
DP98MP08	2-Jun-10	21.5 - 31.5	194.7	194.31	13.14	181.17
	24-Sep-10				22.30	172.01
	20-May-11				25.72	168.59
	12-Sep-11				23.02	171.29
Test Cell No. 3						
DP98INJ-01	2-Jun-10	21.5 - 31.5	195.9	198.54	15.19	183.35
	24-Sep-10				14.43	184.11
	20-May-11				20.31	178.23
	12-Sep-11				18.51	180.03
DP98INJ-02	2-Jun-10	21.0 - 31.0	196.1	199.03	16.31	182.72
	24-Sep-10				15.08	183.95
	20-May-11				21.04	177.99
	12-Sep-11				18.95	180.08

(continued)

Table 3.1 Summary of Groundwater Elevations

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Well/Borehole Identification	Date	Screened Interval (feet bgs)[a/]	Ground Surface Elevation (feet amsl)[b/]	Elevation Top of Casing (feet amsl)	Depth to Water (feet btoc)[c/]	Groundwater Elevation (feet amsl)
Test Cell No. 3						
DP98INJ-03	2-Jun-10	21.0 - 31.0	196.1	199.02	15.51	183.51
	24-Sep-10				14.98	184.04
	20-May-11				21.12	177.90
	12-Sep-11				19.15	179.87
DP98MW-04	2-Jun-10	20.5 - 30.5	196.5	199.28	15.76	183.52
	24-Sep-10				14.64	184.64
	20-May-11				20.70	178.58
	12-Sep-11				18.25	181.03
DP98MW-05	2-Jun-10	21.0 - 31.0	195.5	197.95	15.57	182.38
	24-Sep-10				15.38	182.57
	20-May-11				20.80	177.15
	12-Sep-11				19.79	178.16
DP98MW-06	2-Jun-10	21.0 - 31.0	194.7	197.32	15.59	181.73
	24-Sep-10				15.49	181.83
	20-May-11				20.64	176.68
	12-Sep-11				19.92	177.40
Other Monitoring Wells and Points						
DP98MP10	2-Jun-10	17.0 - 27.0	186.4	186.01	11.24	174.77
	23-Sep-10				11.89	174.12
	20-May-11				14.39	171.62
	15-Sep-11				14.45	171.56
41755-WL04	2-Jun-10	20.1 - 30.1	195.2	198.07	16.48	181.59
	24-Sep-10				NR[d/]	NR
	20-May-11				21.85	176.22
	12-Sep-11				21.74	176.33
41755-WL05	2-Jun-10	13.3 - 23.3	193.6	196.79	15.91	180.88
	24-Sep-10				NR	NR
	20-May-11				19.42	177.37
	12-Sep-11				18.90	177.89
41755-WL09	23-Sep-10	6.6 - 16.6	166.4	170.02	3.75	166.27
	19-May-11				3.63	166.39
	14-Sep-11				4.02	166.00

[a/] feet bgs indicates feet below ground surface.

[b/] feet amsl indicates elevation in feet above mean sea level.

[c/] feet btoc indicates depth in feet below top of casing.

[d/] NR indicates measurement not taken.

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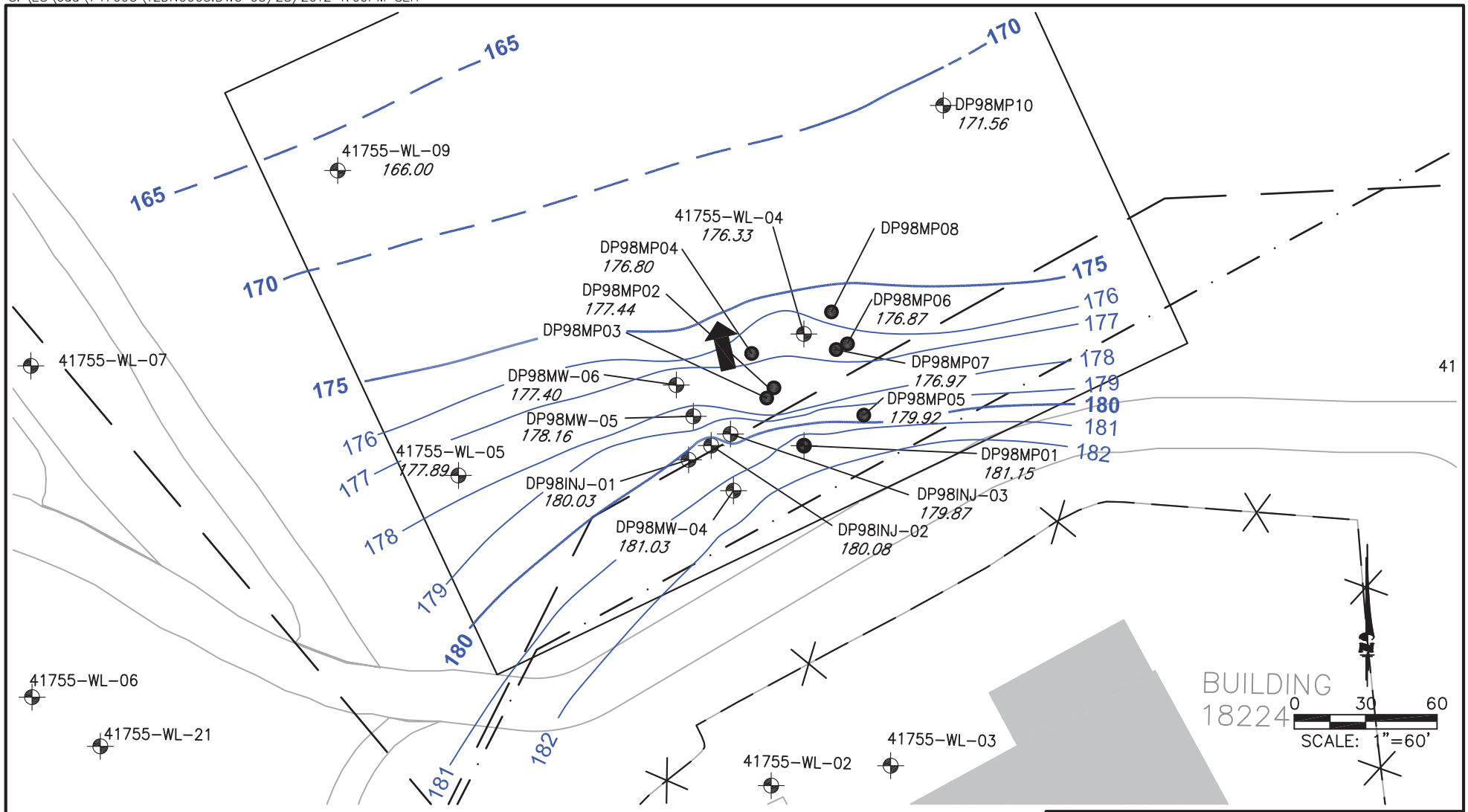

LEGEND

- Well ID — MONITORING WELL
- MONITORING POINT
- SECURITY FENCE
- SANITARY SEWER
- ELECTRICAL (BELOW GROUND)
- INFERRED GROUNDWATER FLOW DIRECTION
- POTENTIOMETRIC SURFACE ELEVATION CONTOUR (DASHED WHERE INFERRED)
- *178.16* POTENTIOMETRIC SURFACE ELEVATION

NOTES:
1. UTILITY LOCATIONS ARE APPROXIMATE.
2. DP98MP03 AND DP98MP08 WERE NOT USED TO DEVELOP GROUNDWATER CONTOURS DUE TO INCONSISTENCY IN DEPTH TO WATER MEASUREMENTS OVER TIME.

FIGURE 3.1

GROUNDWATER POTENTIOMETRIC SURFACE SEPTEMBER 2011

DP98, JBER, Alaska

PARSONS

Denver, Colorado

Table 3.2 Groundwater Biogeochemical Data

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Location	Sampling Location	Sample Date	Temp (°C) [a/]	pH (su) [b/]	Conductivity (µS/cm) [c/]	Dissolved Oxygen (mg/L) [d/]	Redox Potential (mV) [e/]	Dissolved Organic Carbon (mg/L)	Manganese (mg/L)	Ferrous Iron (mg/L)	Hydrogen Sulfide (mg/L)	Carbon Dioxide (mg/L)	Alkalinity (mg/L)	Dissolved Hydrogen (nmol/L) [f/]	Methane (µg/L) [g/]	Ethene (µg/L)	Ethane (µg/L)	Acetylene (µg/L)
Test Cell No. 1 (EHC[h/])																		
DP98MP01	Upgradient	20-May-10	7.4	6.94	1,029	0.55	-291	2.20	4.9	2.1	0.01	85	360	NA [i/]	1,700	0.410	0.500	0.071 F [j/]
		22-Sep-10	7.6	8.71	1,026	0.38	-130	8.90	4.3	1.9	<0.01 [k/]	180	395	12.0	780	0.057	0.055	<0.046
		17-May-11	7.0	6.76	966	0.75	-98	3.33 J [l/]	5.5	4.9	0.01	190	345	NA	1,500	0.180	0.180	<0.044
		13-Sep-11	7.7	6.99	736	0.09	-39	4.52	5.3	2.6	0.01	140	750	NA	1,900	0.130	0.067	<0.044
DP98MP02	Treatment Zone	21-May-10	8.7	7.31	922	4.99	-111	3.20	6.4	<0.1	<0.01	210	360	NA	1,000	3.10	3.20	0.160 F
		22-Sep-10	7.3	8.73	2,100	0.32	-156	532	24	>66	0.09	100 (Int) [m/]	860	18.0	2,400	4.60	4.10	<0.046
		17-May-11	7.2	6.70	1,174	0.98	-157	236 J	15	11.8	0.05	220 (Int)	625	NA	17,000	14.0	1.20	<0.044
		13-Sep-11	8.5	6.75	1,536	0.20	-71	222	9.0	54.8	0.09	410 (Int)	1,060	NA	21,000	120	5.500	<0.044
DP98MP03	Treatment Zone	21-May-10	8.6	6.82	947	3.07	-174	6.60	8.8	0.8	<0.01	250	440	NA	1,000	8.30	11.0	0.120 F
		22-Sep-10	8.4	8.95	2,822	0.32	-177	1,560	72	>66	0.13	Int	1,135	NA	4,000	23.0	19.0	1.40
		17-May-11	7.4	6.88	2,633	0.70	-130	656 J	38	21.8	0.23	300 (Int)	1,230	NA	11,000	15.0	4.50	<0.044
		13-Sep-11	8.7	7.03	2,144	0.11	-149	274	23	61.2	0.03	270 (Int)	1,230	NA	11,000	78.0	6.90	<0.044
DP98MP04	Downgradient	21-May-10	7.8	6.63	1,145	0.39	-132	11.3	24	1.8	<0.01	480	740	NA	10,000	12.0	0.880	0.160 F
		21-Sep-10	7.5	9.46	1,237	0.37	-122	86.6	30	33	0.01	350 (Int)	715	14	3,900	6.20	0.150	<0.046
		18-May-11	7.2	6.97	1,280	2.05	-49	14.0	23	12	<0.01	180 (Int)	675	NA	7,800	12.0	0.500	<0.044
		15-Sep-11	7.2	6.65	1,259	0.33	-67	12.6	16	24	0.02	240 (Int)	645	NA	9,600	19.0	0.600	<0.044
Test Cell No. 2 (EVO[n/], Calcium Sulfate, Hematite)																		
DP98MP05	Upgradient	23-May-10	8.9	7.11	1,226	0.90	-328	2.20	2.4	<0.1	0.04	170	320	NA	1,100	1.70	3.40	<0.044
		22-Sep-10	8.2	8.92	1,209	0.58	-131	2.60	0.8	0.40	<0.01	132	450	3,200	550	0.540	0.540	<0.046
		18-May-11	7.5	6.93	1,206	0.85	-84	3.13	2.0	0.05	0.01	190	465	NA	1,200	2.20	1.70	<0.044
		15-Sep-11	7.2	7.02	1,225	0.52	-10	3.28	1.1	0.19	0.03	164	435	NA	2,000	0.780	0.880	<0.044
DP98MP06	Treatment Zone	23-May-10	7.3	6.75	1,043	1.03	-319	4.00	9.1	1.9	0.08	290	320	NA	2,200	5.800	4.700	0.660
		23-Sep-10	7.3	9.11	2,679	0.24	-148	70.6	7.8	33	0.01	240	470	NA	1,200	1.100	1.300	<0.044
		18-May-11	7.3	7.70	1,861	0.66	-288	43.6	8.0	8.3	>8.0	360 (Int)	1,190	NA	1,300	0.830	0.790	<0.044
		14-Sep-11	7.6	6.89	2,082	0.14	-156	109	14.0	12.9	0.11	308 (Int)	1,055	NA	12,000	0.410	0.190	<0.044
DP98MP07	Treatment Zone	23-May-10	6.8	6.75	1,027	0.46	-303	24.0	8.1	1.2	0.12	270	340	NA	960	2.400	2.900	0.150 F
		22-Sep-10	8.6	8.96	3,009	0.15	-163	164	7.0	1.9	0.03	98	245	2.80	220	0.140	0.160	<0.046
		18-May-11	8.4	7.28	3,448	1.20	-215	361	5.0	3.2	0.15	280 (Int)	690	NA	310	3.000	1.700	<0.044
		14-Sep-11	7.9	7.45	3,066	0.43	-301	7.86	3.5	0.1	2.45	304	1,095	NA	2,200	0.640	0.360	<0.044
DP98MP08	Downgradient	23-May-10	8.9	7.63	975	8.01	-102	9.60	4.5	<0.1	0.02	160	296	NA	270	6.100	4.300	0.110 F
		23-Sep-10	5.8	9.87	989	0.47	-150	22.1	4.9	2.5	<0.01	180	340	NA	850	22.000	13.000	0.380 F
		18-May-11	8.4	7.75	1,043	1.18	-195	7.33	3.7	0.1	0.01	104	425	NA	5,600	1.100	0.920	<0.044
		15-Sep-11	7.4	7.37	1,096	0.52	-170	3.30	2.7	0.3	0.01	150	390	NA	640	0.840	0.670	<0.044

Table 3.2 Groundwater Biogeochemical Data

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Location	Sampling Location	Sample Date	Temp (°C) [a/]	pH (su) [b/]	Conductivity (µS/cm) [c/]	Dissolved Oxygen (mg/L) [d/]	Redox Potential (mV) [e/]	Dissolved Organic Carbon (mg/L)	Manganese (mg/L)	Ferrous Iron (mg/L)	Hydrogen Sulfide (mg/L)	Carbon Dioxide (mg/L)	Alkalinity (mg/L)	Dissolved Hydrogen (nmol/L) [f/]	Methane (µg/L) [g/]	Ethene (µg/L)	Ethane (µg/L)	Acetylene (µg/L)
Test Cell No. 3 (EVO and Ferrous Sulfate)																		
DP98MW-04	Upgradient	24-May-10	7.6	6.70	781	0.70	-90	2.20	6.0	3.2	0.02	270	356	NA	440	0.520	0.290	<0.044
		21-Sep-10	7.1	9.59	667	0.30	-95	4.80	5.9	1.5	0.07	236	410	1.40	190	0.150	0.091	<0.046
		17-May-11	6.3	6.50	736	1.13	-77	3.57 J	9.0	7.8	0.05	184	245	NA	330	0.200	0.085	<0.044
		12-Sep-11	8.0	6.39	809	0.23	26	4.21	5.9	2.8	0.08	168	705	NA	510	0.290	0.150	0.087 F
DP98INJ-01	Treatment Zone	25-May-10	8.2	6.81	1,067	2.02	-77	13.5	13.3	NA	0.02	380	460	NA	23,000	5.400	0.130	0.046 F
		21-Sep-10	7.3	10.85	4,836	0.22	-257	NA	>44	>132	0.04	122 (Int)	1,010	NA	NA	NA	NA	NA
		16-May-11	7.4	6.58	2,895	1.20	-85	NA	26	14.0	0.11	300 (Int)	1,300	NA	NA	NA	NA	NA
		13-Sep-11	8.1	6.55	3,683	0.19	-83	NA	25	>66	0.10	242 (Int)	1,895	NA	NA	NA	NA	NA
DP98INJ-02	Treatment Zone	24-May-10	9.2	6.54	1,137	0.72	-52	105 M [o/]	18.8	2.2	0.04	414	480	NA	19,000	0.470	0.054	0.048 F
		21-Sep-10	8.0	10.80	5,201	1.10	-404	802	>44	>66	<0.01	240 (Int)	530	11,000	6,700	5.100	0.350	<0.046
		17-May-11	7.2	6.96	3,357	0.82	-125	919 J	5.0	25.0	0.05	Int	1,575	NA	12,000	7.100	3.900	<0.044
		13-Sep-11	8.3	6.76	3,023	0.05	-129	38.5	3.5	>66	0.03	Int	1,445	NA	6,300	4.600	1.800	<0.044
DP98INJ-03	Treatment Zone	25-May-10	7.3	6.80	1,202	0.93	-90	33.4	16.8	>3.3	0.02	420	550	NA	21,000	1.200	0.200	0.170 F
		21-Sep-10	7.9	10.14	3,226	2.00	-181	NA	10.2	>66	0.01	120 (Int)	1,115	NA	NA	NA	NA	NA
		16-May-11	8.3	6.69	2,757	0.78	-241	NA	8.0	65.0	0.12	280 (Int)	1,300	NA	NA	NA	NA	NA
		13-Sep-11	8.0	6.72	3,256	0.13	-106	NA	4.0	>66	0.07	208 (Int)	1,490	NA	NA	NA	NA	NA
DP98MW-05	Downgradient	24-May-10	9.1	6.73	1,142	1.31	-19	8.60	21	4.5	<0.01	420	660	NA	7,500	0.860	0.140	<0.044
		20-Sep-10	8.0	7.02	1,524	0.46	-146	17.4	22	4.4	0.01	248	540	1.10	6,500	0.620	0.019	<0.046
		16-May-11	8.0	6.74	1,410	0.66	-119	10.9	27	14	<0.01	490 (Int)	680	NA	8,300	0.970	0.062	<0.044
		12-Sep-11	8.2	6.71	1,339	0.16	-17	13.4	28	2.3	0.01	350 (Int)	1,020	NA	6,300	0.790	0.080	0.070 F
DP98MW-06	Downgradient	24-May-10	8.7	6.49	1,052	1.54	-42	13.6	20	41	<0.01	600	630	NA	13,000	1.100	0.098	<0.044
		20-Sep-10	7.6	6.18	1,429	0.45	-89	33.7	25	25	<0.01	480	705	1.10	4,800	1.300	0.008 F	<0.046
		16-May-11	8.4	6.57	1,049	1.10	-173	15.2	26	2.9	0.02	440 (Int)	490	NA	7,900	1.500	0.320	0.090 F
		12-Sep-11	7.9	6.39	1,124	0.20	-26	27.0	25	2.6	0.02	280 (Int)	1,015	NA	8,200	1.200	0.045	0.110 F
Other Wells and Points																		
DP98MP10	Downgradient	24-May-10	4.7	7.28	770	7.62	-172	NA	3.9	0.08	0.05	150	344	NA	NA	NA	NA	NA
		23-Sep-10	6.8	9.31	811	2.80	-120	NA	6.7	1.9	<0.01	150	370	NA	NA	NA	NA	NA
		18-May-11	5.5	6.74	900	2.64	-135	NA	7.5	0.81	0.01	170	490	NA	NA	NA	NA	NA
		15-Sep-11	5.8	6.92	892	2.08	28	NA	6.8	0.37	<0.01	172	655	NA	NA	NA	NA	NA
41755-WL04	Downgradient	20-May-10	6.8	6.85	1,000	0.39	-57	NA	6.8	2.9	0.05	275	210	NA	NA	NA	NA	NA
		20-Sep-10	7.5	7.10	1,333	0.81	-157	NA	9.8	6.5	<0.01	196	305	NA	NA	NA	NA	NA
		16-May-11	7.2	6.81	1,556	1.19	-187	NA	12.9	3.0	0.07	380 (Int)	745	NA	NA	NA	NA	NA
		12-Sep-11	7.3	6.94	1,335	0.16	-49	NA	5.5	9.2	0.14	190	940	NA	NA	NA	NA	NA
41755-WL08	Downgradient	23-Sep-10	8.6	9.04	549	0.91	-99	NA	1.0	0.10	0.01	86	225	NA	NA	NA	NA	NA
		19-May-11	3.9	5.66	521	1.58	-259	NA	<0.1	<0.1	0.02	240	NA	NA	NA	NA	NA	NA
		14-Sep-11	7.3	6.46	539	0.90	13	NA	<0.1	0.10	0.03	148	225	NA	NA	NA	NA	NA
41755-WL09	Downgradient	23-Sep-10	6.6	9.74	596	0.53	-137	NA	0.60	0.20	<0.01	84	220	NA	NA	NA	NA	NA
		19-May-11	3.7	5.85	676	1.28	-188	NA	0.80	0.01	0.02	140	NA	NA	NA	NA	NA	NA
		14-Sep-11	6.5	7.29	677	0.17	-74	NA	0.60	0.15	0.02	150	320	NA	NA	NA	NA	NA

Table 3.2 Groundwater Biogeochemical Data

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Location	Sampling Location	Sample Date	Temp (°C) [a/]	pH (su) [b/]	Conductivity (µS/cm) [c/]	Dissolved Oxygen (mg/L) [d/]	Redox Potential (mV) [e/]	Dissolved Organic Carbon (mg/L)	Manganese (mg/L)	Ferrous Iron (mg/L)	Hydrogen Sulfide (mg/L)	Carbon Dioxide (mg/L)	Alkalinity (mg/L)	Dissolved Hydrogen (nmol/L) [f/]	Methane (µg/L) [g/]	Ethene (µg/L)	Ethane (µg/L)	Acetylene (µg/L)
Quality Assurance/Quality Control Samples																		
DP98MP02 (dup)		21-May-10	NA	NA	NA	NA	NA	NA	6.90	<0.1	<0.01	220	380	NA	NA	NA	NA	NA
DP98MP24 (dup)		21-May-10	NA	NA	NA	NA	NA	12.1	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98INJ-22 (dup)		21-Sep-10	NA	NA	NA	NA	NA	898	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98MP10-FD		23-Sep-10	NA	NA	NA	NA	NA	NA	6.7	1.9	<0.01	152	360	NA	NA	NA	NA	NA
DP98MP08-FD		23-Sep-10	NA	NA	NA	NA	NA	NA	4.7	2.5	<0.01	178	330	NA	NA	NA	NA	NA
DP98MW04-FD		17-May-11	NA	NA	NA	NA	NA	2.55 J	8.0	7.7	0.05	190	255	NA	NA	NA	NA	NA
DP98MW-14 (dup)		12-Sep-11	NA	NA	NA	NA	NA	4.54	6.0	2.7	0.08	162	710	NA	460	0.28	0.14	0.058 F
DP98MP-11 (dup)		13-Sep-11	NA	NA	NA	NA	NA	3.89	NA	NA	NA	NA	NA	NA	2,100	0.11	0.07	<0.044

[a/] °C = degrees Centigrade.

[b/] su = standard pH units.

[c/] µS/cm = microsiemens per centimeter.

[d/] mg/L = milligrams per liter.

[e/] mV = millivolts.

[f/] nmol/L = nanomoles per liter.

[g/] µg/L = micrograms per liter.

[h/] EHC = controlled release, integrated carbon and zero valent ion source that reduces redox potential.

[i/] NA = not analyzed.

[j/] F-flag indicates the concentration is below the laboratory reporting limit but above the method detection limit (MDL), and the concentration is estimated.

[k/] "<" indicates the concentration is below the indicated laboratory MDL.

[l/] J-flag indicates the analyte was positively identified, but the quantitation is an estimation due to discrepancies in meeting certain analyte-specific quality control criteria.

[m/] Int = Interference due to precipitation or color change; result either could not be reported or is estimated at the indicated concentration.

[n/] EVO = emulsified vegetable oil.

[o/] M-flag indicates recovery/Relative Percent Difference (RPD) poor for matrix spike/matrix spike duplicate (MS/MSD) or for primary/field duplicate sample pair.

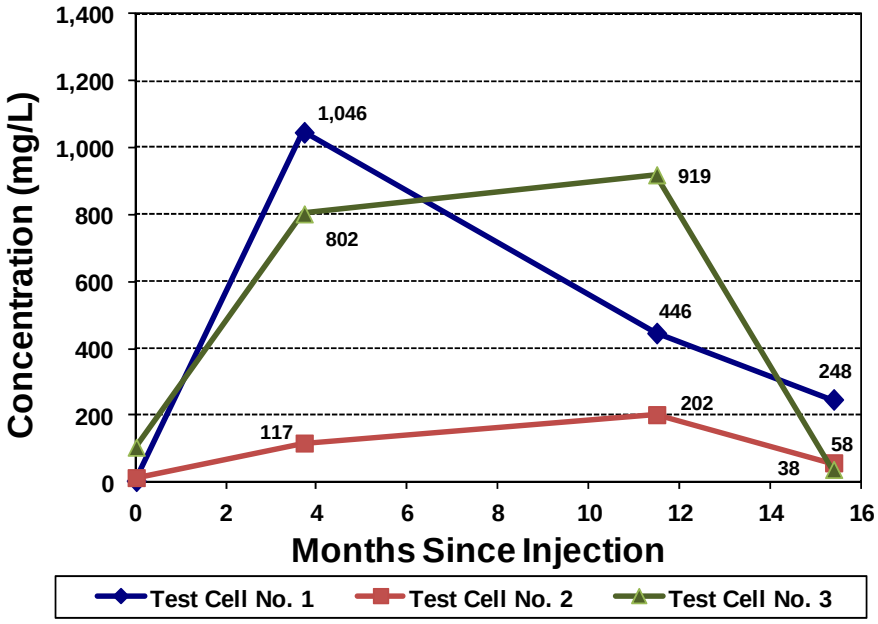

Figure 3.2 Average Concentrations of DOC over Time within the Test Cells

3.2.2 Volatile Fatty Acids

VFAs are degradation products of more complex substrates (e.g., carbohydrates or vegetable oils), and therefore are indicators of the distribution and degradation of organic amendments. Fermentation of VFAs also produces molecular hydrogen for biotic dechlorination processes. Groundwater samples for analysis of VFAs were collected in September 2010 (approximately 3.5 months after injection), and the results are listed in **Table 3.3**.

Acetic, butyric, and propionic acids were detected in several samples. Acetic acid was the primary VFA produced from degradation of the organic amendments injected into the test cells. The maximum concentration of acetic acid was 1,241 mg/L at location DP98MP03 in Test Cell No. 1. Similarly, the maximum concentrations of butyric and propionic acids were also detected in groundwater from location DP98MP03, at estimated concentrations (F-flag) of 769 F mg/L and 512 F mg/L, respectively.

Acetic, butyric, and propionic acids were also detected at well DP98INJ-02 in Test Cell No. 3, with acetic acid at 706 mg/L. Lesser concentrations of acetic and propionic acids were detected in Test Cell No. 2, with a maximum concentration of acetic acid of 133 mg/L at location DP98MP06. These results correlate to the relative concentrations of DOC measured in September 2010, where the highest concentrations of DOC and were measured at Test Cell No. 1 and the lowest concentrations of DOC were measured at Test Cell No. 2.

3.2.3 Dissolved Oxygen

Comparison of pre- and post-injection DO concentrations measured in the field using a direct-reading meter indicate that the organic amendments generally caused concentrations of DO within and downgradient of the test cells to decrease (**Table 3.2**). Concentrations of DO within the test cells prior to the injections ranged from 0.46 to 4.99 mg/L, with the highest concentrations of DO in Test Cell No. 1.

Table 3.3 Volatile Fatty Acids in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Location	Sample Date	Total VFAs (mg/L)[a/]	Volatile Fatty Acids (VFAs)				
			Acetic (mg/L)	Butyric (mg/L)	Hydroxypropanoic (mg/L)	Ketopropionic (mg/L)	Propionic (mg/L)
Test Cell No. 1 (EHC)							
DP98MP01	22-Sep-10	<0.1 [b/]	<0.1	<0.1	<0.1	<0.1	<0.1
DP98MP02	22-Sep-10	**838** [c/]	**447**	**223 F** [d/]	<25	<25	**168 F**
DP98MP03	22-Sep-10	**2,520**	**1,241**	**769 F**	<100	<100	**512 F**
DP98MP04	21-Sep-10	**129**	**90.3**	**23.3 F**	<5	<5	**15.7 F**
Test Cell No. 2 (EVO, Calcium Sulfate, Hematite)							
DP98MP05	22-Sep-10	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
DP98MP06	23-Sep-10	**103**	**103**	<2.5	<2.5	<2.5	<2.5
DP98MP07	22-Sep-10	**167**	**133**	<2.5	<2.5	<2.5	**33.8**
DP98MP08	23-Sep-10	**6.65**	**6.65**	<0.5	<0.5	<0.5	<0.5
Test Cell No. 3 (EVO and Ferrous Sulfate)							
DP98MW-04	21-Sep-10	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DP98INJ-02	21-Sep-10	**1,080**	**706**	**63.6 F**	<20	<20	**308**
DP98MW-05	20-Sep-10	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
DP98MW-06	20-Sep-10	**0.800 F**	<0.2	**0.800 F**	<0.2	<0.2	<0.2

[a/] mg/L = milligrams per liter.

[b/] "<" indicates the concentration is below the indicated laboratory method detection limit (MDL).

[c/] **BOLD** text indicates detected results.

[d/] F-flag indicates the concentration is below the laboratory reporting limit but above the MDL, and the concentration is estimated.

Accurate DO measurements were difficult to obtain at many locations due to low recharge rates and excessive drawdown during purging. However, 17 of 21 DO concentrations measured within the test cells during the three post-injection performance monitoring events were less than 1.0 mg/L. In some instances, concentrations of DO were higher during the May 2011 sampling event when groundwater temperatures were lower, suggesting that higher oxygen solubility and slower rates of microbial respiration at the colder temperatures may have been causative factors.

3.2.4 Oxidation-Reduction Potential

ORP measurements (relative to a silver/silver chloride reference electrode) indicate that groundwater within the test cells was already reducing prior to the injections, ranging from -19 mV at location DP98MW-05 in Test Cell No. 3 to -328 mV at location DP98MP05 in Test Cell No. 2. ORP decreased after the injections at many locations, but not all. For example, for well DP98MP02 in Test Cell No. 1, ORP decreased from -111 mV in May 2010 to -156 to -157 mV in September 2010 and May 2011. In Test Cell No. 3 well DP98MP03, ORP initially remained relatively stable (changing from -174 to -177 mV) before becoming less reducing (-130 mV in May 2011). Eighteen of 21 ORP values measured within the test cells during the performance monitoring period (September 2010 to September 2011) were representative of moderately to highly reducing conditions (i.e., -100 to -300 mV). The other three measurements were still representative of reducing conditions (-71 to -85 mV).

3.2.5 pH

Prior to the injections, pH in the test cell wells ranged from 6.5 to 7.6 standard pH units. pH was generally lower in Test Cell No. 3, the location of the former bioremediation pilot test. After the May 2010 injection, pH increased in all of the test cells, and frequently was higher than 8.0 in September 2010 due to the change in groundwater chemistry. However, the change in groundwater chemistry and the presence of organic amendments also tended to foul the pH probe and the accuracy of the measurements is questionable. In general however, pH increased after the injection, which is beneficial in that FeS minerals are more stable at a pH above 7.

During the May and September 2011 sampling events, pH values were more stable and ranged from 6.7 to 7.0 in Test Cell No. 1 (DP98MP02 and DP98MP03), 6.9 to 7.7 in Test Cell No. 2 (DP98MP06 and DP98MP07), and 6.6 to 7.0 in Test Cell No. 3 (DP98INJ-01 through DP98INJ-03). These relatively neutral pH values are within an optimal range for dechlorinating organisms (pH of 6 to 8), and are also conducive to biogeochemical transformation processes.

3.2.6 Carbon Dioxide and Alkalinity

There is a positive correlation between zones of microbial activity and increased alkalinity. Increases in alkalinity are caused by the dissolution of alkaline minerals (e.g., carbonates) resulting from the production of carbon dioxide by microbial metabolism (USEPA, 1998). Concentrations of carbon dioxide within the test cells generally exhibited moderate increases after the injections, but the increases were not consistent; in some cases concentrations of carbon dioxide decreased. However, the field measurements for carbon dioxide had a high degree of interference from other groundwater constituents and the accuracy of the measurement results are suspect.

Concentrations of alkalinity showed a clearer and more consistent increasing trend. For example, concentrations of alkalinity in Test Cell No. 1 increased from 440 mg/L at location DP98MP03 prior to injection to 1,135 in September 2010 and 1,230 mg/L in May and September 2011. A similar increase was observed for location DP98MP02 in Test Cell No. 1, and for monitoring locations in Test Cells No. 2 and No. 3 (**Table 3.2**). The alkalinity data provide a clear indication that microbial activity was enhanced by the injection of organic amendments.

3.2.7 Anions and Cations

Suites of anions and cations were analyzed during the May and September 2010 monitoring events (**Table 3.4**). Chloride was the primary anion detected in groundwater, followed by sulfate. Concentrations of chloride in May 2010 ranged up to 176 mg/L at location DP98MP05, and concentrations of sulfate in May 2010 ranged up to 8.5 mg/L at location DP98MP02. Concentrations of nitrate, nitrite, fluoride, phosphate and sulfide were typically either non-detect or of low magnitude (i.e., not exceeding 1.5 mg/L).

Both biotic and abiotic reduction of CAHs release chloride ions into groundwater. An increase in chloride concentrations may be an indication that one or both of these processes is occurring, especially if the increase is substantial relative to background or baseline concentrations. However, given that concentrations of CAHs are typically measured in micrograms per liter and concentrations of chloride are typically measured in milligrams per liter (orders of magnitude higher), it may be difficult to distinguish the impact of CAH reduction from natural temporal and spatial variations in chloride concentrations. Nonetheless, a sustained increase in chloride concentrations over time within a test cell reaction zone can indicate that dechlorination of CAHs is occurring.

Concentrations of chloride within Test Cell No. 1 did not increase at location DP98MP02, but did increase at DP98MP03 from 63.3 mg/L in May 2011 to as high as 114 mg/L in May 2011. Concentrations of chloride in Test Cell No. 2 increased slightly at DP98MP06, from 107 mg/L in May 2010 to 122 mg/L in September 2011. Concentrations at DP98MP07 showed a greater increase, from 110 mg/L in May 2010 to 204 mg/L in September 2011. An overall increase in concentrations of chloride in Test Cell No. 3 was not observed.

These data suggest that chloride may not be a suitable indicator of dechlorination of CAHs at DP98, primarily because native chloride concentrations are typically greater than 50 mg/L and may vary over time by 10 mg/L or more (see data for upgradient wells DP98MP01 and DP98MP05), while total CAH concentrations are typically less than 10 mg/L. Thus, the magnitude and natural variation in native chloride concentrations masks the effect of dechlorination processes.

The primary cation in groundwater was calcium, followed by magnesium and sodium. Concentrations of calcium ranged up to 188 mg/L at location DP98MW-05 in May 2011. Following the injections, concentrations of total dissolved iron increased substantially due to the stimulation of biotic iron reduction, as well as the addition of iron in Test Cell No. 1 in the form of ZVI, in Test Cell No. 2 in the form of hematite, and in Test Cell No. 3 in the form of ferrous sulfate. Concentrations of iron in groundwater increased to as high as 328 mg/L in Test Cell No.1 at location DP98MP03 in September 2010, and as high as 600 mg/L in Test Cell No. 2 at location DP09INJ-02 in September 2010. Concentrations of iron in Test Cell No. 2 did not increase above 8 mg/L, possibly due to slow reduction of the iron hematite that was injected. In general, concentrations of total iron measured in the laboratory correlated to field measurements of ferrous iron (**Table 3.2**).

Concentrations of the other cations in the test cells also increased at most locations after injection, indicating that the injection of amendments and the stimulation of biological activity increased total dissolved solids in groundwater. Increases in the concentrations of manganese are attributed to stimulation of manganese reduction.

Table 3.4 Cations and Anions in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

		Cations						Anions						
Sample Location	Sample Date	Calcium (mg/L)[a/]	Iron (mg/L)	Magnesium (mg/L)	Manganese (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Flouride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)
Test Cell No. 1 (EHC)														
DP98MP01	20-May-10	136	2.20	33.0	4.30 J[b/]	1.50	17.5	124.0	<0.08[c/]	1.5	<0.01	<0.215	7.40	<0.60
	22-Sep-10	158	2.48	35.8	4.50	1.51	19.7	140.0	<0.10	<0.03	<0.04	<0.130	1.02	<0.60
	17-May-11	NA[d/]	NA	NA	NA	NA	NA	89.0	NA	NA	NA	NA	<2.60	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	138.3	NA	NA	NA	NA	<0.260	<0.60 J
DP98MP02	21-May-10	129	<0.01	31.7	6.50 J	4.30	17.1	85.5	<0.08	1.30	0.92 F[e/]	<0.215	8.50	<0.60
	22-Sep-10	299	171	62.1	41.5	9.80	28.6	67.4	<0.10	<0.030 J	<0.040 J	1.16 J	24.9	<0.60
	17-May-11	NA	NA	NA	NA	NA	NA	64.4	NA	NA	NA	NA	<2.60	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	81.7	NA	NA	NA	NA	<0.260	<0.60 J
DP98MP03	21-May-10	132	2.10	33.5	6.60 J	2.80	21.5	63.3	0.230 F	<0.004	<0.010	<0.215	4.30	<0.60
	22-Sep-10	410	328	85.9	67.4	19.8	55.2	111	<0.50	<0.150	<0.20	<0.650	9.98	3.09
	17-May-11	NA	NA	NA	NA	NA	NA	114	NA	NA	NA	NA	13.4	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	88.8	NA	NA	NA	NA	<0.260	2.99 J
DP98MP04	21-May-10	153	26.6	42.0	23.3 J	2.20	32.3	44.0	<0.08	0.870 F	<0.01	<0.215	4.80	<0.60
	21-Sep-10	200	45.7	52.9	37.0	2.38	40.6	45.3 J	<0.10	<0.030	<0.04	0.630 F	16.5	<0.60 J
	18-May-11	NA	NA	NA	NA	NA	NA	53.4	NA	NA	NA	NA	22.0	NA
	15-Sep-11	NA	NA	NA	NA	NA	NA	64.4	NA	NA	NA	NA	18.0	<0.60
Test Cell No. 2 (EVO, Calcium Sulfate, Hematite)														
DP98MP05	23-May-10	180	1.27	41.4	1.50	3.60	28.0	176	<0.08	<0.004	<0.01	<0.215	1.70	<0.60
	22-Sep-10	197	0.54	42.5	0.812	2.09	26.7	189	0.140 F	<0.030	<0.04	<0.130	2.03	1.35
	18-May-11	NA	NA	NA	NA	NA	NA	159	NA	NA	NA	NA	<1.30	NA
	15-Sep-11	NA	NA	NA	NA	NA	NA	159	NA	NA	NA	NA	4.92 F	1.99
DP98MP06	23-May-10	160	2.20	38.6	9.00	1.80	13.8	107	<0.08	<0.004	<0.01	<0.215	1.50	0.78 F
	23-Sep-10	444 M[f/]	7.97 M	238 M	16.0 M	2.07	17.4	109 M	<0.20 M	3.46 M	<0.08 M	<0.260	1,260 M	<0.60
	18-May-11	NA	NA	NA	NA	NA	NA	106	NA	NA	NA	NA	38.0	NA
	14-Sep-11	NA	NA	NA	NA	NA	NA	122	NA	NA	NA	NA	15.4	1.78
DP98MP07	23-May-10	159	5.10	36.2	7.30	2.00	18.6	110	<0.08	0.85 F	<0.01	<0.215	4.30	<0.60
	22-Sep-10	824	2.38	212	8.25	2.03	25.0	138	<0.20	<0.06	<0.08	<0.260	2,530	<0.60
	18-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	14-Sep-11	NA	NA	NA	NA	NA	NA	204	NA	NA	NA	NA	895	8.80
DP98MP08	23-May-10	138	0.210	33.9	3.10	7.60	28.1	NA	NA	NA	NA	NA	NA	0.780 F
	23-Sep-10	147	3.34	33.2	4.18	3.79	16.2	136	0.270 F	<0.03	<0.04	<0.130	3.99	<0.60
	18-May-11	NA	NA	NA	NA	NA	NA	131	NA	NA	NA	NA	19.3	NA
	15-Sep-11	NA	NA	NA	NA	NA	NA	138	NA	NA	NA	NA	62.8	1.48

Table 3.4 Cations and Anions in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

		Cations						Anions						
Sample Location	Sample Date	Calcium (mg/L)[a/]	Iron (mg/L)	Magnesium (mg/L)	Manganese (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Flouride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)
Test Cell No. 3 (EVO and Ferrous Sulfate)														
DP98MW-04	24-May-10	121	9.20	26.3	5.80	1.30	11.6	63.5	<0.08	<0.004	<0.01	<0.215	3.40	<0.60
	21-Sep-10	119	8.20	27.0	5.89	1.38	10.6	62.4 J	0.260 F	0.930 F	<0.04	<0.130	5.55	<0.60 J
	17-May-11	NA	NA	NA	NA	NA	NA	58.6	NA	NA	NA	NA	4.82	NA
	12-Sep-11	NA	NA	NA	NA	NA	NA	69.3	NA	NA	NA	NA	3.28	<0.60
DP98INJ-01	25-May-10	158	27.6 J	36.1	13.5	1.40	17.7	64.7	<0.080	<0.004	<0.010	<0.215	0.810 F	<0.60
	21-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	16-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98INJ-02	24-May-10	172 M	31.3 J	36.6	18.5 M	1.50	19.7	69.8	<0.080 M	<0.004	0.77 F	<0.215	1.10	<0.60
	21-Sep-10	242	600	1,210	28.8	2.33	120	47.0 J	<0.20	<0.06	<0.08	<0.26	1,160	5.30 J
	17-May-11	NA	NA	NA	NA	NA	NA	77.4	NA	NA	NA	NA	262	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	63.5	NA	NA	NA	NA	27.6	22.4 J
DP98INJ-03	25-May-10	168	31.8 J	41.2	12.1	1.40	25.7	58.4	<0.080	1.20	<0.010	<0.215	1.50	<0.60
	21-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	16-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	13-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98MW-05	24-May-10	188	7.30 J	45.9	20.5	1.60	35.0	64.3	<0.080	<0.004	<0.010	<0.215	3.10	<0.60
	20-Sep-10	270	21.7	59.2	31.3	1.69	48.5	64.0	0.32 F	<0.03	<0.04	<0.130	32.7	<0.60
	16-May-11	NA	NA	NA	NA	NA	NA	54.0	NA	NA	NA	NA	101	NA
	12-Sep-11	NA	NA	NA	NA	NA	NA	60.6	NA	NA	NA	NA	77.1	<0.60
DP98MW-06	24-May-10	125	38.7 J	37.9	26.8	1.00	24.3	54.1	<0.080	<0.004	<0.010	<0.215	0.870 F	0.860 F
	20-Sep-10	219	61.2	54.4	40.2	1.29	33.9	53.0	0.370 F	0.820 F	<0.04	<0.130	26.9	<0.60
	16-May-11	NA	NA	NA	NA	NA	NA	48.5	NA	NA	NA	NA	23.0	NA
	12-Sep-11	NA	NA	NA	NA	NA	NA	46.4	NA	NA	NA	NA	12.7	<0.60

Table 3.4 Cations and Anions in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

		Cations						Anions						
Sample Location	Sample Date	Calcium (mg/L)[a/]	Iron (mg/L)	Magnesium (mg/L)	Manganese (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Chloride (mg/L)	Flouride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Phosphate (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)
Other Wells and Points														
DP98MP10	24-May-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	23-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	18-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	15-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
41755-WL04	20-May-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	20-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	16-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	12-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
41755-WL08	23-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	19-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	14-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
41755-WL09	23-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	19-May-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	14-Sep-11	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Quality Assurance/Quality Control Samples														
DP98MP02 (dup)	21-May-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98MP24 (dup)	21-May-10	155	27.0	42.0	22.5 J	2.3	30.8	43.9	<0.08	0.89 F	<0.01	<0.215	4.3	<0.6
DP98INJ-22 (dup)	21-Sep-10	244	590	1,160	27.9	2.3	120	34.8 J	<0.1	<0.03	<0.04	<0.13	1,150	6.95 J
DP98MP10-FD	23-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98MP08-FD	23-Sep-10	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
DP98MW04-FD	17-May-11	NA	NA	NA	NA	NA	NA	59	NA	NA	NA	NA	4.3	NA
DP98MW-14 (dup)	12-Sep-11	NA	NA	NA	NA	NA	NA	70	NA	NA	NA	NA	3.4	<0.6
DP98MP-11 (dup)	13-Sep-11	NA	NA	NA	NA	NA	NA	144	NA	NA	NA	NA	<0.26	2.27 J

[a/] mg/L = milligram(s) per liter.

[b/] J-flag indicates the analyte was positively identified, but the quantitation is an estimation due to discrepancies in meeting certain analyte-specific quality control criteria.

[c/] "<" indicates the concentration is below the indicated laboratory method detection limit (MDL).

[d/] NA = not analyzed.

[e/] F-flag indicates the concentration is below the laboratory reporting limit but above the MDL, and the concentration is estimated.

[f/] M-flag indicates the recovery/Relative Percent Difference (RPD) was poor for Matrix Spike/Matrix Spike Duplicate (MS/MSD) or primary/field duplicate sample pair.

3.2.8 Ferrous Iron, Sulfate, and Sulfide

Concentrations of ferrous iron, sulfate, and sulfide are of interest because one of the primary objectives of the injections into Test Cell No. 2 and Test Cell No. 3 was to cause sulfate to be reduced to sulfide, which would in turn combine with ferric or ferrous iron and precipitate as reactive iron-sulfide minerals. The rate at which sulfate is consumed by reduction to sulfide is also an important parameter in considering the potential for production of reactive iron sulfide minerals (Lebron *et al*., 2010). The following paragraphs summarize changes in concentrations of ferrous iron, sulfate, and sulfide within the three test cells.

Test Cell No. 1: The EHC® product injected into Test Cell No. 1 is composed of organic carbon (thought to be primarily cellulose) and ZVI. These constituents were not anticipated to increase concentrations of sulfate. Because natural concentrations of sulfate are low at the site, the addition of EHC® was not anticipated to increase concentrations of sulfide (from sulfate reduction). Ferrous iron could increase due to stimulation of biological iron reduction or corrosion (oxidation) of ZVI. Sulfate concentrations as high as 24.9 mg/L at DP98MP02 in September 2010 and as high as 13.4 mg/L in well DP98MP03 in May 2011 were measured. These concentrations are within the range of naturally occurring sulfate concentrations at the DP98 site. Sulfate was reduced to below detection by September 2011. Concentrations of sulfide as high as 3.09 mg/L (laboratory analysis, **Table 3.4**) were measured at DP98MP03 in September 2010. A sulfide concentration of this magnitude could be produced by reduction of native sulfate. Concentrations of ferrous iron increased substantially within Test Cell No. 1, to greater than 66 mg/L in September 2010 (**Table 3.2**). This increase is likely due to reduction of native iron; similar results were observed during the 2005 treatability study.

Test Cell No. 2: The injection of calcium sulfate (gypsum) into Test Cell No. 2 was anticipated to increase the concentrations of sulfate and sulfide in groundwater. Concentrations of ferrous iron were anticipated to increase due to reduction of both native iron and the iron oxide (hematite) that was injected. At the same time sulfide was anticipated to precipitate with ferrous iron or react with ferric iron to produce iron-sulfide minerals. This process would eventually reduce concentrations of sulfide and ferrous iron in groundwater. Sulfate did increase after injection, to as high as 2,530 mg/L at DP98MP07 in September 2010. Concentrations of sulfate at this location subsequently decreased to 895 mg/L and to 15.4 mg/L at DP98MP06 in September 2011, indicating that sulfate reduction was occurring. Sulfate increased from 19.3 mg/L in May 2011 to 62.8 mg/L at DP98MP08 in September 2011, indicating that some of the injected sulfate was migrating out of the test cell.

Concentrations of sulfide were as high as 8.8 mg/L (laboratory analysis) at DP98MP07, and a strong hydrogen sulfide odor was observed in the field. This confirms that sulfate reduction was stimulated. In contrast to Test Cell No. 1, measured concentrations of ferrous iron only increased to a maximum of 33 mg/L at DP98MP06 in May 2011. The lower magnitude of this increase relative to Test Cell No. 1 suggests that much of the ferrous iron that was produced precipitated with sulfide to form iron-sulfide minerals.

Test Cell No. 3: The injection of soluble ferrous sulfate into Test Cell No. 3 was anticipated to immediately increase the concentrations of sulfate and ferrous iron in groundwater. Following an initial increase, the concentration of ferrous iron was anticipated to decrease as sulfate was reduced to sulfide, and as sulfide precipitated with ferrous iron. The concentration of sulfate increased to 1,160 mg/L at DP98INJ-02 in September 2010, and subsequently decreased to 27.6 mg/L in September 2011. Concentrations of sulfide at DP98INJ-02 were 5.30 J mg/L (estimated concentration) in September 2010 and 22.4 J mg/L in September 2011. The sulfide concentration measured at DP98INJ-02 in September 2011 was the highest sulfide concentration

measured during the demonstration, providing a strong indication that sulfate reduction was stimulated in Test Cell No. 3. Concentrations of ferrous iron at Test Cell No. 3 remained substantially elevated, exceeding 66 mg/L at all three injection wells in September 2011. The ferrous iron data suggest that an excess of ferrous iron was present in Test Cell No. 3 over the course of the demonstration.

3.2.9 Methane, Ethene, Ethane, and Acetylene

Analysis of dissolved gases including methane, ethane, ethene, and acetylene was performed by Microseeps using method AM-20GAX. Methane is produced by biodegradation of an organic substrate, while ethene and ethane are produced by dechlorination of VC. Acetylene is a byproduct of the abiotic dechlorination of CAHs by reactive iron-sulfide minerals.

Methane: Methane concentrations during the baseline sampling event in May 2010 ranged from 23,000 µg/L at DP98INJ-03 within the former enhanced bioremediation pilot test area to 270 µg/L at DP98MP08 downgradient of Test Cell No. 2. Outside of the former enhanced bioremediation pilot test area, baseline concentrations of methane typically ranged from about 1,000 to 2,000 µg/L (**Table 3.2**). The concentrations of methane after the biogeochemical transformation injections generally increased in Test Cells No. 1 and No. 2, with the highest concentration being 21,000 µg/L at DP98MP02 in Test Cell No. 1. Conversely, post-injection concentrations of methane in Test Cell No. 3 either decreased or remained relatively stable. This may be due to the injection of sulfate, which favored sulfate reduction over methanogenesis.

Ethene and Ethane: Elevated concentrations of ethene provide direct evidence that biotic dechlorination of VC is occurring, resulting in the complete transformation of chlorinated ethenes. Baseline concentrations of ethene and ethane in the test cells ranged up to 8.3 µg/L and 11 µg/L, respectively; both detections occurred at DP98MP03 in Test Cell No. 1. After the injections, concentrations of ethene in Test Cell No. 1 increased to a maximum of 120 µg/L at DP98MP02 in September 2011. The maximum concentration of ethene detected in wells associated with Test Cell No. 2 was 22 µg/L at downgradient well DP98MP08 in September 2010. In contrast, ethene concentrations within Test Cell No. 2 generally decreased or remained stable relative to baseline concentrations. Concentrations of ethene at DP98INJ-02 in Test Cell No. 3 increased slightly, from less than 0.5 µg/L during baseline sampling to 7.1 µg/L in May 2011. Concentrations of ethane in test cell wells were generally more stable than ethene concentrations over time. The ethene data suggest that Test Cell No. 1 had the greatest potential for complete biotic reductive dechlorination of CAHs.

Acetylene: Precipitated iron sulfide minerals exist in a reduced state and may react rapidly with oxidized compounds such as TCE to form acetylene, as described in **Section 1.4**. However, a lack of acetylene detections does not necessarily demonstrate that biogeochemical reduction of CAHs is not occurring because acetylene is volatile and labile and is difficult to detect when biological activity is stimulated. Acetylene was detected at very low concentrations (less than 0.7 µg/L) during the baseline sampling event. The highest baseline concentration of acetylene was 0.66 µg/L at DP98MP06. Acetylene was only sporadically detected after the injections; the highest post-injection concentration of acetylene was 1.4 µg/L at DP98MP03 in September 2010. Therefore, results of analysis for acetylene are inconclusive regarding the stimulation of abiotic dechlorination processes.

3.3 CHLORINATED ALIPHATIC HYDROCARBONS IN GROUNDWATER

Concentrations of CAHs and a few other select VOCs in groundwater over time are listed in **Table 3.5**. The effect of the May 2010 injections on degradation of CAHs in the three test cells is assessed in the following subsections by evaluating the performance metrics in **Section 1.1.2**.

Table 3.5 Summary of Chlorinated Aliphatic Hydrocarbons in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Months from Injection	PCE[a/] (µg/L)[b/]	TCE[a/] (µg/L)	*cis*-1,2-DCE[a/] (µg/L)	*trans*-1,2-DCE (µg/L)	1,1-DCE (µg/L)	VC[a/] (µg/L)	1,1-DCA[a/] (µg/L)	Methylene Chloride (µg/L)	Acetone (µg/L)	2-Butanone (MEK) (µg/L)	Naphthalene (µg/L)	Benzene (µg/L)
Test Cell No. 1 (EHC)															
DP98MP01	Upgradient	20-May-10	0	<0.15 [c/]	**610** [d/]	**2,400**	**7.00**	**16.0**	**0.77 F** [e/]	<0.19	<0.35	<0.95	<0.6	<0.36	**1.70**
		22-Sep-10	4	<0.06	**136 J** [f/]	**1,910**	**2.05 J**	**3.39 J**	**0.56 J**	<0.07	<0.35	**45.7 J**	**3.35 J**	<0.07	**0.66 J**
		17-May-11	11	<0.06	**100**	**7,550**	**5.25**	**25.9**	**1.93 J**	<0.07	<0.35	**20.1**	<0.22	<0.07 J	**2.02**
		13-Sep-11	15	<0.06	**117**	**1,660**	**5.25**	**9.65**	**0.90 F**	**0.34 F**	<0.35	<2.8	<0.22	<0.07	**1.40**
DP98MP-11	(duplicate)	13-Sep-11	15	<0.06	**133**	**1,750**	**4.63**	**9.06**	**0.99 F**	**0.38 F**	<0.35	<2.8	<0.22	<0.07	**1.36**
DP98MP02	Injection	21-May-10	0	<0.15	**350**	**2,100**	**6.40**	**9.20**	**5.90**	<0.19	<0.35	**9.80 F**	**5.4 F**	<0.36	**1.00**
		22-Sep-10	4	<0.06	**5.73 J**	**2,560**	**3.24 J**	**6.3 J**	**34.3 J**	<0.07	<0.35	**562 B** [g/]	**148**	**1.66 J**	**0.54 J**
		17-May-11	11	<0.06	**5.58**	**2,080**	**6.49**	**8.10**	**385 J**	<0.07	<0.35	**1,250**	<0.22	<0.07 J	**0.62**
		13-Sep-11	15	<0.06	**1.36**	**446**	**3.86**	**2.03**	**2,200 M** [h/]	<0.07	<0.35	**362 F**	**179 F**	**0.37 F**	**0.79**
DP98MP03	Injection	21-May-10	0	<0.15	**290**	**1,900**	**7.40**	**7.80**	**11.0**	<0.19	<0.35	**17**	**7.80 F**	<0.36	**0.78**
		22-Sep-10	4	<0.06	**88.0**	**1,900**	**5.88**	**8.25**	**41.5**	<0.07	<0.35	**3,610 B**	**342 F**	**1.10**	**0.69**
		17-May-11	11	<6	**19.1 F**	**3,690**	<8	<12	**140 J**	<7	<35	**2,540**	<22	<7 J	<7
		13-Sep-11	15	<0.06	**1.77**	**85.4**	**2.46**	**0.59 F**	**1,690**	<0.07	<0.35	**918**	**269 F**	<0.07	**0.51**
DP98MP04	Downgradient	21-May-10	0	<0.15	**150**	**4,700**	**17.0**	**25.0**	**150**	<0.19	<0.35	<0.95	<0.6	**7.40**	**1.40**
DP98MP24	(duplicate)	21-May-10	0	<0.15	**150**	**4,300**	**15.0**	**25.0**	**140**	<0.19	<0.35	<0.95	<0.6	**7.70**	**1.50**
		21-Sep-10	4	<0.06	**6.89 J**	**3,670**	**5.82 J**	**8.55 J**	**207 F**	<0.07	<0.35	**194 J**	**50.3 J**	**12.7 J**	**0.64 J**
		18-May-11	12	<0.06	**89.9**	**6,630**	**31.9 J**	**41.8 J**	**483 J**	**0.72 F**	<0.35	<2.8	<0.22	**15.4**	**2.00**
		15-Sep-11	15	<0.06	**87.9**	**4,290**	**35.2**	**24.9**	**618**	<0.07	<0.35	<2.8	<0.22	**9.32**	**1.31**
Test Cell No. 2 (EVO + Gypsum + Hematite)															
DP98MP05	Upgradient	23-May-10	0	<0.15	**270**	**280**	**1.80**	**2.80**	**0.77 F**	<0.19	<0.35	<0.95	<0.6	<0.36	**1.10**
		22-Sep-10	4	<1.2	**426**	**606**	**4.89 F**	<2.4	<1.6	<1.4	**69.6 B**	<56	<4.4	<1.4	<1.4
		18-May-11	12	<0.06	**306**	**1,360**	**4.52 J**	**7.86 J**	**2.72 J**	**0.93 F**	<0.35	<2.8	<0.22	**0.34 F**	**1.74**
DP98MP05-FD	(duplicate)	18-May-11	12	<0.06	**317**	**1,480**	**3.29 J**	**5.36 J**	**1.27 J**	**0.82 F**	<0.35	<2.8	<0.22	<0.07	**1.61**
		15-Sep-11	15	<0.06	**327**	**517**	**2.20**	**3.76**	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	**1.34**
DP98MP06	Injection	23-May-10	0	<0.15	**230**	**3,900**	**13.0**	**22.0**	**2.50**	<0.19	<0.35	<0.95	<0.6	**1.10**	**2.90**
		23-Sep-10	4	<6	**187**	**4,000 M**	**46.67 F**	<12	<8	<7	**473 M**	<280	<22	<7	<7
DP98MP-26	(duplicate)	23-Sep-10	4	<6	**190**	**4,150 M**	**49.2 F**	<12	**31.7 F**	<7	**543 M**	<280	<22	<7	<7
		18-May-11	12	<0.06	**5.94**	**3,790**	**18.52 J**	**14.2 J**	**26.0 J**	**0.61 F**	<0.35	<2.8	<0.22	<0.07	**1.75**
		14-Sep-11	15	<0.06	**1.28**	**2,430 J**	**9.53**	**7.79**	**33.1 F**	**0.43 F**	<0.35	<2.8	<0.22	<0.07	**1.05**
DP98MP07	Injection	23-May-10	0	<0.15	**200**	**3,100**	**9.20**	**17.0**	**1.30**	<0.19	<0.35	<0.95	<0.6	**1.10**	**2.40**
		22-Sep-10	4	<6	**79.2 F**	**2,460**	**46.1 F**	<12	<8	<7	**524 B**	<280	<22	<7	<7
		18-May-11	12	**0.17 F**	**7.78**	**266**	**3.80 J**	**0.96 J**	**2.50 J**	<0.07	<0.35	<2.8	**3.11 F**	<0.07	**0.31 F**
		14-Sep-11	15	<0.06	**5.01**	**339**	**3.73**	<0.12	**6.01**	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98MP08	Downgradient	23-May-10	0	<0.15	**96.0**	**1,500**	**4.60**	**6.60**	**3.80**	<0.19	<0.35	**18.0**	<0.6	<0.36	**1.50**
		23-Sep-10	4	<3	**60.1**	**1,720**	**27.2 F**	<6	<4	<3.5	**232 B**	<140	<11	<3.5	<3.5
		18-May-11	12	<0.06	**7.04**	**1,170**	**15.6 J**	**4.33 J**	**2.88 J**	**0.27 F**	<0.35	<2.8	<0.22	<0.07	**0.63**
		15-Sep-11	15	<0.06	**23.9**	**504**	**1.91**	**1.74**	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07

Table 3.5 Summary of Chlorinated Aliphatic Hydrocarbons in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Months from Injection	PCE[a/] (µg/L)[b/]	TCE[a/] (µg/L)	*cis*-1,2-DCE[a/] (µg/L)	*trans*-1,2-DCE (µg/L)	1,1-DCE (µg/L)	VC[a/] (µg/L)	1,1-DCA[a/] (µg/L)	Methylene Chloride (µg/L)	Acetone (µg/L)	2-Butanone (MEK) (µg/L)	Naphthalene (µg/L)	Benzene (µg/L)
Test Cell No. 3 (EVO + Ferrous Sulfate)															
DP98MW-04	20' Upgradient	24-May-10	0	**1.8**	**2,400**	**3,100**	**13.0**	**15.0**	**1.00**	<0.19	<0.35	<0.95	<0.6	**1.30**	**1.10**
		21-Sep-10	4	**0.79 J**	**2,230**	**2,860**	**3.29 J**	**6.19 J**	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07 J	**0.59 J**
		17-May-11	11	**1.67**	**2,850**	**3,900**	**4.46**	**17.6**	**2.57 J**	<0.07	<0.35	**27.5**	<0.22	**2.79 J**	**0.77**
DP98MW-04FD	(duplicate)	17-May-11	11	**1.62**	**2,930**	**3,940**	**4.48**	**17.1**	**1.52 J**	<0.07	<0.35	**27.3**	<0.22	<0.07 J	**0.75**
		12-Sep-11	15	<6	**1,790**	**2,520**	<8	<12	<8	<7	<35	<280	<22	<7	<7
DP98MW-14	(duplicate)	12-Sep-11	15	<6	**1,900**	**2,490**	<8	<12	<8	<7	<35	<280	<22	<7	<7
DP98INJ-01	Injection	25-May-10	0	<0.15	**0.98 F**	**4,900**	**9.50**	**15.0**	**710**	<0.19	<0.35	**2.30 F**	<0.6	**35.0**	**0.89**
		21-Sep-10	4	<0.06	**12.9**	**1,776**	**7.08 J**	**4.76**	**506**	<0.07	<0.35	**11.5**	**23.5**	**5.59 J**	**0.50**
		16-May-11	11	<0.06	**1.01**	**755**	**17.4**	**4.14**	**2,120**	<0.07	<0.35	**60.4**	**41.6**	**5.18**	**0.97**
		13-Sep-11	15	<0.06	**0.54 F**	**212**	**19.8**	**1.65**	**2,340**	<0.07	<0.35	**36.1**	**19.0**	**10.1**	**1.21**
DP98INJ-02	Injection	24-May-10	0	**0.58 F**	**1.40**	**7,100**	**75.0**	**35.0**	**73.0**	<0.19	<0.35	<0.95	<0.6	**42.0**	**1.10**
		21-Sep-10	4	<0.06	**3.40 J**	**2,740**	**2.29 J**	**3.04 J**	**67.3 J**	<0.07	<0.35	**10.4 J**	**5.56 J**	**1.40 J**	**0.19 J**
DP98INJ-22	(duplicate)	21-Sep-10	4	<0.06	**2.17 J**	**2,600**	**2.84 J**	**3.66 J**	**66.0 J**	<0.07	<0.35	<2.8	**6.48 J**	**1.11 J**	**0.25 J**
		17-May-11	11	<0.06	**25.0**	**10,100**	**13.8**	**21.5**	**196 J**	<0.07	<0.35	**56.7**	**85.5**	**1.07 J**	**0.82**
		13-Sep-11	15	<0.06	**5.57**	**5,690**	**20.4**	**17.2**	**331**	<0.07	<0.35	**21.2**	**12.5**	**1.12**	**1.05**
DP98INJ-03	Injection	25-May-10	0	<0.15	**3.20**	**6,500**	**16.0**	**31.0**	**75.0**	<0.19	<0.35	<0.95	<0.6	**44.0**	**1.20**
		21-Sep-10	4	<0.06	**3.95**	**1,050**	**5.44 J**	**1.61**	**257**	<0.07	<0.35	**27.8**	**9.88 F**	**1.71 J**	**0.25 F**
		16-May-11	11	<0.06	**0.56 F**	**177**	**13.7**	<0.12	**1,200**	<0.07	<0.35	**89.1**	**25.2**	**1.70**	**0.50**
		13-Sep-11	15	<0.06	**0.43 F**	**117**	**13.8**	**0.84 F**	**1,670**	<0.07	<0.35	**28.7**	**12.1**	**3.22**	**0.66**
DP98MW-05	10' Downgradient	24-May-10	0	**0.21 F**	**45.0**	**8,200**	**43.0**	**39.0**	**45.0**	<0.19	<0.35	<0.95	<0.6	**23.0**	**1.70**
		20-Sep-10	4	<0.06	**3.28 J**	**8,600**	**22.4 J**	**22.9 J**	**40.7 J**	<0.07	<0.35	<2.8	<0.22	**51.6 J**	**1.49 J**
		16-May-11	11	<6	**48.0 F**	**14,600**	**47.3 F**	**80.3 F**	**55.8 F**	<7	**143**	<280	<22	**56.3 F**	<7
		12-Sep-11	15	<15	**82.5 F**	**7,310**	<20	<30	<20	<17.5	<87.5	<700	<55	<17.5	<17.5
DP98MW-06	20' Downgradient	24-May-10	0	<0.15	**2.60**	**4,200**	**24.0**	**20.0**	**40.0**	<0.19	<0.35	<0.95	<0.6	**320**	**1.60**
		20-Sep-10	4	<0.06	**3.90 J**	**5,040**	**17.5 J**	**10.7 J**	**49.2 J**	<0.07	<0.35	<2.8	<0.22	**315 F**	**1.04 J**
		16-May-11	11	<0.06	**44.5**	**7,080**	**19.1**	**29.1**	**52.5**	<0.07	<0.35	**27.4**	<0.22	**237**	**1.53**
		12-Sep-11	15	<6	**33.4 F**	**3,640**	<8	<12	**65.7 F**	<7	<35	<280	<22	**330**	<7

Table 3.5 Summary of Chlorinated Aliphatic Hydrocarbons in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Months from Injection	PCE[a/] (µg/L)[b/]	TCE[a/] (µg/L)	*cis*-1,2-DCE[a/] (µg/L)	*trans*-1,2-DCE (µg/L)	1,1-DCE (µg/L)	VC[a/] (µg/L)	1,1-DCA[a/] (µg/L)	Methylene Chloride (µg/L)	Acetone (µg/L)	2-Butanone (MEK) (µg/L)	Naphthalene (µg/L)	Benzene (µg/L)
Other Wells and Points															
DP98MP10	Downgradient	24-May-10	0	<0.15	**570**	**330**	**1.40**	**2.30**	**1.20**	<0.19	<0.35	**9.00 F**	<0.6	<0.36	**0.63**
		23-Sep-10	4	<1.2	**222**	**910**	**14.3 F**	**3.92 F**	<1.6	<1.4	**69.8 B**	<56	<4.4	<1.4	<1.4
		19-May-11	12	<0.06	**86.2**	**311**	**3.78**	**1.32**	**0.47 F**	**0.46 F**	<0.35	<2.8	<0.22	<0.07	**0.31 F**
		15-Sep-11	15	<0.06	**140**	**233**	**0.67 F**	**1.42**	**2.23**	<0.07	<0.35	<2.8	<0.22	<0.07	**0.32 F**
41755-WL04	Downgradient	20-May-10	0	<0.15	**270**	**3,700**	**13.0**	**22.0**	**5.50**	<0.19	<0.35	<0.95	<0.6	**1.30**	**1.70**
		20-Sep-10	4	<6	**156 J**	**2,140 J**	<8	<12	<8	<7	<35	<280	<22	**53.8 J**	<7
		16-May-11	11	<0.06	**2.05**	**2,450**	**5.75**	**11.6**	**1,316**	<0.07	<0.35	**1,010**	<0.22	<0.07	**0.83**
		12-Sep-11	15	<3	<2.5	**493**	<4	<6	**900**	<3.5	<17.5	**271 F**	<11	<3.5	<3.5
41755-WL08	Downgradient	23-Sep-10	4	<1.2	**376**	**286**	<1.6	<2.4	<1.6	<1.4	**72.6 B**	<56	<4.4	<1.4	<1.4
		19-May-11	12	<0.06	**236**	**173**	**0.28 F**	**0.72 F**	<0.08	**0.23 F**	<0.35	<2.8	<0.22	<0.07	<0.07
		14-Sep-11	15	<0.06	**259**	**200**	**0.66 F**	**0.94 F**	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
41755-WL09	Downgradient	23-Sep-10	4	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
		19-May-11	12	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
		14-Sep-11	15	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
Quality Assurance/Quality Control Samples															
Trip Blank #1	Trip Blank	21-May-10	0	<0.15	<0.16	<0.16	<0.19	<0.3	<0.23	<0.19	<0.35	<0.95	<0.6	<0.36	<0.16
Trip Blank	Trip Blank	25-May-10	0	<0.15	<0.16	<0.16	<0.19	<0.3	<0.23	<0.19	<0.35	<0.95	<0.6	<0.36	<0.16
DP98TB01	Trip Blank	21-Sep-10	4	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98TB02	Trip Blank	22-Sep-10	4	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98FB03	Field Blank	23-Sep-10	4	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98FB04	Field Blank	23-Sep-10	4	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98TB02-051811	Trip Blank	16-May-11	11	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
DP98TB02-051811	Trip Blank	18-May-11	12	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
Trip Blank DP98091211	Trip Blank	12-Sep-11	15	<0.06	<0.05	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07
Trip Blank/DP98091311	Trip Blank	13-Sep-11	15	<0.06	<0.05 J	<0.07	<0.08	<0.12	<0.08	<0.07	<0.35	<2.8	<0.22	<0.07	<0.07

[a/] PCE = tetrachloroethene, TCE = trichloroethene, DCE = dichloroethene, VC = vinyl chloride, DCA = dichloroethane, MEK = methyl ethyl ketone.

[b/] µg/L = micrograms per liter.

[c/] "<" indicates the concentration is below the indicated laboratory method detection limit (MDL).

[d/] **BOLD** text indicates detected results.

[e/] F-flag indicates the concentration is below the laboratory reporting limit but above the MDL, and the concentration is estimated.

[f/] J-flag indicates the analyte was positively identified, but the quantitation is an estimation due to discrepancies in meeting certain analyte-specific quality control criteria.

[g/] B-flag indicates the analyte was detected in the method blank.

[h/] M-flag indicates the recovery/Relative Percent Difference (RPD) was poor for Matrix Spike/Matrix Spike Duplicate (MS/MSD) or primary/field duplicate sample pair.

Ideally, the differing degradation patterns described in **Section 1.4** should be evident on time-versus-concentration graphs for the various CAHs, and on graphs of molar fractions over time. Concentrations of CAHs over time were graphed to facilitate evaluation of degradation patterns prior to and following the May 2010 injection event. Graphs were prepared for all wells sampled from May 2010 to September 2011, and are provided in **Attachment B**. For molar fraction and total molar chloroethene calculations, non-detects were assigned a value equal to one-half the method detection limit, and primary and duplicate sample results were averaged.

It should be noted that many wells may not exhibit idealized degradation patterns. Seasonal changes in groundwater levels may influence the flux of CAH mass through the test cells over time, and variations in temperature may impact rates of both biological and geochemical processes.

Average pre-injection degradation rates for TCE and *cis*-DCE in groundwater in the vicinity of the test cells were calculated using historical data for wells 41755WL-02, 41755WL-03, and 41755WL-04. The rates were calculated using the linear regression technique described in Appendix A of the document titled *An Approach for Evaluating the Progress of Natural Attenuation in Groundwater* (USEPA, 2011). The average pre-injection degradation rates calculated for TCE and cis-DCE are 4.6×10^{-4} per day (day^{-1}) and 2.5×10^{-4} day^{-1}, respectively. These rates are compared in the following paragraphs to post-injection rates calculated using data for test cell interior monitoring locations to assess whether the targeted rate increase identified in Performance Metric #2 (listed in **Section 1.1.2**) was attained.

3.3.1 Test Cell No. 1

Concentrations of chlorinated ethenes for Test Cell No. 1 are listed in **Table 3.5**, and concentration graphs for wells DP98MP01 through DP98MP04 are included as Figures B.1 through B.4 in **Attachment B**. Average concentrations of chlorinated ethenes and total molar CAHs within the Test Cell No. 1 reaction zone (DP98MP02 and DP98MP03) are shown on **Figure 3.3**. Concentrations of TCE decreased to 1.36 µg/L at DP98MP02 and 1.77 µg/L at DP98MP03 by September 2011 (**Table 3.5**); the September 2011 concentrations are less than the performance objective of 5.0 µg/L.

The average concentration of total DCE (sum of the three isomers) initially increased from 2,015 µg/L in May 2010 to 2,899 µg/L in May 2011, before decreasing to 270 µg/L in September 2011 (i.e., substantially lower than the initial pre-injection concentrations). The average concentration of VC consistently increased from 8.5 µg/L in May 2010 to 1,949 µg/L in September 2011, indicating that TCE and DCE were transformed primarily by sequential biotic dechlorination. Average concentrations of ethene + ethane increased to 105 µg/L in September 2011, indicating that transformation of VC to ethene occurred but not at a rate sufficient to prevent the accumulation of VC within the test cell. Performance metric #3 (**Section 1.1.2**) was met for *cis*-DCE in Test Cell No. 1, but VC concentrations increased and did not meet the target metric.

An observed 45% increase in the total molar concentration of CAHs within Test Cell No. 1 over time reflects the incomplete transformation of TCE and DCE to VC. Therefore, Performance Metric #4 (**Section 1.1.2**) for total molar CAH concentrations was not met. A significant portion of this increase is likely due to the lower sorption potentials for DCE and VC. As TCE is transformed to DCE and VC, a greater percentage of the compound will be soluble in groundwater relative to that sorbed to the soil matrix.

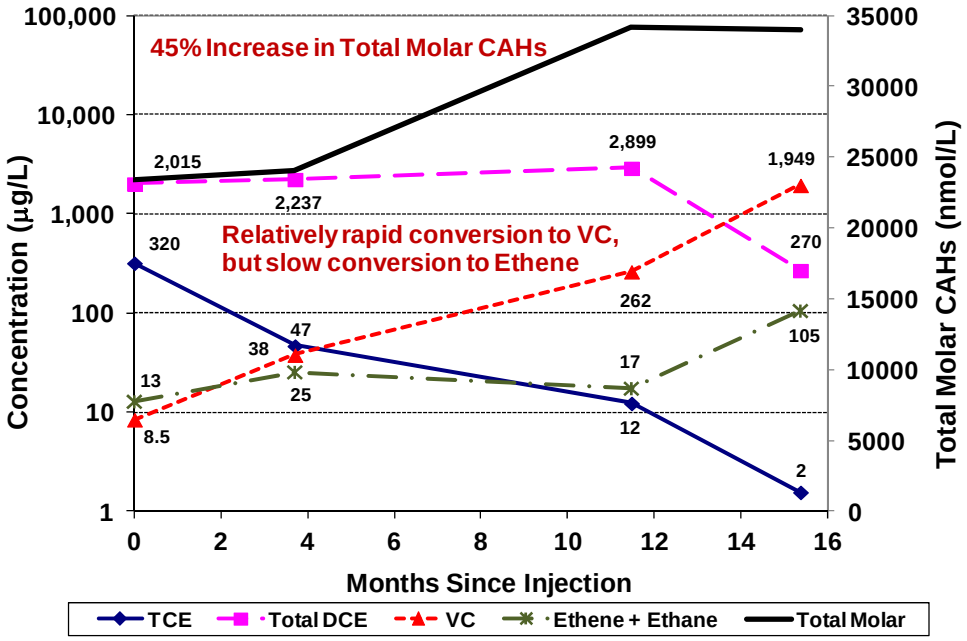

Figure 3.3 Concentrations of Chlorinated Ethenes at Test Cell No. 1
(EHC®: Average of DP98MP02 and DP98MP03)

The average post-injection degradation rates for TCE and *cis*-DCE in Test Cell No. 1, calculated using data from monitoring points DP98MP02 and DP98MP03, were 9.5 x 10^{-3} day^{-1} and 3.7 x 10^{-3} day^{-1}, respectively. The rate for *cis*-DCE is conservative because DCE was continually produced from dechlorination of TCE migrating into the treatment cell. Comparison of these rates to the pre-injection rates presented above in **Section 3.3 (**4.6 x 10^{-4} day^{-1} for TCE and 2.5 x 10^{-4} day^{-1} for *cis*-DCE) indicates that the rates increased by at least an order of magnitude following the substrate / amendment injection. Therefore, Performance Metric # 2 was met at Test Cell No. 1.

3.3.2 Test Cell No. 2

Concentrations of chlorinated ethenes for Test Cell No. 2 are listed in **Table 3.5**, and concentration graphs for wells DP98MP05 through DP98MP08 are included in Figures B.5 through B.8 in **Attachment B**. Average concentrations of chlorinated ethenes and total molar CAHs within Test Cell No. 2 are shown on **Figure 3.4**. Concentrations are the average of the two monitoring locations within the test cell reaction zone (DP98MP06 and DP98MP07). Similar to Test Cell No. 1, concentrations of TCE steadily decreased to 1.18 µg/L at DP98MP06 and to 5.01 µg/L at DP98MP07 by September 2011 (**Table 3.5**), less than or very close to the performance objective of 5.0 µg/L.

However, unlike Test Cell No. 1, the average concentration of total DCE consistently decreased during the performance monitoring period, with an overall decrease of 61% from May 2010 to September 2011. The average VC concentration increased during the same period, but only to 20 µg/L, and was relatively stable compared to the other two test cells. Concentrations of ethene did not increase. These data suggest that the transformation of TCE and DCE was primarily by an abiotic pathway that did not produce significant amounts of VC or ethene. The performance metric for *cis*-DCE was met in Test Cell No. 2, but VC concentrations increased and did not meet the target metric.

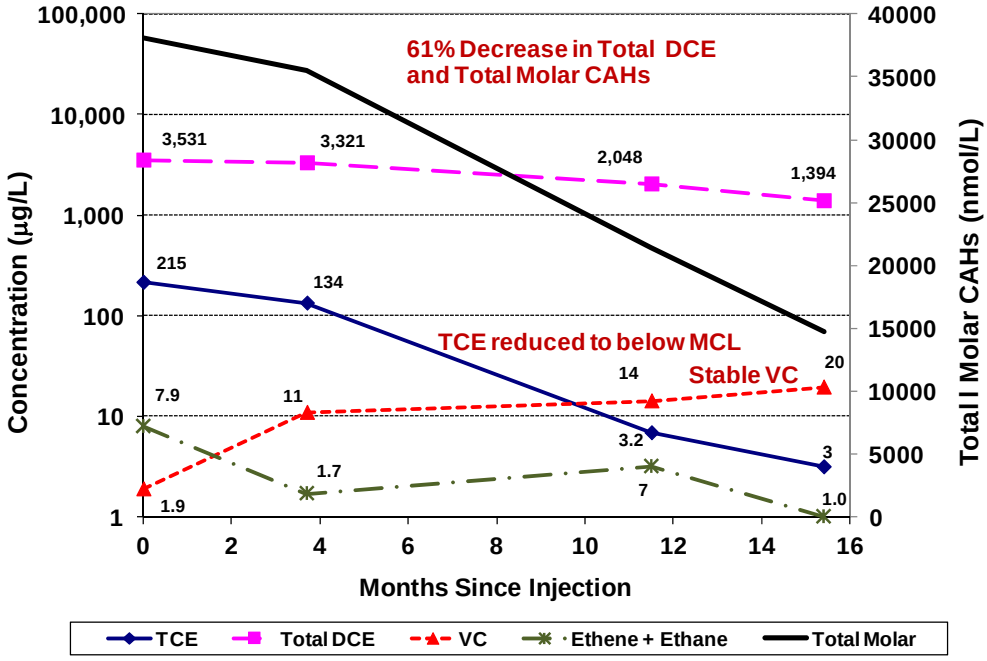

Figure 3.4 Concentrations of Chlorinated Ethenes at Test Cell No. 2
(Hematite + Gypsum + EVO: Average of DP98MP06 and DP98MP07)

The total molar concentration of CAHs within Test Cell No. 2 decreased by 61% during the performance monitoring period, providing a further indication that abiotic degradation was stimulated by biogeochemical transformation without significant accumulation of DCE or VC. Although the observed decrease did not meet the 90% performance metric, the decreasing trends in concentrations of TCE, DCE, and total molar concentrations are a promising indication that remediation of chlorinated ethenes in groundwater at the DP98 site by biogeochemical processes can be effective.

Linear regression analysis of post-injection data for TCE and cis-DCE data yields degradation rates of 9.8×10^{-3} for TCE and 3.2×10^{-3} day^{-1}, respectively. The rate for *cis*-DCE is conservative because some DCE was continually produced from dechlorination of TCE migrating into the treatment cell. Comparison of these rates to the pre-injection rates presented above in **Section 3.3** (4.6×10^{-4} day^{-1} for TCE and 2.5×10^{-4} day^{-1} for *cis*-DCE) indicates that the rates increased by at least an order of magnitude following the substrate / amendment injection. Therefore, Performance Metric # 2 was met at Test Cell No. 2. Extrapolation of the regression trend for total DCE to a cleanup level 70 µg/L for cis-DCE yields a period of approximately 4.5 years to achieve the target concentration. This is only an estimate; several conditions would have to be met for this to become a reality, including sustaining the appropriate biogeochemical conditions in the reaction zone.

3.3.3 Test Cell No. 3

Concentrations of chlorinated ethenes for Test Cell No. 3 are listed in **Table 3.5**, and concentration graphs for injection wells DP98INJ-01 through DP98INJ-03 and monitoring wells DP98MW-04 through DP98MW-06 are included on Figures B.9 through B.14 in **Attachment B**. Average concentrations of chlorinated ethenes and total molar CAHs within Test Cell No. 3 are shown on **Figure 3.5**. Concentrations are the average of the three monitoring locations within

the test cell reaction zone (DP98INJ-01 through DP98INJ-03). Unlike the other two test cells, concentrations of TCE were already below 5.0 µg/L within the reaction zone at Test Cell No. 3 due to a prior bioremediation treatability study. The intent of injecting into Test Cell No. 3 was to see if further degradation of DCE and VC could be enhanced.

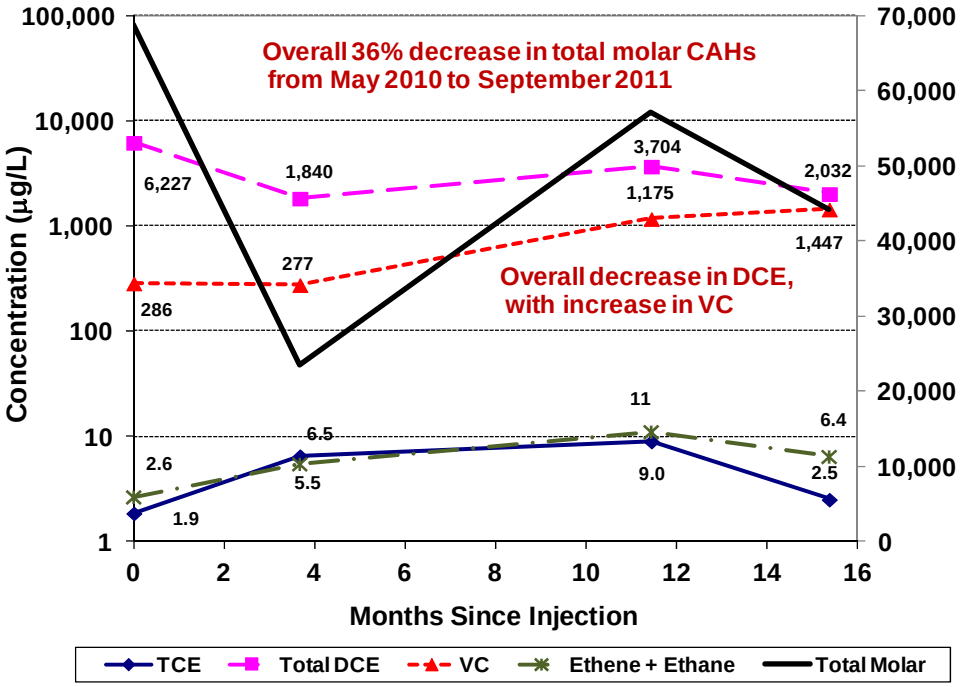

Figure 3.5 Concentrations of Chlorinated Ethenes at Test Cell No. 3
(Ferrous Sulfate + EVO: Average of DP98INJ-01 Through DP98INJ-03)

The average concentration of total DCE was variable, initially decreasing from 6,227 µg/L to 1,840 µg/L in September 2010, but then increasing in May 2011 before decreasing to 2,032 µg/L in September 2011. Overall the average concentration of total DCE within Test Cell No. 3 decreased by 67% from May 2010 to September 2011. The average concentration of VC within Test Cell No. 3 increased from September 2010 to September 2011. These data suggest that DCE was transformed to VC via a primarily biotic pathway. Concentrations of ethene only increased from 3 µg/L to a high of 11 µg/L, indicating that further biotic dechlorination of VC was limited. The performance metric for *cis*-DCE was met in Test Cell No. 3, but VC concentrations increased and did not meet the target metric.

The observed changes in the total molar concentration of CAHs within Test Cell No. 3 correlated to the changes in concentration of total DCE, with an overall reduction of 36% from May 2010 to September 2011. Although the overall decrease in concentrations of total DCE is a positive result. this decrease did not meet the 90% performance metric (**Section 1.1.2**). The persistence of VC in Test Cell No. 3 prevented a greater decrease in total molar concentration.

A post-injection degradation rate for TCE in Test Cell No. 3 was not calculated because TCE concentrations were less than 5.0 µg/L during the baseline and performance monitoring events. The average post-injection degradation rate for *cis*-DCE in Test Cell No. 3, calculated using data from wells DP98INJ-01 through DP98INJ-03, was 7.1 x 10^{-3} day^{-1}. This rate is conservative because some DCE was likely produced from dechlorination of TCE migrating into the treatment

cell. Comparison of this rate to the pre-injection rate presented above in **Section 3.3** (2.5×10^{-4} day^{-1}) indicates that the rate increased by at least an order of magnitude following the substrate / amendment injection. Therefore, Performance Metric # 2 was met at Test Cell No. 3.

3.3.4 Summary and Supporting Data for CAH Degradation Processes

Degradation patterns for TCE, DCE, and VC observed for the three test cells indicate that both biotic sequential dechlorination and abiotic biogeochemical transformation processes were operating, but not always in the same place at the same time. The following summarizes the degradation processes evident at each test cell location:

- **Test Cell No. 1:** A substantial increase in VC indicates that biotic dechlorination of TCE and DCE to VC occurred. The production of ethene towards the end of the monitoring period indicates that dechlorination of VC to ethene also occurred, but not at a rate sufficient to prevent the accumulation and persistence of VC.
- **Test Cell No. 2:** Concentrations of TCE and DCE consistently decreased in Test Cell No. 2, with only a slight increase in VC and no production of ethene. These trends suggest an abiotic degradation pathway for TCE and DCE that produced little VC or ethene.
- **Test Cell No. 3:** Concentrations of total DCE in Test Cell No. 3 were variable, but exhibited an overall decrease of 67% from May 2011 to September 2011. A substantial increase in VC was observed, indicating that biotic dechlorination of DCE to VC was a primary degradation pathway. Little ethene was produced, suggesting that biotic dechlorination stalled at VC. However, an overall decrease in the total molar CAH concentration of 36% suggests that some abiotic degradation of DCE occurred. Therefore, both biotic and abiotic degradation likely occurred in Test Cell No. 3.

The dechlorination of VC to ethene observed in Test Cell No. 1 is only known to occur when *Dehalococcoides* species are present. To test for the presence of *Dehalococcoides*, groundwater samples from select locations were collected in May 2011 and submitted for molecular analyses of *Dehalococcoides* and reductase enzymes for TCE and VC (Bio-Dechlor Census) by Microbial Insights, Inc. of Nashville, Tennessee (**Table 3.6**). Results from a June 2008 sampling event performed at the prior enhanced bioremediation pilot test area (Test Cell No. 3) are also included for comparison.

Only a single estimated concentration of *Dehalococcoides* was detected in June 2008, approximately 3 years after the enhanced bioremediation pilot test injection. However, multiple detections of *Dehalococcoides* and reductase enzymes were measured in May 2011 for all three test cells. Many of these detected concentrations are less than the laboratory detection limits obtained in 2008, apparently due to improvements in the laboratory method. However, several results were substantially higher than the 2008 detection limits.

The maximum concentration of *Dehalococcoides* in May 2011 was 2.59E+04 cells per milliliter (cells/ml) at location DP98MP02 in Test Cell No. 1. The highest concentration of the TCE reductase enzyme was also detected in the sample from this location (2.71E+04 cells/ml). *Dehalococcoides* was detected in Test Cell No. 2, but at much lower concentrations ranging up to 4.4E+00 cells/ml at upgradient location DP98MP05. Concentrations of *Dehalococcoides* in Test Cell No. 3 location DP98INJ-02 were below detection. *Dehalococcoides* was detected in downgradient well DP98MW-05 at a maximum concentration of 4.73E+01 cells/ml in a duplicate sample. This result is lower than results for in Test Cell No. 1, but higher than for Test Cell No. 2. Overall these results are consistent with the observations of degradation processes discussed above, where the biotic dechlorination was most evident in Test Cell No. 1 and No. 3, and abiotic dechlorination was most evident in Test Cell No. 2.

Table 3.6 Bio-Dechlor Census Screening Results

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Dehalococcoides species (cells/mL) [b/]	Functional Genes [a/]		
				TCE R-Dase (cells/mL)	BAV1 VC R-Dase (cells/mL)	VC R-Dase (cells/mL)
DP98 Groundwater Samples - 2008 Bioremediation Study						
DP98MW-04	Upgradient	19-Jun-08	<2.0E+00 [c/]	<2.0E+00	<2.0E+00	<2.0E+00
DP98INJ-02	Treatment Zone	19-Jun-08	<2.5E+00	<2.5E+00	<2.5E+00	<2.5E+00
DP98INJ-12 (duplicate)		19-Jun-08	<2.5E+00	<2.5E+00	<2.5E+00	<2.5E+00
DP98MW-05	Downgradient	19-Jun-08	**1.73E-01 J** [d/]	<6.67E-01	<6.67E-01	<6.67E-01
Test Cell No. 1 (EHC) [e/]						
DP98MP-01	Upgradient	19-May-11	**1.40E+01**	<3.0E-01	<3.0E-01	**1.00E-01 J**
DP98MP-02	Treatment Zone	19-May-11	**2.59E+04**	**2.71E+04**	<9.00E-01	<9.00E-01
DP98MP-03	Treatment Zone	19-May-11	**1.16E+02**	**7.93E+01**	<9.00E-01	**4.00E-01 J**
Test Cell No. 2 (Hematite + Gypsum + EVO) [f/]						
DP98MP-05	Upgradient	19-May-11	**4.40E+00**	**1.00E-01 J**	<3.00E-01	**3.00E-01**
DP98MP-06	Treatment Zone	19-May-11	**1.30E+00**	**4.00E-01 J**	<5.00E-01	**3.00E-01 J**
DP98MP-07	Treatment Zone	19-May-11	**1.70 E+00**	<7.00E-01	<7.00E-01	**1.00E+00**
Test Cell No. 3 (Ferrous Sulfate + EVO)						
DP98MW-04	Upgradient	19-May-11	**3.00E-01 J**	**1.00E-01 J**	<3.00E-01	**3.00E-01**
DP98INJ-02	Treatment Zone	19-May-11	<5.00E-01	<5.00E-01	<5.00E-01	<5.00E-01
DP98MW-05	Downgradient	19-May-11	**4.35E+01**	**3.71E+01**	<3.00E-01	**2.00E-01 J**
DP98MW-15 FD [g/]		19-May-11	**4.73E+01**	**4.25E+01**	<3.00E-01	**1.00E-01 J**

[a/] TCE R-Dase = trichloroethene (TCE) reductase enzyme responsible for reductive dechlorination of TCE; BAV1 VC R-Dase = vinyl chloride (VC) reductase enzyme and VC R-Dase = VC reductase enzyme both responsible for reductive dechlorination of VC.

[b/] cells/mL = cells per milliliter of sample.

[c/] "<" indicates the result was not detected above the indicated practical quantitation limit (PQL).

[d/] **BOLD** text indicates detected results. J-flag indicates the estimated gene copies are below the PQL but above the laboratory quantification limit (LQL).

[e/] EHC = controlled release, integrated carbon and zero valent ion source that reduces redox potential.

[f/] EVO = emulsified vegetable oil.

[g/] FD indicates a field duplicate.

The VC and BAV1 reductase enzymes are two enzymes that have been isolated that demonstrate the ability of the *Dehalococcoides* species present to directly transform VC to ethene. The VC reductase enzyme was detected in all three test cells, with the highest concentration being 1.00E+00 cells/ml at DP98MP07 in Test Cell No. 2. These results are encouraging as they indicate a potential for native *Dehalococcoides* species to transform VC to ethene, as was observed in Test Cell No.1. However, the low cell concentrations measured suggest that that the process will be slow relative to dechlorination of TCE and DCE to VC.

Another indication of the degradation of chlorinated ethenes is provided by carbon isotope fractionation. CSIA results for stable carbon isotopes are listed in **Table 3.7** for sampling events in May 2010, September 2010, and May 2011. Carbon isotope ratios are reported as a measure of the ratio of carbon 13 to carbon 12 (δC^{13}) in parts per thousand (‰, also known as parts per mil). If fractionization of carbon occurred by biotic or abiotic degradation processes, then values of δC^{13} would increase (become less negative) within the test cells (USEPA, 2008).

Isotope ratios for TCE in the upgradient wells ranged from -25.09 to -27.73 ‰. Values of δC^{13} for TCE within Test Cell No. 1 increased from a pre-injection ratio of -25.94 ‰ to a maximum post-injection ratio of -18.91 ‰, indicating that active dechlorination of TCE was occurring. Values of δC^{13} for TCE within Test Cell No. 2 increased slightly from a pre-injection ratio of -26.76 ‰ to a maximum post-injection ratio of -23.51 ‰; this small increase does not provide substantial evidence of active dechlorination of TCE. Concentrations of TCE within Test Cell No. 3 were too low to obtain fractionization results.

3.4 RESULTS OF SOIL SAMPLING

As described in **Section 2.4.1**, select soil samples were collected from the three test cells and analyzed for iron and sulfide mineralogy by CDM using a SEM, and select samples were analyzed for mineral speciation (i.e., bulk iron and sulfide content) by Microseeps. The results of these analyses are summarized in this section. A more detailed report of the SEM analyses prepared by CDM, including SEM photographs, is provided in the supporting data package. The analytical data reports provided by Microseeps are also contained in the supporting data package.

3.4.1 Baseline Soil Characterization

Select soil samples collected during installation of monitoring points for Test Cell No. 2 and Test Cell No. 3 were submitted for analysis of VOCs by USEPA Method SW8260B (**Table 3.8**). The only chlorinated ethenes detected in soil were TCE and *cis*-DCE. The maximum concentrations of TCE and *cis*-DCE were 3.1 mg/kg and 0.95 mg/kg, respectively, with both detections from a sample collected at a depth of 28.5 to 29 feet bgs at boring DP98MW02 (located adjacent to monitoring point DP98MP02 in Test Cell No. 1).

Select soil samples were also submitted for analysis of total iron, phosphorous, and potassium by USEPA Method SW6010B (**Table 3.9**). Concentrations of total iron ranged from 23,800 to 26,000 mg/kg. Concentrations of this magnitude indicate that the sediments at the DP98 site have a high potential for iron reduction under anaerobic conditions, although not all the iron in the sediments is likely to be bioavailable. Potassium and phosphorus can be utilized as trace nutrients for biological processes. Concentrations of total potassium and total phosphorous ranged from 562 to 662 mg/kg and 502 to 955 mg/kg, respectively.

3.4.2 SEM Analyses

The primary objective of the iron/sulfate injections into Test Cells No. 2 and No. 3 was to stimulate the production of reactive iron-sulfide minerals that are strongly reduced and that facilitate the reduction of CAHs. Select soil samples were collected in September 2010 and

Table 3.7 Summary of Chlorinated Ethenes and Isotope Fractionization in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Location Description	Analysis (units) [b/]	Sample Date	Months from Injection	Dilution Factor	PCE [a/] (µg/L)		TCE [a/] (µg/L)		*cis* -1,2-DCE [a/] (µg/L)		VC [a/] (µg/L)	
Test Cell No. 1													
DP98MP01	Upgradient	APPL Laboratory VOCs (µg/L)	20-May-10	0	1	1.0	U [c/]	610		2,400		0.77	F [d/]
		VOCs with CSIA Screen (µg/L)	20-May-10	0	1/10/200	5.0	U	500		3,000		5.0	U
		Carbon Fractionization- $\delta^{13}C$ (‰)	20-May-10	0	1	NR [e/]		-26.30		-28.62		NR	
		APPL Laboratory VOCs (µg/L)	22-Sep-10	4	1	1.0	U	140		1,900		0.56	F
		VOCs with CSIA Screen (µg/L)	22-Sep-10	4	1/20	NA [f/]		200		3,000		1.0	J [g/]
		Carbon Fractionization- $\delta^{13}C$ (‰)	22-Sep-10	4	1	NA		-25.09		-24.83		NR	
		APPL Laboratory VOCs (µg/L)	17-May-11	11	1	1.0	U	100		7,754		1.9	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	1/100	NA		65		4,900		0.8	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		-27.39		-26.58		NR	
DP98MP02	Within Test Cell	APPL Laboratory VOCs (µg/L)	21-May-10	0	1	1.0	U	350		2,100		5.9	
		VOCs with CSIA Screen (µg/L)	21-May-10	0	1/10/100	5.0	U	300		3,000		5.0	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-May-10	0	1	NR		-25.94		-27.27		NR	
		APPL Laboratory VOCs (µg/L)	22-Sep-10	4	1	1.0	U	88		1,900		42	
		VOCs with CSIA Screen (µg/L)	22-Sep-10	4	1/40	NA		7.0		5,000		80	
		Carbon Fractionization- $\delta^{13}C$ (‰)	22-Sep-10	4	1	NA		NR		-24.81		-37.07	
		APPL Laboratory VOCs (µg/L)	17-May-11	11	1	1.0	U	5.6		2,080		385	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	1/10	NA		1.8	J	900		380	
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		-23.85		-25.53		-21.74	
DP98MP03	Within Test Cell	APPL Laboratory VOCs (µg/L)	21-May-10	0	1/200	1.0	U	290		1,900		11	
		VOCs with CSIA Screen (µg/L)	21-May-10	0	1	NA		NA		NA		NA	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-May-10	0	1	NA		NA		NA		NA	
		APPL Laboratory VOCs (µg/L)	22-Sep-10	4	1/400	1.0	U	5.7		2,600		34	
		VOCs with CSIA Screen (µg/L)	22-Sep-10	4	1/40	NA		50		4,000		60	
		Carbon Fractionization- $\delta^{13}C$ (‰)	22-Sep-10	4	1	NA		-18.91		-24.01		-35.31	
		APPL Laboratory VOCs (µg/L)	17-May-11	11	100	100	U	19.1		3,690		140	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	1/50	NA		3.7	J	1,700		120	
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		-28.26		-23.93		-31.32	
DP98MP04	Downgradient	APPL Laboratory VOCs (µg/L)	21-May-10	0	1/200	1.0	U	150		4,700		150	
		VOCs with CSIA Screen (µg/L)	21-May-10	0	1/10/200	5.0	U	100		5,000		80	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-May-10	0	1	NR		-28.23		-25.20		-28.66	
		APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1/400	1.0	U	69		3,700		210	F
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/40	NA		9		6,000		1,000	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		NR		-24.83		-28.79	
		APPL Laboratory VOCs (µg/L)	18-May-11	12	1	1.0	U	90		6,630		483	
		VOCs with CSIA Screen (µg/L)	18-May-11	12	1/25	5.0	U	40		3,100		390	
		Carbon Fractionization- $\delta^{13}C$ (‰)	18-May-11	12	1	NR		-26.22		-25.84		-31.98	

Table 3.7 Summary of Chlorinated Ethenes and Isotope Fractionization in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Location Description	Analysis (units) [b/]	Sample Date	Months from Injection	Dilution Factor	PCE [a/] (µg/L)		TCE [a/] (µg/L)		*cis* -1,2-DCE [a/] (µg/L)	VC [a/] (µg/L)	
Test Cell No. 2					1							
DP98MP05	Upgradient	APPL Laboratory VOCs (µg/L)	23-May-10	0	1	1.0	U	270		280	0.77	F
		VOCs with CSIA Screen (µg/L)	23-May-10	0	1/10	5.0	U	300		300	0.6	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-May-10	0	1	NR		-27.27		-25.23	NR	
		APPL Laboratory VOCs (µg/L)	22-Sep-10	4	20	20	U	430		610	20	U
		VOCs with CSIA Screen (µg/L)	22-Sep-10	4	1/10	NA		200		600	3.0	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	22-Sep-10	4	1	NA		-27.73		-25.24	NR	
		APPL Laboratory VOCs (µg/L)	18-May-11	12	1	1.0	U	306		1363	2.72	
		VOCs with CSIA Screen (µg/L)	18-May-11	12	1/10	5.0	U	140		620	1.2	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	18-May-11	12	1	NR		-27.17		-26.36	NR	
DP98MP06	Within Test Cell	APPL Laboratory VOCs (µg/L)	23-May-10	0	1	1.0	U	230		3,900	2.5	
		VOCs with CSIA Screen (µg/L)	23-May-10	0	10/100	50	U	200		5,000	50	U
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-May-10	0	1	NR		-26.76		-26.11	NR	
		APPL Laboratory VOCs (µg/L)	23-Sep-10	4	100	100	U	190		4,200	32	F
		VOCs with CSIA Screen (µg/L)	23-Sep-10	4	1/40	NA		100		5,000	110	
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-Sep-10	4	1	NA		-26.61		-25.90	-43.63	
		APPL Laboratory VOCs (µg/L)	18-May-11	12	1	1.0	U	5.94		3,790	26	
		VOCs with CSIA Screen (µg/L)	18-May-11	12	1/20	5.0	U	2.1	J	1,700	19	
		Carbon Fractionization- $\delta^{13}C$ (‰)	18-May-11	12	1	NR		NR		-26.40	-38.97	
DP98MP07	Within Test Cell	APPL Laboratory VOCs (µg/L)	23-May-10	0	1	1.0	U	200		3,100	1.3	
		VOCs with CSIA Screen (µg/L)	23-May-10	0	NA	NA		NA		NA	NA	
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-May-10	0	NA	NA		NA		NA	NA	
		APPL Laboratory VOCs (µg/L)	22-Sep-10	4	100	100	U	79		2,500	100	U
		VOCs with CSIA Screen (µg/L)	22-Sep-10	4	1/20	NA		40		2,000	80	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	22-Sep-10	4	1	NA		-27.78		-25.87	NR	
		APPL Laboratory VOCs (µg/L)	18-May-11	12	1	0.2	F	7.78		266	2.5	
		VOCs with CSIA Screen (µg/L)	18-May-11	12	1/5	5.0	U	3.4	J	310	1.6	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	18-May-11	12	1	NR		-23.51		-26.07	-37.34	
DP98MP08	Downgradient	APPL Laboratory VOCs (µg/L)	23-May-10	0	1/200	1.0	U	96		1,500	3.8	
		VOCs with CSIA Screen (µg/L)	23-May-10	0	1/100	5.0	U	200		2,000	4.0	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-May-10	0	1	NR		-24.74		-25.15	NR	
		APPL Laboratory VOCs (µg/L)	23-Sep-10	4	50	50	U	60		1,700	50	U
		VOCs with CSIA Screen (µg/L)	23-Sep-10	4	1/20	NA		20		2,000	30	
		Carbon Fractionization- $\delta^{13}C$ (‰)	23-Sep-10	4	1	NA		-20.51		-24.11	NR	
		APPL Laboratory VOCs (µg/L)	18-May-11	12	1	1.0	U	7.04		1,167	2.88	
		VOCs with CSIA Screen (µg/L)	18-May-11	12	1/10	5.0	U	2.5	J	360	1.5	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	18-May-11	12	1	NR		-24.02		-24.94	-32.69	

Table 3.7 Summary of Chlorinated Ethenes and Isotope Fractionization in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Location Description	Analysis (units) [b/]	Sample Date	Months from Injection	Dilution Factor	PCE [a/] (µg/L)		TCE [a/] (µg/L)		*cis* -1,2-DCE [a/] (µg/L)		VC [a/] (µg/L)	
Test Cell No. 3													
DP98MW-04	Upgradient	APPL Laboratory VOCs (µg/L)	24-May-10	0	1	1.8		2,400		3,100		1.0	
		VOCs with CSIA Screen (µg/L)	24-May-10	0	1/100	3.0	J	2,000		3,000		0.6	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	24-May-10	0	1	NR		-26.33		-25.98		NR	
		APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1	0.8	F	2,200		2,900		1.0	U
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/40	NA		2,000	B [h/]	4,000		1.0	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		-25.86		-25.54		NR	
		APPL Laboratory VOCs (µg/L)	17-May-11	11	1	1.6		2,850		3,900		2.6	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	1/50	NA		1,200		1,900		5.0	U
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		-26.93		-26.78		NR	
DP98INJ-01	Injection	APPL Laboratory VOCs (µg/L)	25-May-10	0	1	1.0	U	0.98		4,900		710	
		VOCs with CSIA Screen (µg/L)	25-May-10	0	1/20/200	5.0	U	2.0	J	20,000		500	
		Carbon Fractionization- $\delta^{13}C$ (‰)	25-May-10	0	1	NR		NR		-26.01		-30.77	
		APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1	1.0	U	13.0		1,800		510	
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/40	NA		7.0		3,000		2,000	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		NR		-24.87		-23.94	
DP98INJ-02	Injection	APPL Laboratory VOCs (µg/L)	24-May-10	0	1	0.6	F	1.4		7,100		73	M [i/]
		VOCs with CSIA Screen (µg/L)	24-May-10	0	1/200	5.0	U	3.0	J	30,000		50	
		Carbon Fractionization- $\delta^{13}C$ (‰)	24-May-10	0	1	NR		NR		-25.51		-50.92	
		APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1	1.0	U	3.4		2,700		67	
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/40	NA		1.0	J	3,000		130	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		NR		-25.24		-30.96	
		APPL Laboratory VOCs (µg/L)	17-May-11	11	1	1.0	U	25		10,110		196	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	5/50	NA		26		4,400		140	
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		NR		-26.13		-36.98	
DP98INJ-03	Injection	APPL Laboratory VOCs (µg/L)	25-May-10	0	1	1.0	U	3.2		6,500		75	
		VOCs with CSIA Screen (µg/L)	25-May-10	0	1/200	5.0	U	6.0		20,000		60	
		Carbon Fractionization- $\delta^{13}C$ (‰)	25-May-10	0	1	NR		NR		-25.46		-43.77	
		APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1	1.0	U	3.9		1,000		260	
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/20	NA		3.0	J	1,000		1,000	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		NR		-24.04		-19.87	

Table 3.7 Summary of Chlorinated Ethenes and Isotope Fractionization in Groundwater

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Location Description	Analysis (units) [b/]	Sample Date	Months from Injection	Dilution Factor	PCE [a/] (µg/L)		TCE [a/] (µg/L)		*cis* -1,2-DCE [a/] (µg/L)		VC [a/] (µg/L)	
DP98MW-05	Downgradient	APPL Laboratory VOCs (µg/L)	24-May-10	0	1	0.2	F	45		8,200		45	
		VOCs with CSIA Screen (µg/L)	24-May-10	0	1/200	5.0	U	90		30,000		20	
		Carbon Fractionization- $\delta^{13}C$ (‰)	24-May-10	0	1	NR		-27.07		-25.99		-40.26	
		APPL Laboratory VOCs (µg/L)	20-Sep-10	4	1	1.0	U	3.3		8,600		41	
		VOCs with CSIA Screen (µg/L)	20-Sep-10	4	1/100	NA		4.0	J	20,000		200	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	20-Sep-10	4	1	NA		NR		-26.43		-36.91	
		APPL Laboratory VOCs (µg/L)	16-May-11	11	<100	100	U	48		14,600		56	
		VOCs with CSIA Screen (µg/L)	16-May-11	11	1/100	NA		21		6,500		36	
		Carbon Fractionization- $\delta^{13}C$ (‰)	16-May-11	11	1	NA		-24.34		-28.30		-34.45	
DP98MW-06	Downgradient	APPL Laboratory VOCs (µg/L)	24-May-10	0	1	1.0	U	2.6		4,200		40	
		VOCs with CSIA Screen (µg/L)	24-May-10	0	1/200	5.0	U	3.0	J	8,000		40	
		Carbon Fractionization- $\delta^{13}C$ (‰)	24-May-10	0	1	NR		-23.36		-26.41		-31.60	
		APPL Laboratory VOCs (µg/L)	20-Sep-10	4	1	1.0	U	3.9		5,000		49	
		VOCs with CSIA Screen (µg/L)	20-Sep-10	4	1/100	NA		5.0	J	7,000		200	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	20-Sep-10	4	1	NA		NR		-25.85		-24.59	
		APPL Laboratory VOCs (µg/L)	16-May-11	11	1	1.0	U	44		7,080		52	
		VOCs with CSIA Screen (µg/L)	16-May-11	11	1/100	NA		23		3,500		30	
		Carbon Fractionization- $\delta^{13}C$ (‰)	16-May-11	11	1	NA		-25.37		-27.31		-27.44	
QA/QC													
DP98MP24	Duplicate DP98MP04	APPL Laboratory VOCs (µg/L)	21-May-10	0	1	NA		NA		NA		NA	
		VOCs with CSIA Screen (µg/L)	21-May-10	0	1/10/200	5.0	U	100		5,000		20	J
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-May-10	0	1	NR		-27.73		-25.07		-28.67	
DP98INJ-22	Duplicate DP98INJ-02	APPL Laboratory VOCs (µg/L)	21-Sep-10	4	1	1.0	U	2.20		2,600		66	
		VOCs with CSIA Screen (µg/L)	21-Sep-10	4	1/20	NA		2.00	J	3,000		120	
		Carbon Fractionization- $\delta^{13}C$ (‰)	21-Sep-10	4	1	NA		NR		-25.39		-29.66	
DP98MW-04-FD	Duplicate DP98MW-04	APPL Laboratory VOCs (µg/L)	17-May-11	11	1	1.6		2,930		3,940		1.50	
		VOCs with CSIA Screen (µg/L)	17-May-11	11	1/50	NA		1,200		1,900		5.0	U
		Carbon Fractionization- $\delta^{13}C$ (‰)	17-May-11	11	1	NA		-26.98		-26.78		NR	

[a/] PCE = tetrachloroethene, TCE = trichloroethene, DCE = dichloroethene, VC = vinyl chloride.

[b/] µg/L = micrograms per liter; $\delta^{13}C$ (‰) = a measure of the ratio of stable isotopes ^{13}C : ^{12}C, reported in parts per thousand (per mil ‰).

[c/] U-flag indicates the concentration is below the indicated laboratory reporting limit.

[d/] F-flag indicates the concentration is below the laboratory reporting limit but above the method detection limit, and the concentration is estimated.

[e/] NR = the compound was not detected by the isotope ratio mass spectrometer.

[f/] NA = not analyzed.

[g/] J-flag indicates the analyte was positively identified, but the quantitation is an estimation due to discrepancies in meeting certain analyte-specific quality control criteria.

[h/] B-flag indicates the analyte was detected in the method blank.

[i/] M-flag indicates the concentration is estimated due to a matrix effect.

Table 3.8 Summary of Volatile Organic Compounds Detected in Soil

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Percent Moisture (%)	PCE[a/] (mg/kg)[b/]	TCE[a/] (mg/kg)	*cis* -1,2-DCE[a/] (mg/kg)	*trans* -1,2-DCE (mg/kg)	1,1-DCE (mg/kg)	VC[a/] (mg/kg)	n-Butyl benzene (mg/kg)	sec-Butyl benzene (mg/kg)
Test Cell No. 1											
DP98MW10/24.0-24.5	DP98MP10	18-May-10	9.1	<0.0055 [c/]	0.63	0.16	<0.0110	<0.0170	<0.0110	0.017 F [d/]	0.010 F
DP98MW10/24.5-25.0	DP98MP10	18-May-10	9.8	<0.0055	0.62	<0.0110	<0.0110	<0.0170	<0.0110	<0.0055	<0.0055
DP98MW07/25.0-25.5	DP98MP07	18-May-10	8.3	<0.0055	<0.0110	<0.0110	<0.0110	<0.0160	<0.0110	<0.0055	<0.0055
DP98MW02/28.5-29.0	DP98MP02	19-May-10	7.3	<0.0024	3.1	0.95	<0.0047	<0.0071	<0.0047	<0.0024	0.019 F

[a/] PCE = tetrachloroethene, TCE = trichloroethene, DCE = dichloroethene, VC = vinyl chloride.

[b/] mg/kg = milligram(s) per kilogram.

[c/] less than (<) indicates the concentration is below the indicated laboratory method detection limit (MDL).

[d/] F-flag indicates the concentration is below the laboratory reporting limit but above the MDL, and the concentration is estimated.

Table 3.9 Summary of Iron, Potassium and Phosphorous in Soil

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Identification	Sampling Location	Sample Date	Percent Moisture (%)	Total Iron (mg/kg)[a/]	Total Phosphorous (mg/kg)	Total Potassium (mg/kg)
Test Cell No. 1						
DP98MW10/24.0-24.5	DP98MP10	18-May-10	9.1	25,200	526	573
DP98MW10/24.5-25.0	DP98MP10	18-May-10	9.8	23,800	502	562
DP98MW07/25.0-25.5	DP98MP07	18-May-10	8.3	26,000	526	611
DP98MW02/28.5-29.0	DP98MP02	19-May-10	7.3	25,700	955	662

[a/] mg/kg = milligram(s) per kilogram.

analyzed by CDM using a SEM at the University of Colorado in Boulder (see supporting data package for full report). The reduced iron phases identified in the DP98 samples included hematite (Fe2O3), magnetite (Fe3O4), and pyrite (FeS2). A summary of the identified reduced iron phases is presented in **Table 3.10**.

Table 3.10 Summary of Reduced Iron Phases in DP98 Samples Analyzed by Scanning Electron Microprobe

Sample ID	Sample Location	Phase and Association
DP98SB04/25-25.5	Test Cell No. 1	A single grain of pyrite measuring 1 by 6 microns (μm).
DP98SB05/24.5-25	Test Cell No. 1	Hematite and magnetite. No iron sulfide grains were found.
DP98SB01/26-27	Test Cell No. 2	Hematite and magnetite. No iron sulfide grains were found.
DP98SB02/25-26	Test Cell No. 2	Hematite and magnetite. No iron sulfide grains were found.
DP98SB07/26-26.5	Test Cell No. 3	Large crystalline pyrite grains
DP98SB08/27-29	Test Cell No. 3	Large, partially oxidized, crystalline pyrite grains.

An example of a ~10 micron (μm) diameter hematite grain is shown on **Figure 3.6** for a sample from within Test Cell No. 2. The iron and oxygen concentrations of the phase (70% iron and 30% oxygen) are very close to the stoichiometric concentrations for pure hematite. In addition, the grain size is similar to that of the hematite powder that was injected. Therefore, it is likely that much of the hematite observed in the soil samples was from the injection and had not reacted with any sulfides as of the September 2010 sampling event (3.5 months post-injection). Crystalline magnetite grains were also observed that also had oxygen and iron concentrations that are very close to the stoichiometric amounts for pure magnetite (72% iron and 28% oxygen). Magnetite at the site could have been naturally occurring (i.e., deposited with the sediment) or produced by post-depositional biogenic processes.

Iron sulfide grains were present, but were relatively scarce. These grains were large, crystalline, and partially oxidized. An example of a partially oxidized pyrite grain is shown on **Figure 3.7** for a soil sample from Test Cell No. 3. The grain is 5 to 10 μm thick with a rind of partially oxidized iron disulfide. The rind contained 40.6% iron, 27% oxygen, and 28.8% sulfur, which corresponds to a formula of $FeS_{1.2}O_{2.3}$. However, the interior of the grain had a composition consistent with pyrite (FeS_2).

Pyrite is a relatively stable, and potentially less reactive, iron-sulfide mineral that is not the optimal mineral form for biogeochemical transformation of CAHs. The oxidized nature of some of the pyrite grains suggests that any iron-monosulfide (FeS) minerals produced were not stable and were oxidized to iron disulfides (FeS_2 – pyrite). The size of the pyrite grains that were observed were coarse, ranging from 6 to 50 μm in diameter. The coarse and crystalline nature of the grains suggests that the groundwater system was relatively stagnant (low rates of groundwater flow and mixing), and that crystal growth was favored over nucleation of smaller grains or crystals.

Past researchers have specifically investigated the reductive reactivity of reduced iron minerals such as pyrite. They demonstrated that a suspension of pyrite was able to dechlorinate carbon tetrachloride (Kriegman-King and Reinhard, 1994) and reduce dinitrotoluene (DNT)

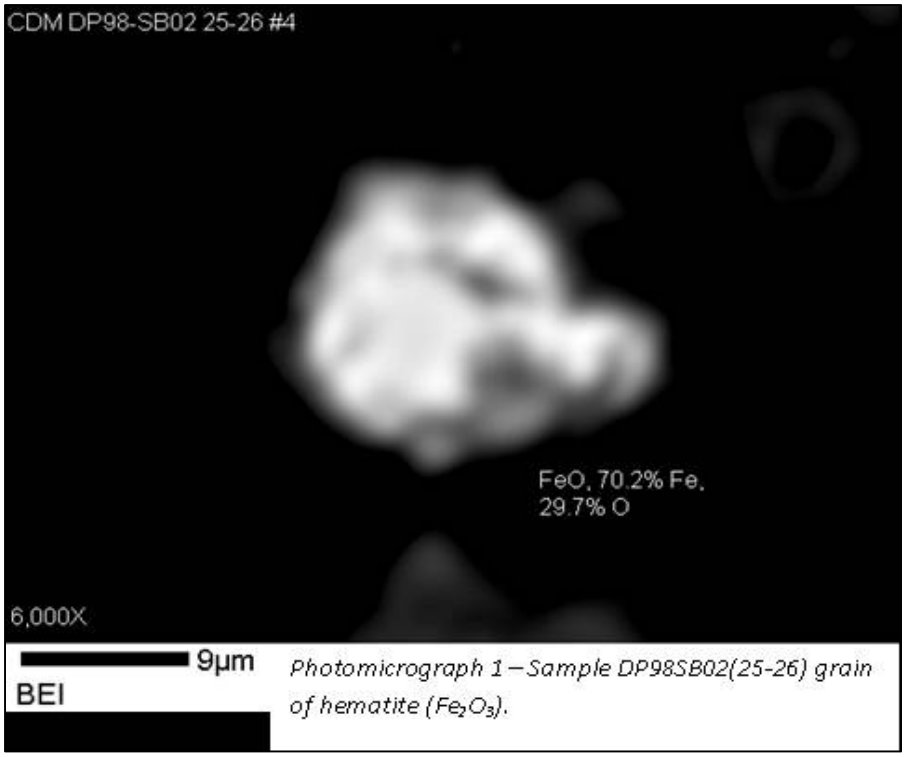

Figure 3.6 Hematite Grain from Test Cell No. 2 Soil Sample

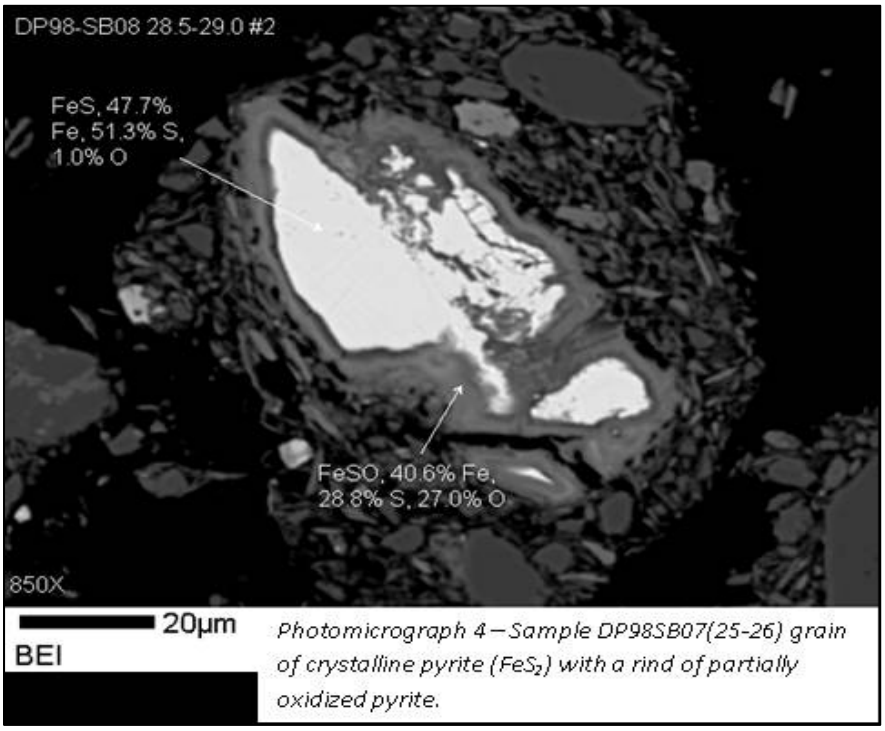

Figure 3.7 Partially Oxidized Pyrite Grain from Test Cell No. 3

(Jiayang *et al*., 1996). Attendees at a workshop on *in situ* biogeochemical transformation of chlorinated solvents (Becvar *et al*., 2008) concurred that pyrite could play a role in biogeochemical transformation of these compounds. Lee and Batchelor (2002) also observed measurable dechlorination rates for PCE, *cis*-DCE, and VC by reaction with pyrite. Therefore, biogeochemical transformation of CAHs in the presence of pyrite may still be an environmentally significant process.

3.4.3 Analysis of Iron and Sulfide in Soil

Soil samples were collected in May 2010, prior to the test cell injections, and again in September 2010 approximately 3.5 months after the injections. These samples were analyzed to evaluate the potential for production of reduced iron sulfides. The following paragraphs describe these analyses (from Appendix D of AFCEE, 2008). Additional descriptions can be found in AFCEE (2002), Kennedy *et al.* (1999), Wilkin (2003), and Wilkin and Bischoff (2006).

Bioavailable ferric iron (Fe^{3+}) and manganese (Mn^{4+}) are measures of iron and manganese that can be utilized as electron acceptors for microbially mediated iron and manganese reduction. Bioavailable ferric iron may be measured with a bioassay test (New Horizons test kit; Evans and Koenigsberg, 2001) that estimates the concentration of bioavailable ferric iron in a soil sample from biogenic ferrous iron (Fe^{2+}) created by the microbial reduction of ferric iron. Experience has shown that concentrations detected using the bioavailable ferric iron assay test are higher than detected using a weak acid extraction, indicating that the bioassay test may be a better indicator of bioavailable iron concentrations. Oxidized iron was also calculated by Microseeps when conducting the bioavailable iron assay. Any increase in ferric iron over the incubation period may result from oxidation of biogenic ferrous iron. If this occurs, it is reported as oxidized iron. The sum of the bioavailable ferric iron and oxidized iron concentrations is an approximation of the 'total' concentration of bioavailable ferric iron in the sediment sample.

Strong acid extractable (SAE) iron and manganese represents iron and manganese extracted by strong acid solution as an estimate of the total amount present in soils. The SAE extracts a greater quantity of native iron and manganese in sediments than a weak acid extraction or a bioavailable iron assay. Comparing the ratio of Fe^{2+} to Fe-total between the SAE and bioavailable iron may aid in differentiating zones where Fe^{3+} reduction has occurred (AFCEE, 2002). Microbial Fe^{3+} reduction often only converts a small amount of the total Fe present in sediment to Fe^{2+}.

Acid volatile sulfide (AVS) and **chromium reducible sulfur (CRS)** are indicative of the amount of reduced metal sulfides in the sediment. In particular, the sulfide in iron mono-sulfide (FeS) is most susceptible to AVS extraction; therefore, AVS is often used as an approximation of the amount of FeS present in the sediment. CRS is an indicator of the fraction of total mineral sulfides that is reducible by chromium solution. When CRS extraction is performed following AVS extraction, then CRS is an indication of iron disulfide (FeS_2) and elemental sulfur (S^o) remaining in the sediment sample. If CRS extraction follows AVS extraction, then the concentration of AVS plus the concentration of CRS can be used to yield a total sulfide mineral mass number. Because minerals extracted by the AVS method are reduced and reactive, they typically do not persist for long periods of time in the subsurface environment and the presence of AVS is used as a general indicator of recent sulfate reduction. High CRS concentrations relative to AVS concentrations suggests older microbial activity or an increase in the oxidation potential of the groundwater. Therefore, environments rich in AVS relative to CRS may indicate recent or ongoing iron- and sulfate-reducing processes.

The mineral speciation results provided by Microseeps are summarized in **Table 3.11**. Samples collected ***prior*** to the injections had the following characteristics:

- Bioavailable ferric iron (Fe^{3+}) averaged 783 mg/kg, and SAE ferric iron averaged 5,447 mg/kg. Compared to an average concentration of SAE ferrous iron of 6,060 mg/kg, a significant proportion of bioavailable ferric iron had already been reduced at the site.
- Concentrations of AVS and CRS both averaged 493 mg/kg for the baseline soil samples, with less variability than the iron concentrations. The concentration of AVS suggests that production of more reduced iron sulfide minerals has occurred in the recent past (possibly a result of a fuel release at the site).

Samples collected in September 2010, approximately 3.5 months ***after*** the injections, had the following characteristics:

- Average concentrations of bioavailable ferric iron (Fe^{3+}) increased relative to baseline concentrations. Concentrations of bioavailable iron were the highest in Test Cell No. 1, averaging 1,857 mg/kg. This could be a result of the ZVI injected in the EHC® product. The average concentration of bioavailable iron in Test Cell No. 2 was 856 mg/kg, which is likely a result of injecting ferric iron oxide in the form of hematite. Bioavailable iron was also relatively high in the samples from Test Cell No. 3, averaging 1,543 mg/kg. This was not anticipated because the iron product injected was soluble ferrous iron, and native iron in this area should have been greatly reduced during the prior bioremediation pilot test.
- Concentrations of SAE ferric iron were variable, but average concentrations increased in Test Cells No. 1 and No. 2 relative to baseline concentrations. A greater increase in average SAE ferrous iron concentrations relative to the average baseline concentration was observed. Average concentrations of SAE ferrous iron increased from 6,060 mg/kg in baseline samples to 18,200 mg/kg in Test Cell No. 1, 10,913 mg/kg in Test Cell No. 3, and 8,637 mg/kg in Test Cell No. 2. Thus, most iron in the post-injection soil samples was present as ferrous iron relative to ferric iron.
- Average concentrations of AVS and CRS in Test Cells No. 1 and No. 3 increased after injection, but did not increase in Test Cell No. 2. The highest post-injection concentration of AVS was 841 mg/kg in the sample collected at a depth of 26.5 feet in Test Cell No. 3. Similar increases in the average concentrations of CRS were observed in Test Cells No. 1 and No. 3. An increase in the average concentration of CRS in Test Cell No. 2 was also observed, suggesting that any iron sulfide minerals produced in that test cell were oxidized to iron disulfide (pyrite).

In theory, sufficient iron and sulfate amendments were added to Test Cell No. 2 and Test Cell No. 3 in May 2010 to produce approximately 2,000 mg/kg of FeS. The target concentration of AVS (2,000 mg/kg) was not achieved in any of the post-injection soil samples, and only moderate increases in concentrations of AVS were observed in Test Cell No. 1 and Test Cell No. 3. The combined average concentration of AVS and CRS in baseline samples was 986 mg/kg. The combined average AVS + CRS concentrations in post-injection samples were 1,293 mg/kg in Test Cell No. 1 (an increase of 31%), 911 mg/kg in Test Cell No. 2 (no increase), and 1,455 mg/kg in Test Cell No. 3 (48% increase). Therefore, only a modest increase in iron sulfides was observed.

It should be noted that the soil cores from the DP98 site showed a high degree of heterogeneity, and it was not possible to isolate thin layers of permeable sediment or fracture zones in the field without losing sample integrity. Therefore, it is difficult to assess whether these soil results are representative of changes in mineral composition that may have occurred in more permeable sediments where the amendments were preferentially distributed.

Table 3.11 Summary of Iron and Sulfide Soil Analytical Results

Demonstration of Biogeochemical Transformation, DP98, JBER, Alaska

Sample Location	Test Cell	Sample Date	Sample Depth (feet bgs) [a/]	Percent Solids	Bio Fe^{3+} [c/] (mg/kg) [b/]	Bio Mn [c/] (mg/kg)	Oxidized Iron (mg/kg)	SAE Fe^{3+} [c/] (mg/kg)	SAE Fe^{2+} [c/] (mg/kg)	SAE Mn [c/] (mg/kg)	AVS [c/] (mg/kg)	CRS [c/] (mg/kg)
Baseline Sampling Event - May 2010												
DP98MW02	Test Cell No. 1	19-May-10	28.0-28.5	91%	847 BM [d/]	31.3	21.0	4,090	2,920	NA [e/]	430 B	450 B
DP98MW07	Test Cell No. 2	18-May-10	25.5-26.0	90%	<5.6 BM [f/]	<5.6	8.6	8,240	11,200	NA	520 B	560 B
DP98MW10	Downgradient	18-May-10	24.5-25.0	90%	1,500 BM	10.3	11.2	4,010	4,060	NA	530 B	470 B
			Averages		**783**	**15**	**14**	**5,447**	**6,060**	**NA**	**493**	**493**
Second Sampling Event - September 2010												
DP98SB05/23.5	Test Cell No. 1	20-Sep-10	23.5	99%	1,860 BM	51.1	<5.0 B	9,310	11,400	385	612	666
DP98SB04/25.5	Test Cell No. 1	20-Sep-10	25.5	90%	2,390 BM	52.7	268 B	1,350	30,800	401	699	496
DP98SB04/26.5	Test Cell No. 1	20-Sep-10	26.5	91%	1,320 BM	40.8	260 B	9,620	12,400	387	752	654
			Averages		**1,857**	**48**	**177**	**6,760**	**18,200**	**391**	**688**	**605**
DP98SB01/25.5	Test Cell No. 2	20-Sep-10	25.5	92%	955 BM	33.7	<5.4 B	5,520	4,560	268	<108.7	485
DP98SB01/27.0	Test Cell No. 2	20-Sep-10	27.0	92%	830 BM	8.8	8.8 B	2,980	5,950	211	476	765
DP98SB02/24.5	Test Cell No. 2	20-Sep-10	24.5	90%	784 BM	<5.6	<5.6 B	12,900	15,400	352	392	559
			Averages		**856**	**15**	**4.6**	**7,133**	**8,637**	**277**	**308**	**603**
DP98SB07/25.0	Test Cell No. 3	20-Sep-10	25.0	94%	1,460 BM	45.6	180 B	2,570	3,640	169	602	738
DP98SB07/26.5	Test Cell No. 3	20-Sep-10	26.5	90%	1,650 BM	202.0	<5.6 B	5,990	11,900	436	841	722
DP98SB08/27.5	Test Cell No. 3	20-Sep-10	27.5	91%	1,520 BM	41.3	128 B	4,820	17,200	437	751	712
			Averages		**1,543**	**96**	**103**	**4,460**	**10,913**	**347**	**731**	**724**

[a/] feet bgs = feet below ground surface.

[b/] mg/kg = milligram(s) per kilogram, dry weight.

[c/] Bio Fe^{3+} = bioavailable ferric iron; Bio Mn = bioavailable manganese; SAE = strong acid extractable ferric iron, ferrous iron, or manganese; AVS = acid volatile sulfide; CRS = chromium reducible sulfide.

[d/] B-flag indicates analyte was detected in the sample blank; M-flag indicates recovery/Relative Percent Difference (RPD) poor for Matrix Spike/Matrix Spike Duplicate (MS/MSD).

[e/] NA = not analyzed.

[f/] "<" indicates the concentration is below the indicated laboratory method detection limit.

4.0 DISCUSSION AND CONCLUSIONS

The primary objective of the DP98 technology demonstration was to determine the extent to which biogeochemical transformation processes can be used to reduce concentrations of CAHs in groundwater to levels protective of human health and the environment. Performance metrics were developed to measure and evaluate the ability of engineered biogeochemical transformation to increase rates of contaminant degradation and to reduce concentrations of CAHs in groundwater.

Iron, sulfate, and organic amendments were injected into two shallow subsurface treatment zones in May 2010 (Test Cells No. 1 and No. 3), and a commercial ISCR product was injected into Test Cell No. 3. Soil and groundwater samples were collected before and after injection of the amendments. The following sections summarize monitoring results for the two test cells.

4.1 MONITORING RESULTS

4.1.1 Impact of Injections on Groundwater Biogeochemistry

The injection of organic substrates increased concentrations of DOC, but differences in the magnitude of DOC concentrations in the three test cells were observed. DOC concentrations were the highest in Test Cell No. 1 amended with EHC®, and lowest in Test Cell No. 2 amended with hematite, gypsum, and EVO. The presence of low concentrations of DO, low ORP, neutral pH, and elevated concentrations of dissolved methane indicate that redox conditions in all three test cells were conducive to anaerobic degradation of CAHs. However, the higher concentrations of DOC in Test Cells No. 1 and No. 3 stimulated greater biotic reductive dechlorination relative to biogeochemical transformation processes.

The EHC® product injected into Test Cell No. 1 caused an increase in DOC and more reducing conditions, as expected. Concentrations of ferrous iron increased substantially within Test Cell No. 1, to greater than 66 mg/L in September 2010. This is likely due to reduction of native iron and possibly oxidation of the ZVI in the product.

The injection of calcium sulfate (gypsum) into Test Cell No. 2 was anticipated to immediately increase the concentration of sulfate in groundwater. Sulfate increased after injection to a maximum of 2,530 mg/L in September 2010, and subsequently decreased indicating that sulfate reduction occurred. Concentrations of sulfide were as high as 8.8 mg/L at DP98MP07. A strong hydrogen sulfide odor was observed in the field, confirming that sulfate reduction was stimulated. Concentrations of ferrous iron also increased to a maximum of 33 mg/L at DP98MP06 in May 2011. This suggests that the iron hematite and/or native iron were reduced. Together, these processes indicate a strong potential for the formation of reduced iron sulfide minerals in Test Cell No. 2.

The injection of soluble ferrous sulfate into Test Cell No. 3 was anticipated to immediately increase the concentrations of sulfate and ferrous iron in groundwater. For example, the concentration of sulfate increased to 1,160 mg/L at DP98INJ-02 in September 2010 and subsequently decreased to 27.6 mg/L in September 2011. The highest concentrations of sulfide detected during the demonstration were in Test Cell No. 3, a strong indication that sulfate reduction was stimulated. Concentrations of ferrous iron remained very high at Test Cell No. 3 (i.e., greater than 66 mg/L at all three injection wells in September 2011), an indication that an excess of ferrous iron was present over the course of the demonstration.

4.1.2 Impact of Injections on CAHs in Groundwater

Degradation patterns for TCE, DCE, and VC within the three test cells indicate that both biotic sequential dechlorination and abiotic biogeochemical transformation processes occurred, as summarized below:

- **Test Cell No. 1:** A substantial increase in VC indicates that biotic dechlorination of TCE to DCE and DCE to VC was the primary transformation process stimulated by the injection of EHC®. The production of ethene towards the end of the monitoring period indicates that dechlorination of VC to ethene occurred, but not at a rate sufficient to prevent the accumulation and persistence of VC.
- **Test Cell No. 2:** Concentrations of TCE and DCE consistently decreased from one monitoring event to the next, with only a slight increase in VC and no production of ethene. These trends suggest an abiotic degradation pathway for TCE and DCE that produced little VC or ethene.
- **Test Cell No. 3:** Concentrations of DCE in Test Cell No. 3 were variable, but overall decreased by about 67% from May 2011 to September 2011. A substantial increase in VC was observed, indicating that biotic dechlorination to VC was a primary degradation pathway. Little ethene was produced, suggesting that biotic dechlorination stalled at VC. However, an overall decrease in the total molar CAH concentration of 36% suggests that some abiotic degradation of DCE occurred. Therefore, both biotic and abiotic degradation processes were enhanced in Test Cell No. 3.

4.1.3 Soil Analyses

In theory, sufficient iron and sulfate amendments were added to Test Cells No. 2 and No. 3 in May 2010 to produce approximately 2,000 mg/kg of FeS. The target concentration of AVS (2,000 mg/kg) was not achieved for any of the post-injection soil samples, and increases in concentrations of AVS relative to pre-injection conditions were only observed in Test Cell No. 1 and Test Cell No. 3. The combined average concentrations of AVS and CRS in baseline samples from the three test cells was 986 mg/kg. The combined average concentration in post-injection samples was 1,293 mg/kg in Test Cell No. 1 (an increase of 31%), 911 mg/kg in Test Cell No. 2 (no increase), and 1,455 mg/kg in Test Cell No. 3 (a 48% increase). Therefore, only a modest increase in total iron sulfides was observed for Test Cell No. 1 and Test Cell No. 3.

The results of the SEM evaluation and mineral speciation results were internally consistent and suggest that any reduced iron mono-sulfide minerals (FeS) that were produced were subsequently oxidized to the more stable, less reactive forms of pyrite (FeS_2). However, pure hematite grains were observed in Test Cell No. 2. This suggests that reduction of iron and subsequent formation of reduced iron sulfide minerals had not progressed within the 3.5-month period following injection when the soil samples were collected, to the extent that an increase in AVS or CRS could measured.

4.2 CONCLUSIONS

The degree to which the demonstration performance metrics were met at the three test cells is summarized in **Table 4.1**. The most promising results were observed at Test Cell No. 2, where a combination of natural hematite iron powder, powdered calcium sulfate, and a buffered EVO product were injected. Test Cell No. 2 exhibited a 61 % decrease in the average total molar concentration of CAHs within the test cell, substantially higher than the other two test cells. However, analysis of soil collected from Test Cell No. 2 did not show an increase in AVS at 3.5

Table 4.1 Comparison of Demonstration Results to Performance Metrics

Performance Metric	Test Cell No. 1 (EHC®)	Test Cell No. 2 (Hematite + Gypsum + EVO)	Test Cell No. 3 (Ferrous Sulfate + EVO)
Generate at least 2,000 mg/kg of AVS within the treatment zone	Not applicable – Used EHC® for comparison	Not achieved (average AVS concentration = 308 mg/kg)	Not achieved (average AVS concentration = 731 mg/kg)
Enhance the rates of *in situ* anaerobic degradation of TCE and *cis*-DCE by at least 1 order of magnitude relative to rates of natural attenuation at the site	Achieved	Achieved	Achieved
Reduce concentrations of TCE in the reaction zone to less than 5 µg/L, and limit increases in DCE and VC	Achieved for TCE and *cis*-DCE but not for VC	Achieved	TCE < 5 µg/L prior to injection; achieved for *cis*-DCE but not for VC
Reduce total molar concentrations of CAHs within the reaction zone by at least 90%	Not achieved (increased by 45%)	Not achieved (decreased by 61%)	Not achieved (decreased by 36%)

months after injection. The presence of hematite grains in Test Cell No. 2 at 3.5 months post-injection suggests the process was ongoing. The rate of dechlorination of TCE and DCE at Test Cell No. 2 increased after the 3.5-month sample event. Therefore, the concentrations of AVS and CRS may not be representative of the extent to which the formation of iron sulfide minerals was ultimately achieved.

Results for Test Cell No. 1 (EHC®) and Test Cell No. 3 (soluble ferrous sulfate and buffered EVO) indicate that sequential biotic dechlorination occurred, with a significant accumulation of VC. This may be a result of higher concentrations of DOC in these two test cells, which may have preferentially stimulated biotic dechlorination relative to abiotic dechlorination by biogeochemical transformation. Ethene was produced, indicating the potential for sequential biotic dechlorination to go to completion. However, the low concentrations of *Dehalococcoides* measured in groundwater, and the relatively slow rate at which VC is transformed to ethene, raises concern whether sequential biotic dechlorination can be an effective remedy at cold temperature sites like DP98.

The results of the SEM evaluation and mineral speciation analyses suggest that any reduced iron sulfide minerals that were produced were oxidized to more stable, less reactive forms of pyrite. The rate at which biogeochemical processes produce iron sulfide minerals from the amendments injected is not well understood. The presence of hematite grains in Test Cell No. 2 at 3.5 months post-injection suggests the process was ongoing, with the potential for greater concentrations of iron sulfide to be produced over time.

While engineered biogeochemical transformation shows promise for remediation of chlorinated solvents in groundwater, particularly for sites with chlorinated ethenes where sequential biotic dechlorination stalls at DCE or VC, challenges to successful implementation of the technology remain. Based on the observations from this demonstration, future applications of engineered biogeochemical transformation should consider the following:

- Over-stimulation of biological processes (e.g., resulting from concentrations of DOC over 100 to 200 mg/L) may favor biotic dechlorination processes over abiotic biogeochemical processes.
- Additional research is needed to understand the rates at which sulfate and iron reduction occur, and the rates at which iron sulfide minerals are formed. Engineered designs should consider the bioavailability of differing iron and sulfate products, and the impact of groundwater flow, mixing, and temperature on the rates of the individual biogeochemical processes that lead to formation of reduced iron sulfide minerals.
- Soluble forms of iron and sulfate may migrate out of the treatment zone before they are utilized. Groundwater flow should be evaluated to determine if multiple injections of iron and sulfate amendments are necessary; for example, at sites where the rate of groundwater flow exceeds 0.2 to 0.5 foot per day.
- Iron or sulfate may become a limiting factor depending on the rate at which the amendments are utilized and the quantities of native iron and sulfate present. Groundwater monitoring may be useful to determine appropriate modifications to the ratio of iron and sulfate amendments for sites where multiple injections are used.
- Uniform distribution of iron and sulfate amendments is a challenge at low permeability or highly heterogeneous sites. Alternative distribution methods such as those employing groundwater re-circulation may provide better distribution.
- The ability to differentiate between abiotic and biotic dechlorination processes is difficult given conventional monitoring tools. Better tools are needed to fully understand the complex biological and chemical processes that occur in the subsurface when attempting to engineer the production of reactive iron sulfide minerals.

It is anticipated that future research and field experience with biogeochemical transformation processes will lead to a more robust understanding of how to optimally engineer and implement the technology.

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ATTACHMENT A
DESIGN CALCULATIONS

Rev	Date	By	Check	Subject
0	30-Mar-10	BMH	JRH	Design Calculations
				Biogeochemical Transformation Demonstration
				Project Location: DP98, Elmendorf AFB, Alaska

Note: Shaded cells are user input

1 Calculate Percent Reduction Desired

Influent Concentration (C_o) =	**3,000**	µg/L
Target Concentration (C_t) =	**30.0**	µg/L
Percent Reduction =	**99.000%**	percent

2 Bulk Density of the Reaction Zone

Bulk Density of Soil =	**1.68**	gm/cm^3	=	**1,680**	kg/m^3

3 Pore Volume

Effective Porosity =	22%
Total Porosity =	30%
Percent Solids =	70%
Liters per m^3 =	1,000
Liters Pore Water/m^3 =	300

The solution to the first order decay rate is:

$C_t = C_o e^{-(kt)}$

4 Calculate Rates (per day) Given Initial AVS Concentration (rates from Shen and Wilson, 2007)

Enter mg/kg AVS	mg AVS/m^3	gm AVS/liter pore water	moles AVS/liter pore water	Rate at 0.53 per mole AVS per day	Rate at 2.3 per mole AVS per day
500	840,000	2.8	0.08725	0.046	0.201
1000	1,680,000	5.6	0.17451	0.092	0.401
1500	2,520,000	8.4	0.26176	0.139	0.602
2000	3,360,000	11.2	0.34902	0.185	0.803
3000	5,040,000	16.8	0.52353	0.277	1.204

5 Calculate Percent Reduction Given Residence Time and Using Lower Rate

mg/kg AVS	Initial TCE Concentration (µg/L)	Rate (per day)	Days (t)	Concentration of TCE at Day t	Percent Reduction
500	3,000	0.046	36.0	568	81.077%
1000	3,000	0.092	36.0	107	96.419%
1500	3,000	0.139	36.0	20	99.322%
2000	**3,000**	**0.185**	**36.0**	**4**	**99.872%**
3000	3,000	0.277	36.0	0	99.995%

6 Calculate Percent Reduction Given Residence Time and Using Upper Rate

mg/kg AVS	Initial TCE Concentration (µg/L)	Rate (per day)	Days (t)	Concentration of TCE at Day t	Percent Reduction
500	3,000	0.201	36.0	2	99.927%
1000	**3,000**	**0.401**	**36.0**	**0.0**	**100.000%**
1500	3,000	0.602	36.0	0.0	100.000%
2000	3,000	0.803	36.0	0.0	100.000%
3000	3,000	1.204	36.0	0.0	100.000%

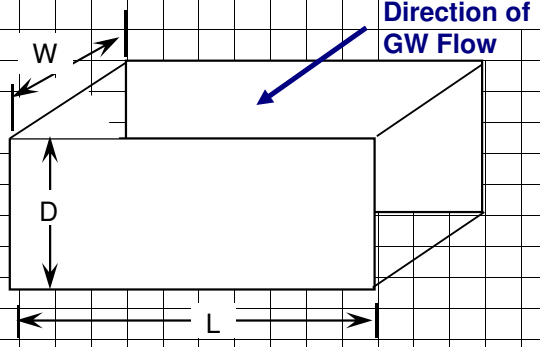
Rev	Date	By	Check	Subject
0	30-Mar-10	BMH	JRH	Design Calculations
				Biogeochemical Transformation Demonstration
				Project Location: DP98, Elmendorf AFB, Alaska

Note: Shaded cells are user input

1 Calculation of Reaction Zone Volume

Given:

D = 10 feet
L = 20 feet
W = 13 feet (along direction of GW flow)



Calculate Reaction Zone Volume (V_R)

V_R = (L*W*D)

V_R = **2600** cubic feet = **96.3** cubic yards

V_R = **73.6** cubic meters

2 Calculate Residence Time

Distance along Direction of Groundwater Flow:	**13**	feet
Average/Assumed Rate of Groundwater Flow	**0.333**	ft/day
Residence Time in the Reaction Zone:	**39.0**	days

3 Estimate Pore Volume of Reaction Zone:

Total Porosity =	**30%**	percent			
Effective Porosity =	**22%**	percent			
Total Pore Volume=	**22.1**	cubic meters	=	**5,835**	gallons
Effective Pore Volume=	**16.2**	cubic meters	=	**4,279**	gallons

4 Estimate Mass of Soil

Bulk Density = **1.68** gm/cm^3 = **1680** kg/m^3

Total Mass Soil = Density X Volume = **123,684** kg

5 Estimate Mass of AVS Required

Concentration of AVS = **2,000** mg/kg (from Sheet 1)

Concentration of AVS = **3.4E+06** mg/m^3 = **3.36** kg/m^3

Total Mass of AVS for Reaction Zone = **247.4** kg

6 Estimate Stoichiometric Mass of Sulfate and Ferric/Ferrous Iron Required

Assumptions: (from Appendix D of AFCEE, 2008)

1. Mass of AVS is approximation of mass of FeS required
2. It takes approximately 1.64 kg of SO_4^{2-} to produce 1.0 kg FeS
3. It takes approximately 0.64 kg of Fe^{3+} to produce 1.0 kg FeS

Mass of Sulfate =	**406**	kg	=	**894** pounds
Mass of Ferric/Ferrous Iron =	**158**	kg	=	**349** pounds

Rev	Date	By	Check	Subject
0	30-Mar-10	BMH	JRH	Design Calculations
				Biogeochemical Transformation Demonstration
				Project Location: DP98, Elmendorf AFB, Alaska

Note: Shaded cells are user input

1 Product Specifications

A. Ferrous Sulfate from Advanced Scientific ($FeSO_4 \cdot 7H_2O$) MW = 278.0

Percent Sulfate **34.6%**

Percent Iron **20.1%**

B. Calcium Sulfate Dihydrate (powdered calcium sulfate) ($CaSO_4 \cdot 2H_2O$) MW = 172.2

Percent Sulfate **55.8%**

C. Magnesium Sulfate Heptahydrate ($MgSO_4 \cdot 7H_2O$) MW = 246.5

Percent Sulfate **40.0%**

D. Ferrous Lactate from Advanced Scientific ($Fe(C_3H_5O_3)_2$) MW = 234.0

Percent Ferrous Iron **23.9%**

E. Ferrous Chloride Heptahydrate ($FeCl_3.7H_2O$) MW = 270.3

Percent Ferrous Iron **20.7%**

F. Powdered Hematite (Fe_2O_3) MW = 159.7

Percent Ferric Iron **68.0%**

2 Sulfate and Iron Requirements

Amount Sulfate Required (from Sheet 2) **894** pounds

Amount iron Required (from Sheet 2) **349** pounds

3 Product Requirements

A. Amount Ferrous Sulfate to Meet Sulfate Requirement **2,589** pounds

Amount Ferrous Sulfate to Meet Iron Requirement **1,737** pounds

Assume **2,500** pounds of ferrrous sulfate

Then **864** pounds of sulfate will provide **1.0** times the sulfate requirement

502 pounds of ferrous iron will provide **1.4** times the iron requirement

B. Amount of Calcium Sulfate Dihydrate to Meet Sulfate Requirement **1,603** pounds

C. Amount of Magnesium Sulfate to Meet Sulfate Requirement **2,238** pounds

D. Amount of Ferrous lactate to Meet Iron Requirement **1,462** pounds

E. Amount of Ferric Chloride Heptahydrate to Meet Iron Requirement **1,689** pounds

F. Amount of Colloidal Hematite to Meet Iron Requirement **513** pounds

4 Effective Concentration per Effective Pore Volume

A. Effective Pore Volume **16.2** Cubic meters = **16,197** liters = **4,279** gallons

B. Sulfate = **3.92E+08** milligrams

C. Sulfate Concentration = **24,189** mg/L

D. Ferrous Iron = **2.28E+08** milligrams

E. Iron Concentration = **14,066** mg/L or = **1,842** mg/kg

ATTACHMENT B
CONCENTRATION PLOTS OVER TIME

FIGURE A.1A - CONCENTRATIONS OF CHLOROETHENES AT UPGRADIENT LOCATION DP98MP01

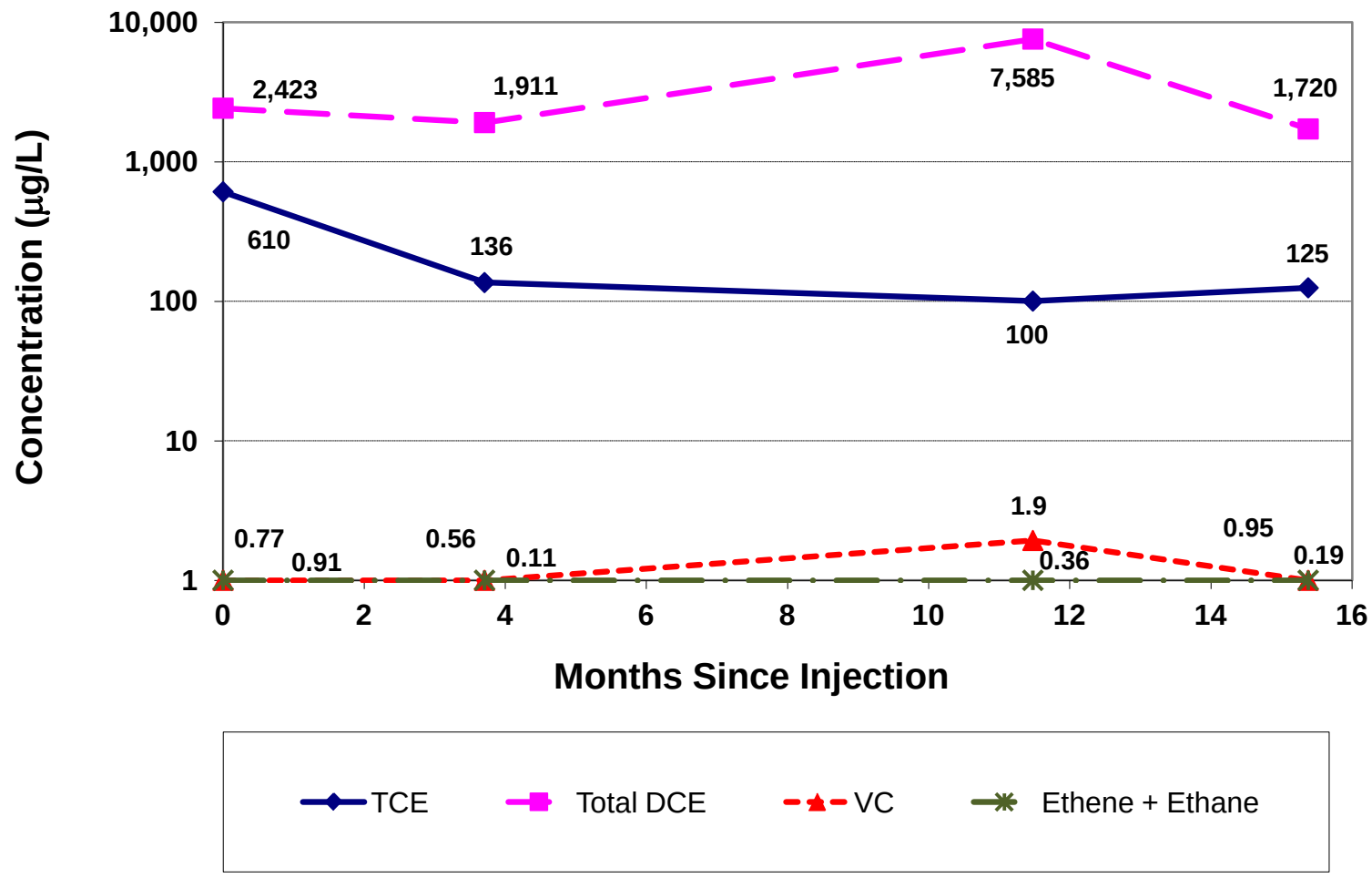


FIGURE A.1B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT UPGRADIENT LOCATION DP98MP01

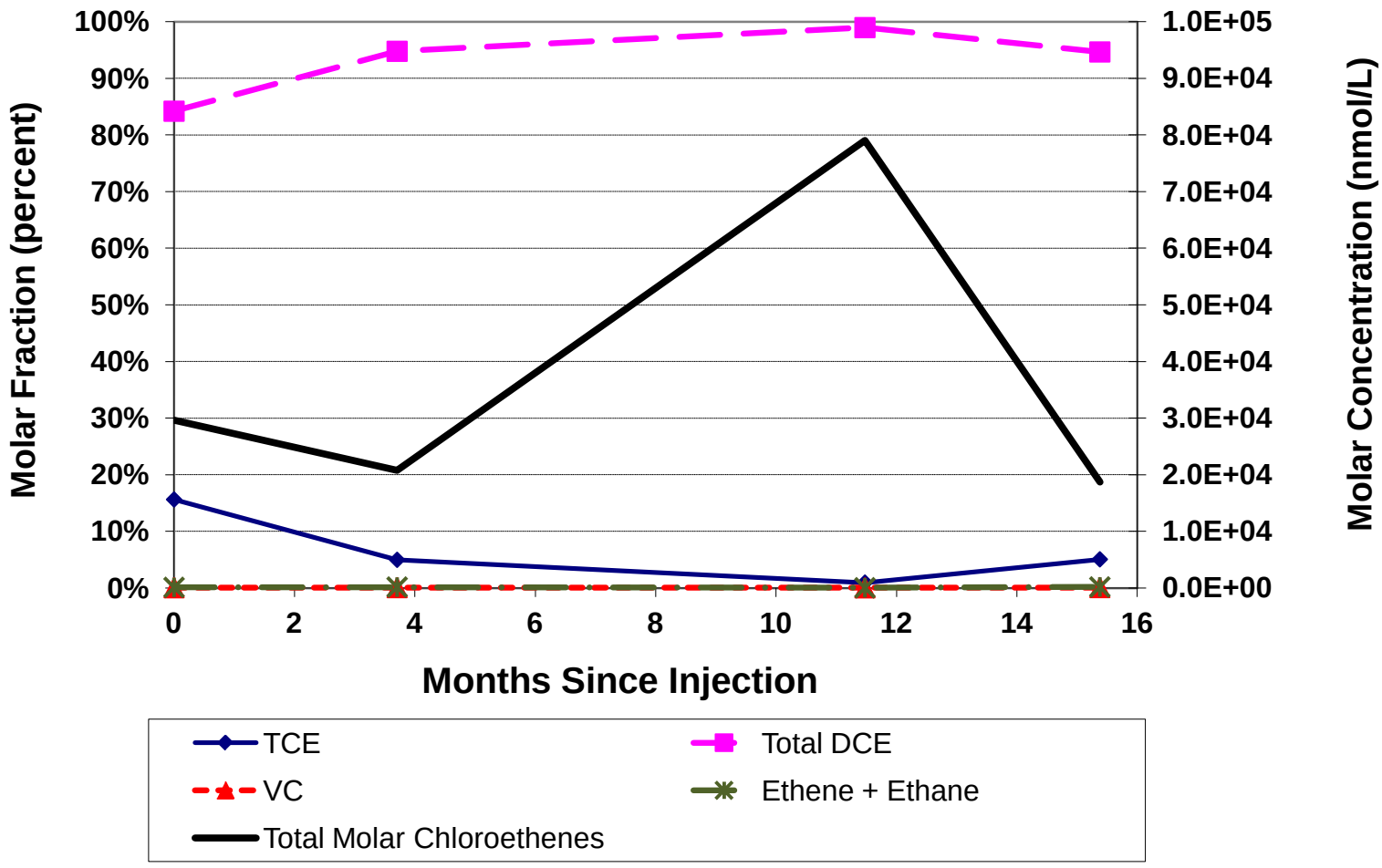


FIGURE A.2A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98MP02

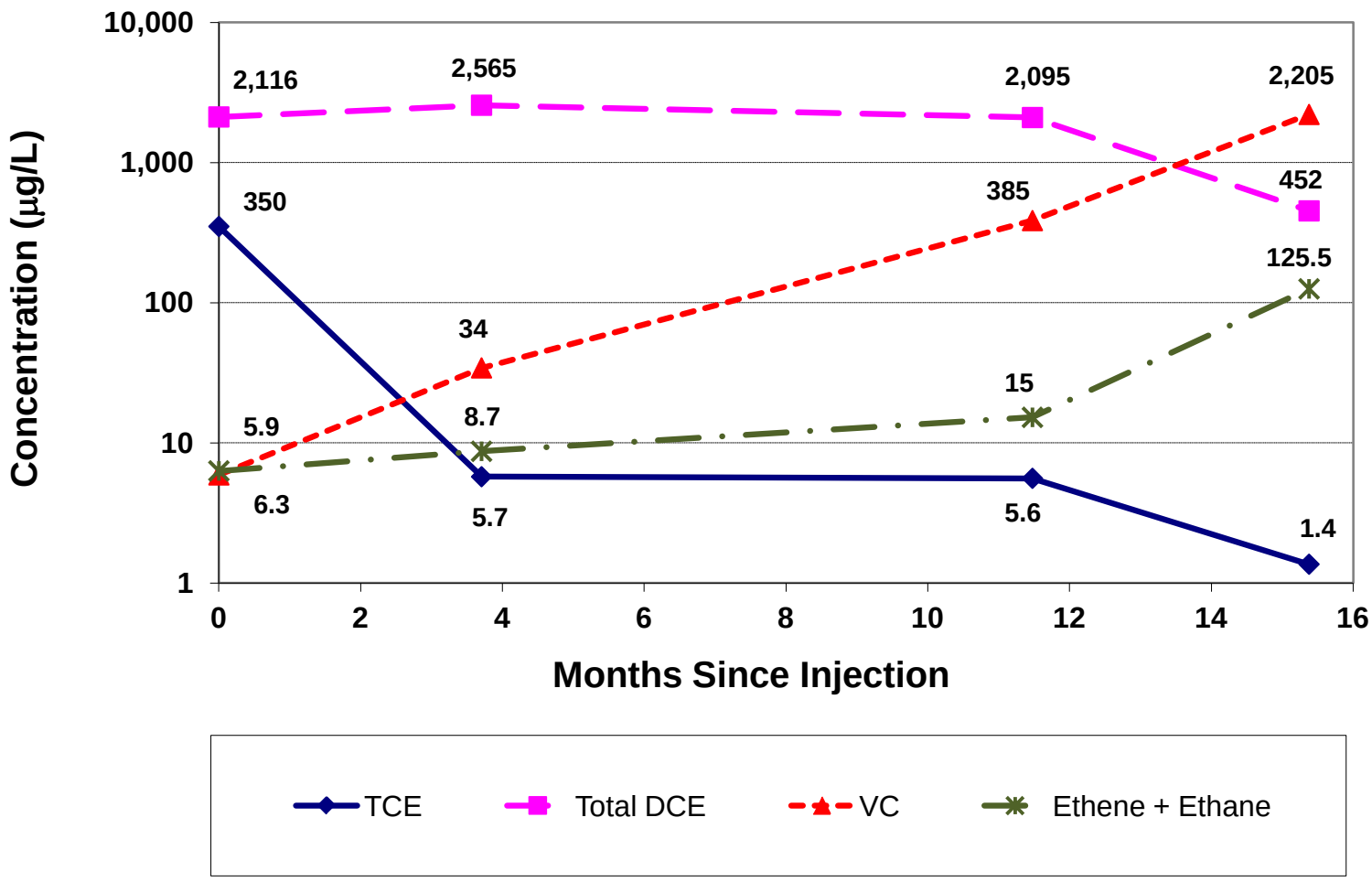


FIGURE A.2B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98MP02

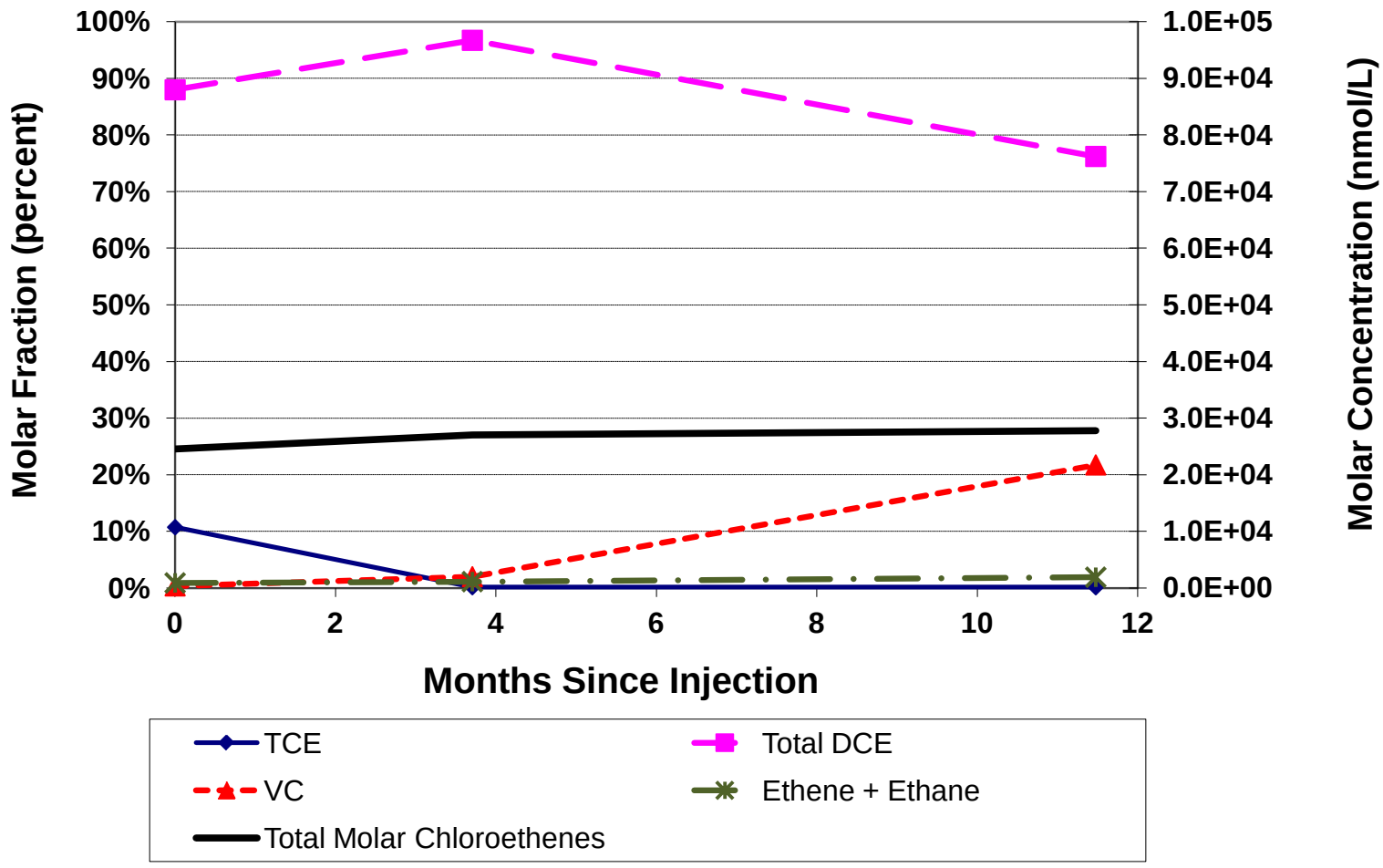


FIGURE A.3A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98MP03

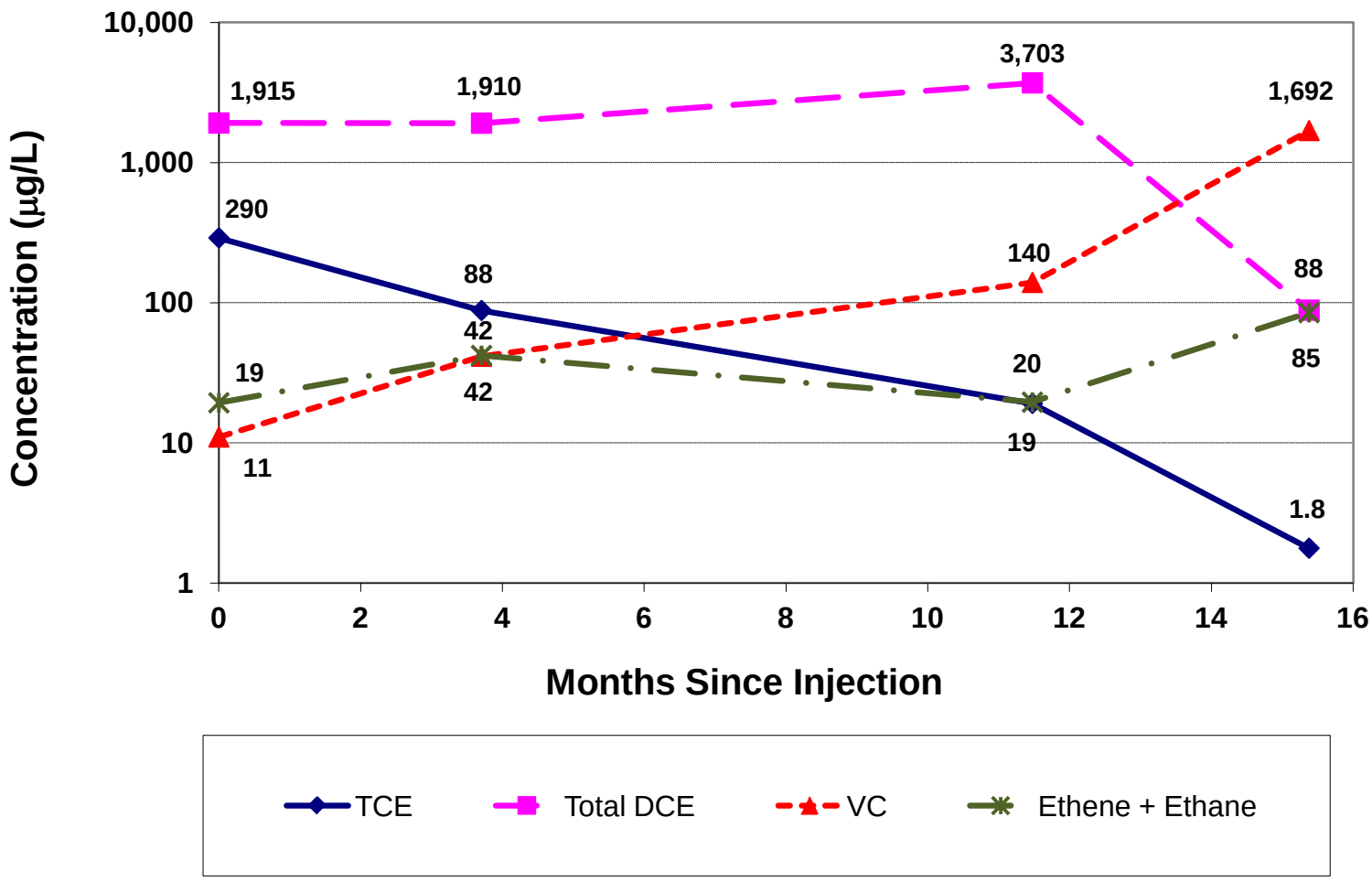


FIGURE A.3B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98MP03

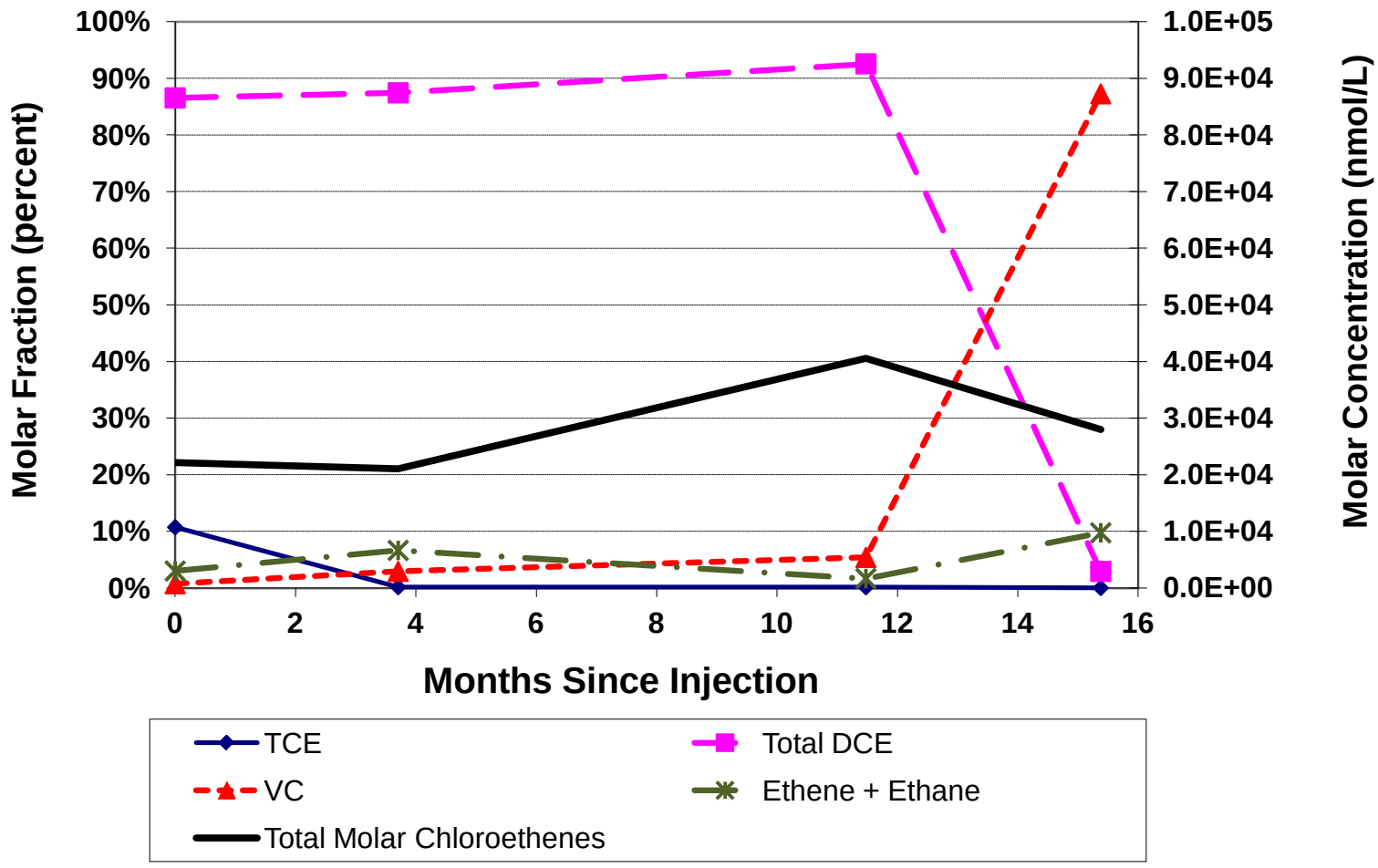


FIGURE A.4A - CONCENTRATIONS OF CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MP04

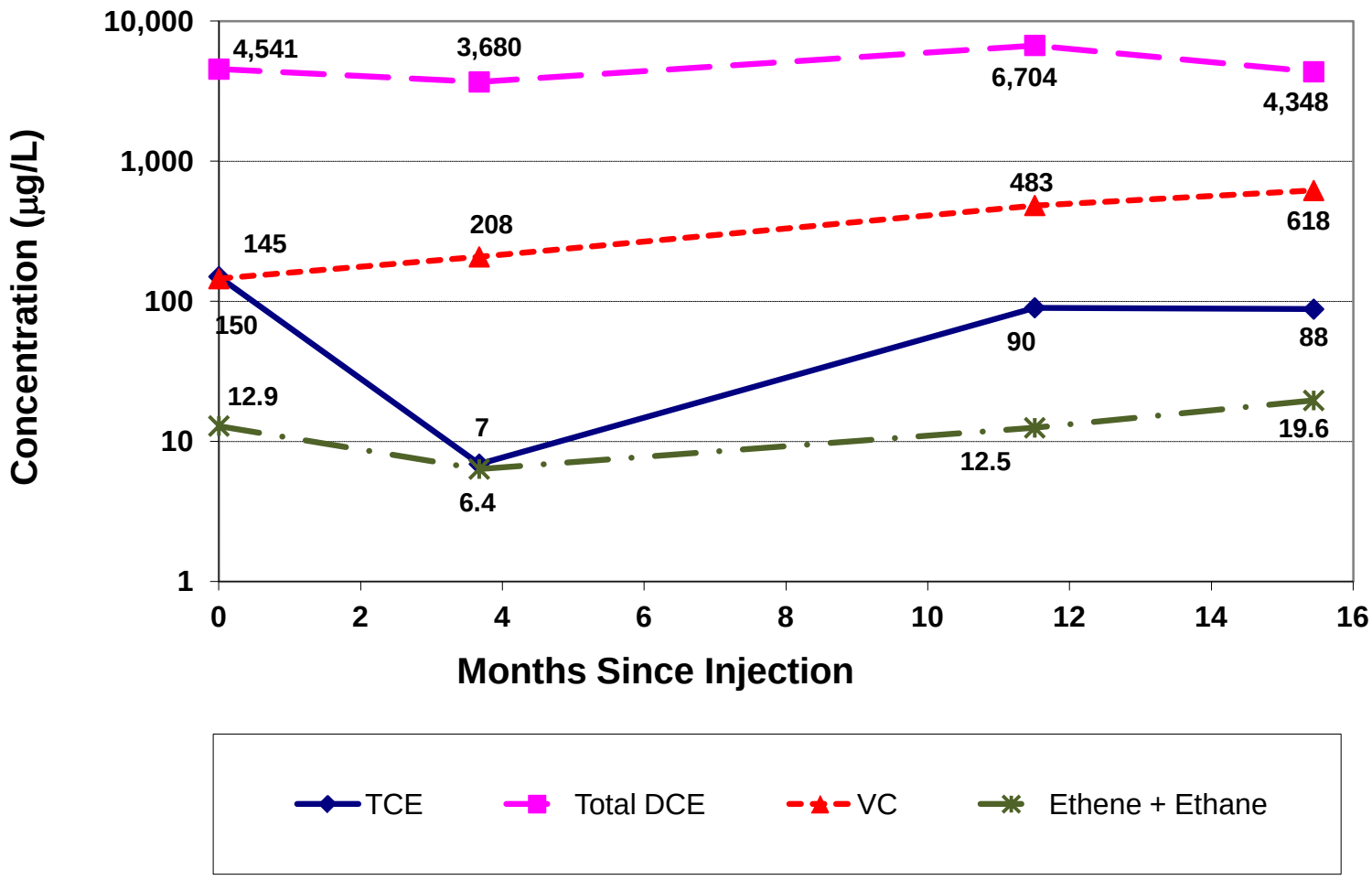


FIGURE A.4B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MP04

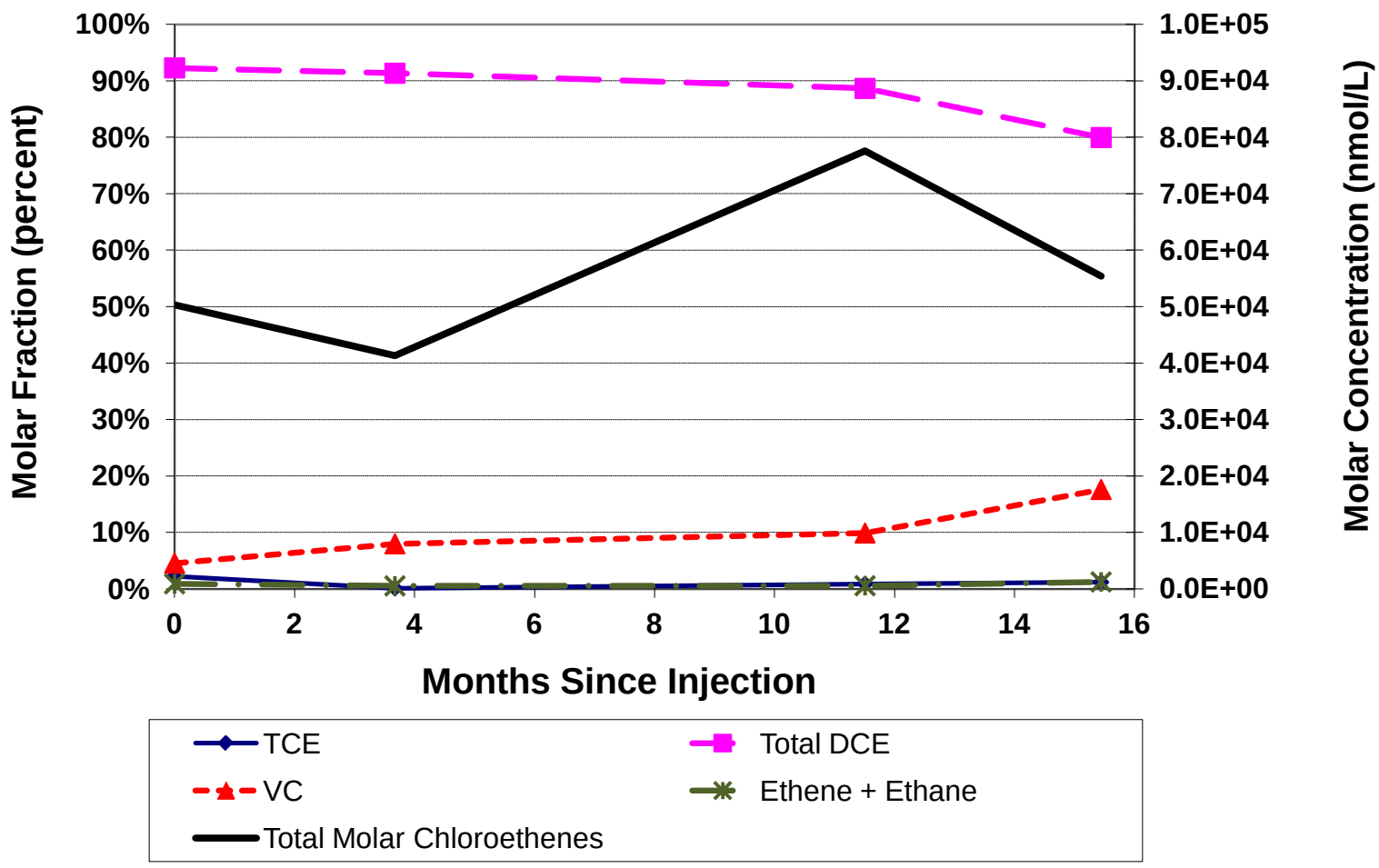
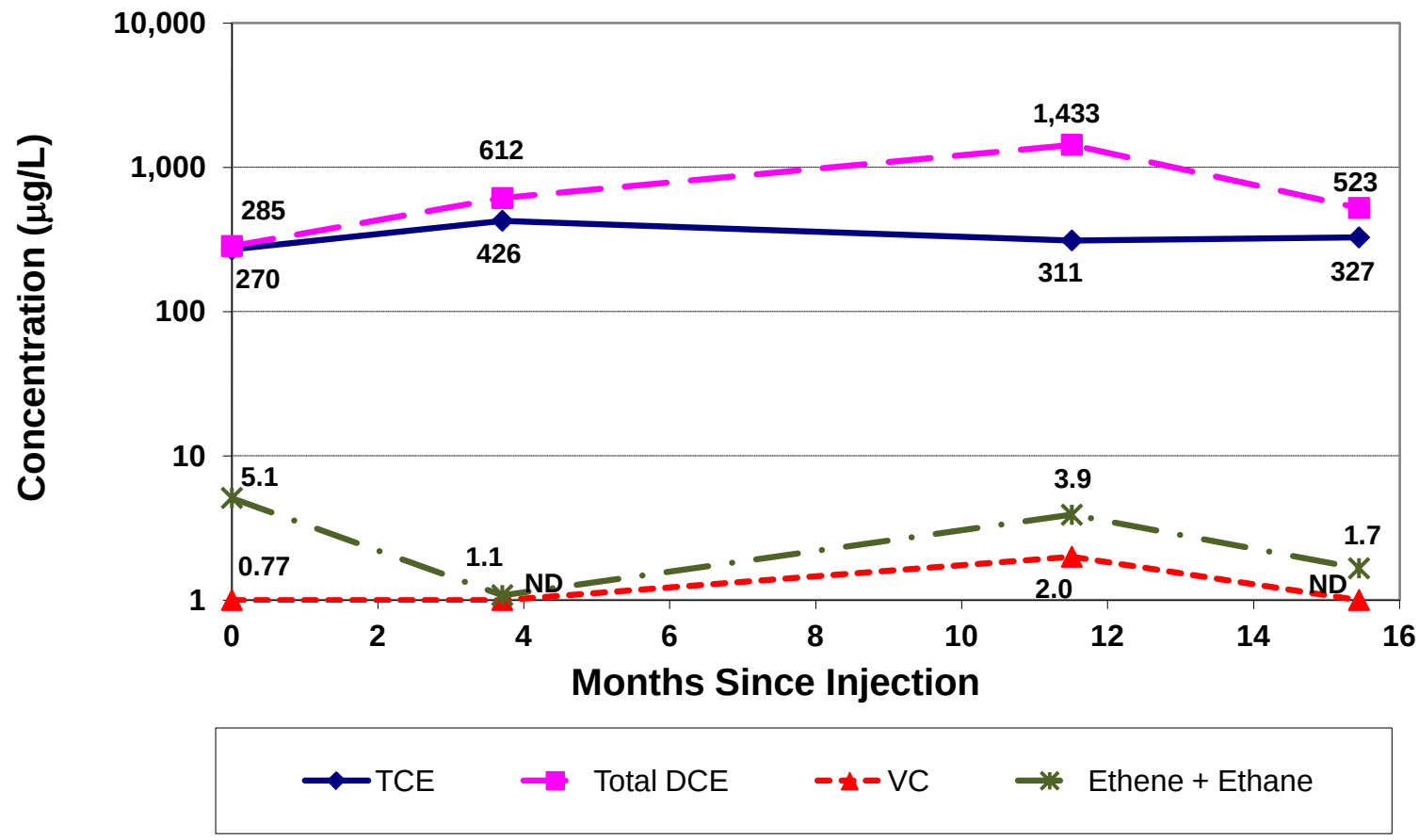


FIGURE A.5A - CONCENTRATIONS OF CHLOROETHENES AT UPGRADIENT LOCATION DP98MP05



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.5B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT UPGRADIENT LOCATION DP98MP05

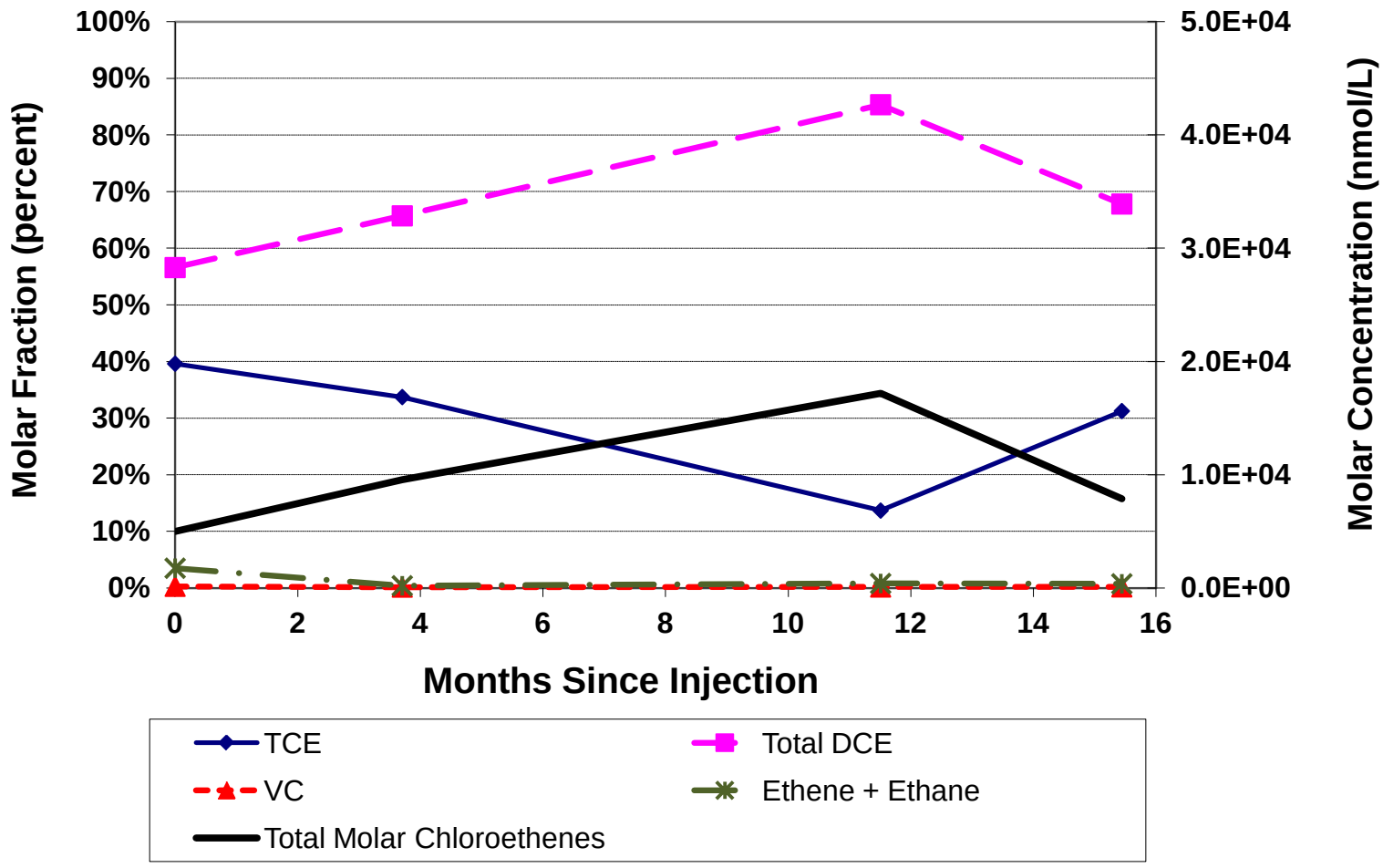


FIGURE A.6A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98MP06

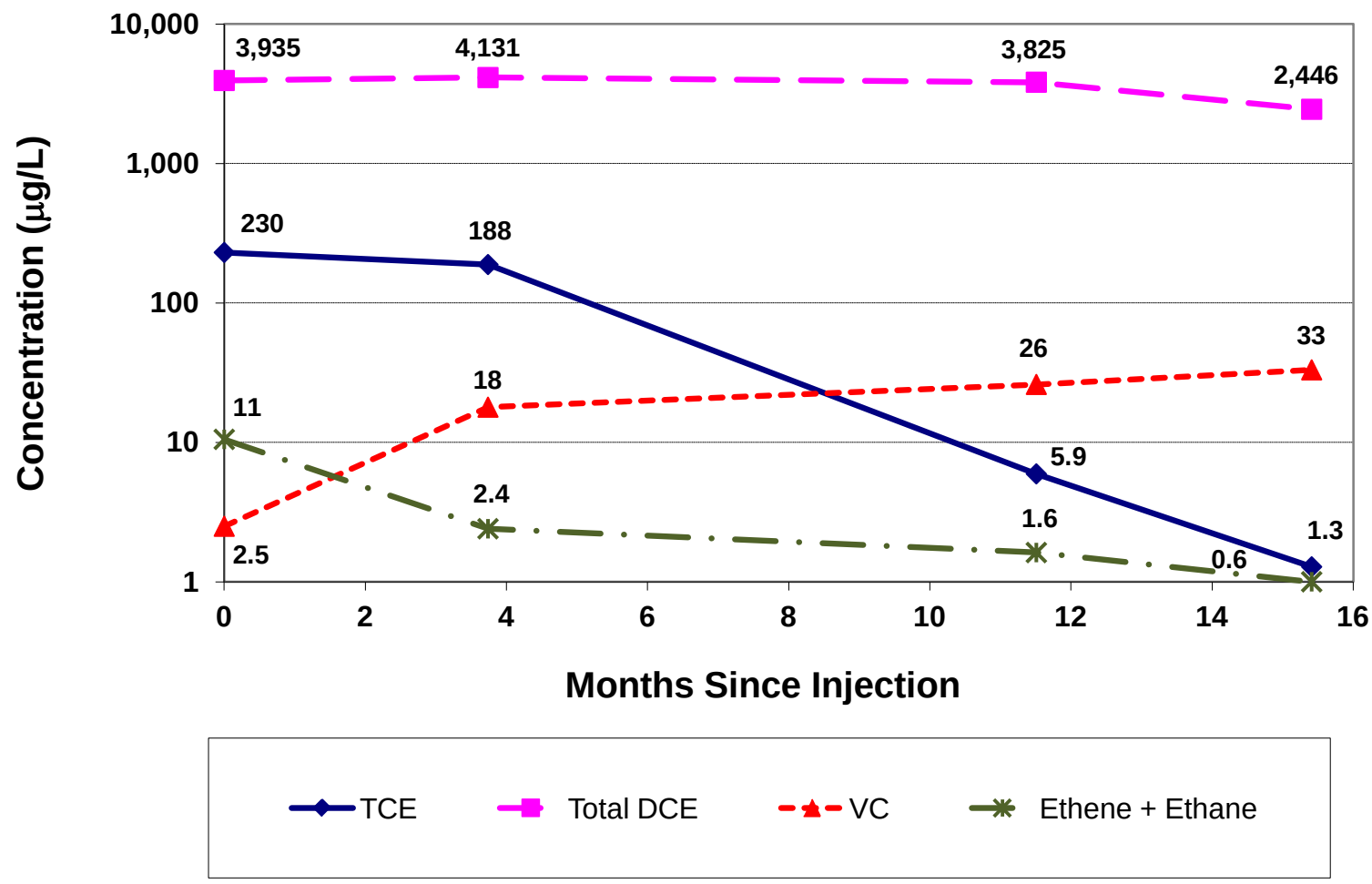


FIGURE A.6B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98MP06

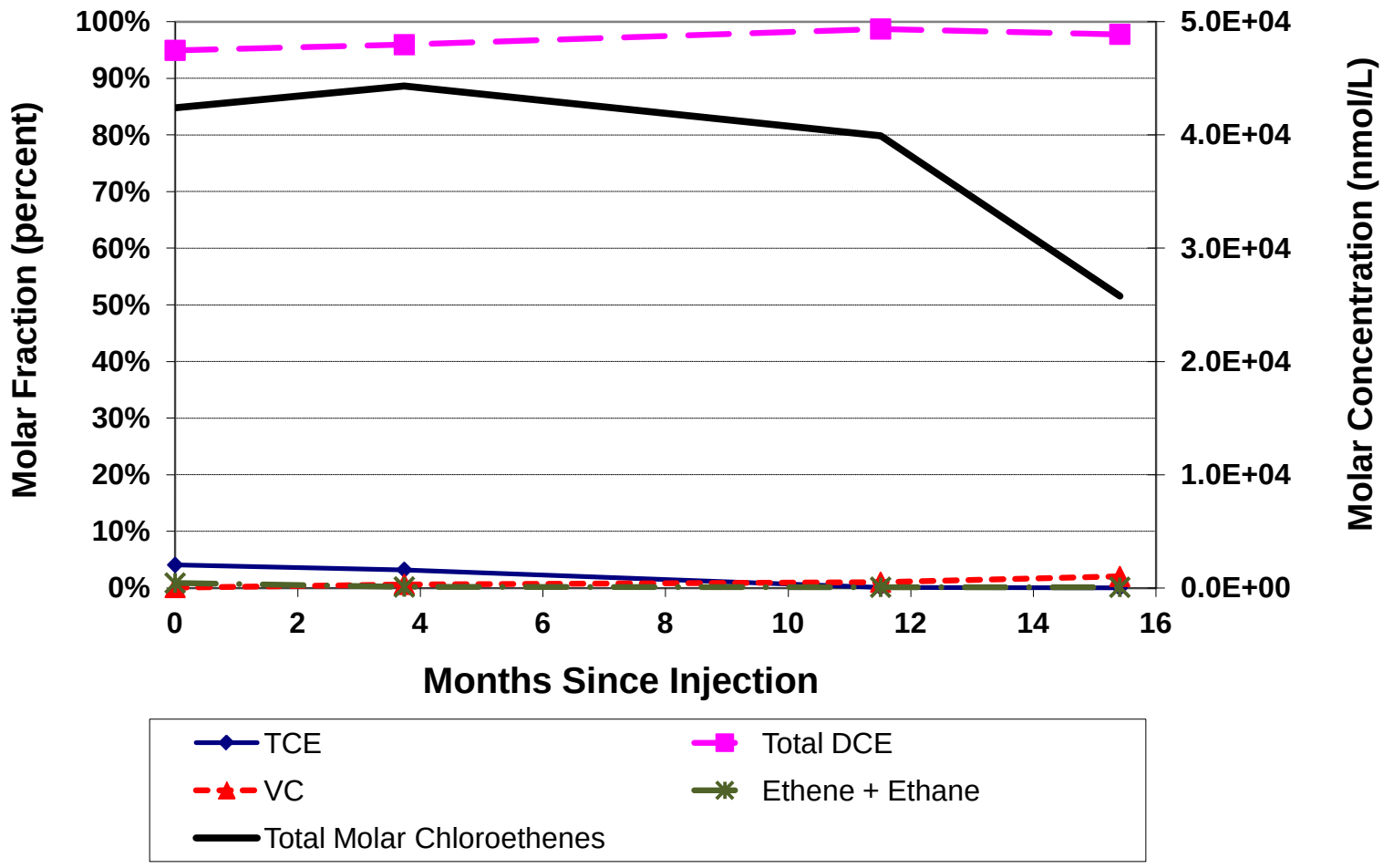
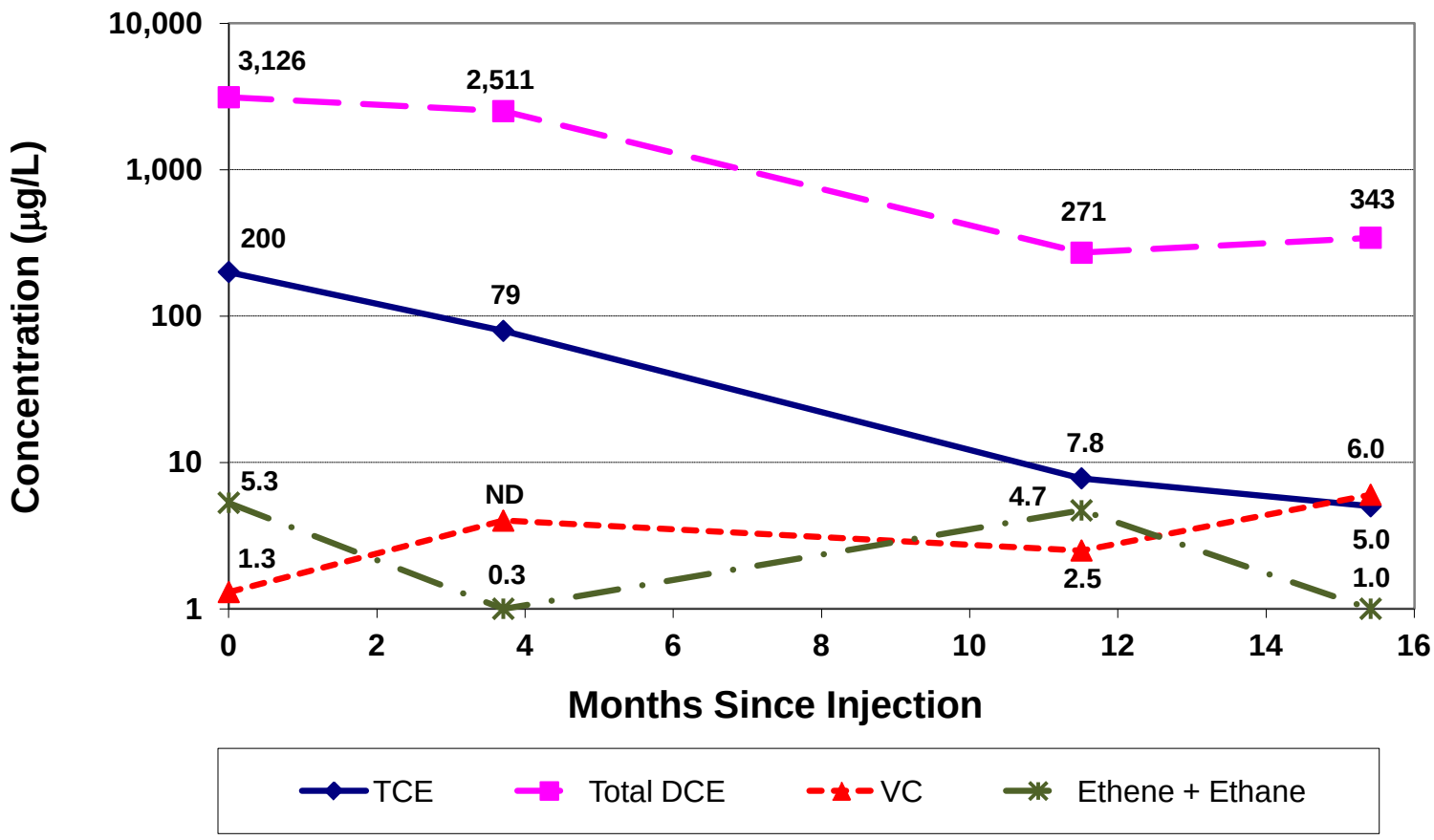


FIGURE A.7A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98MP07



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.7B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98MP07

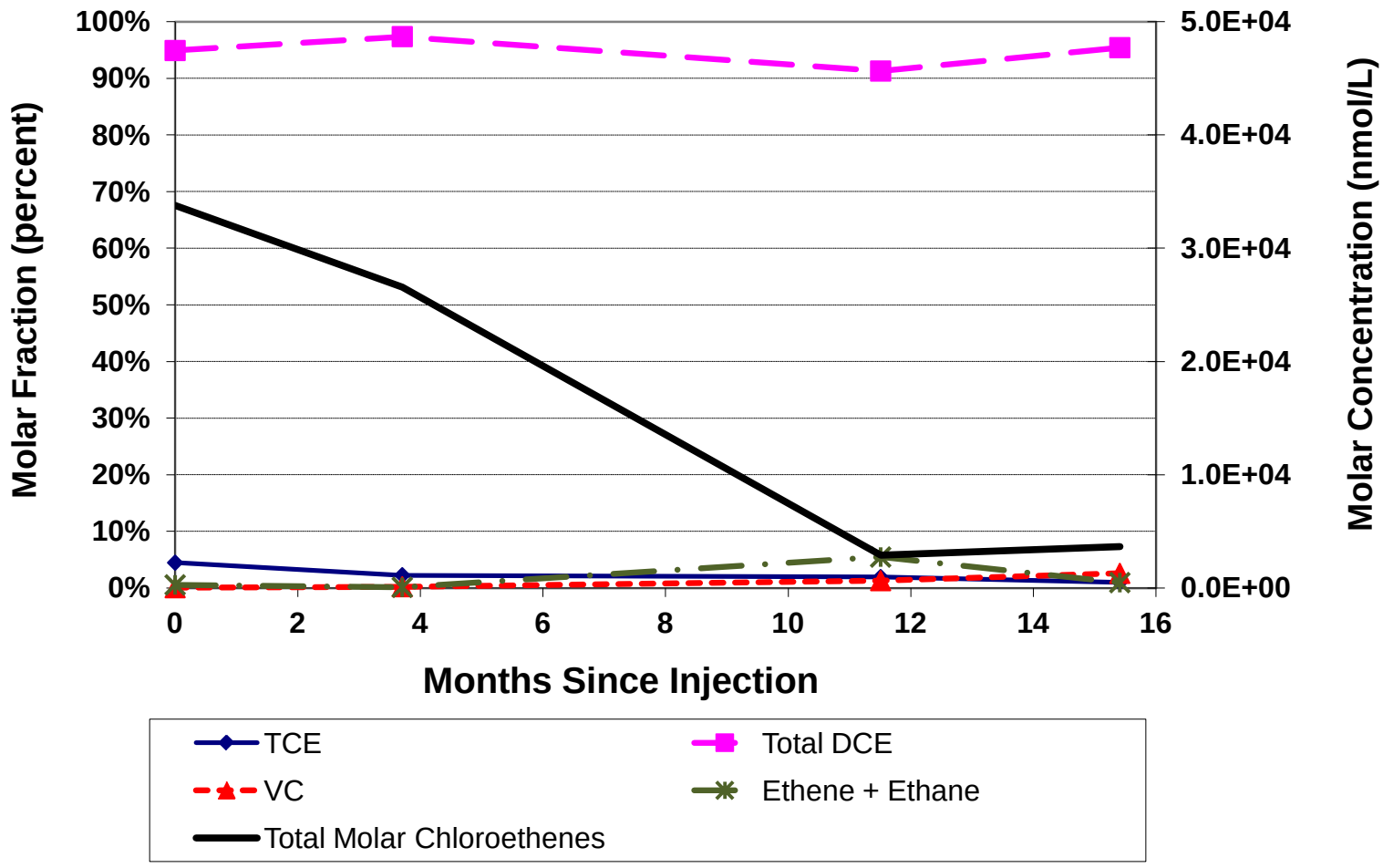
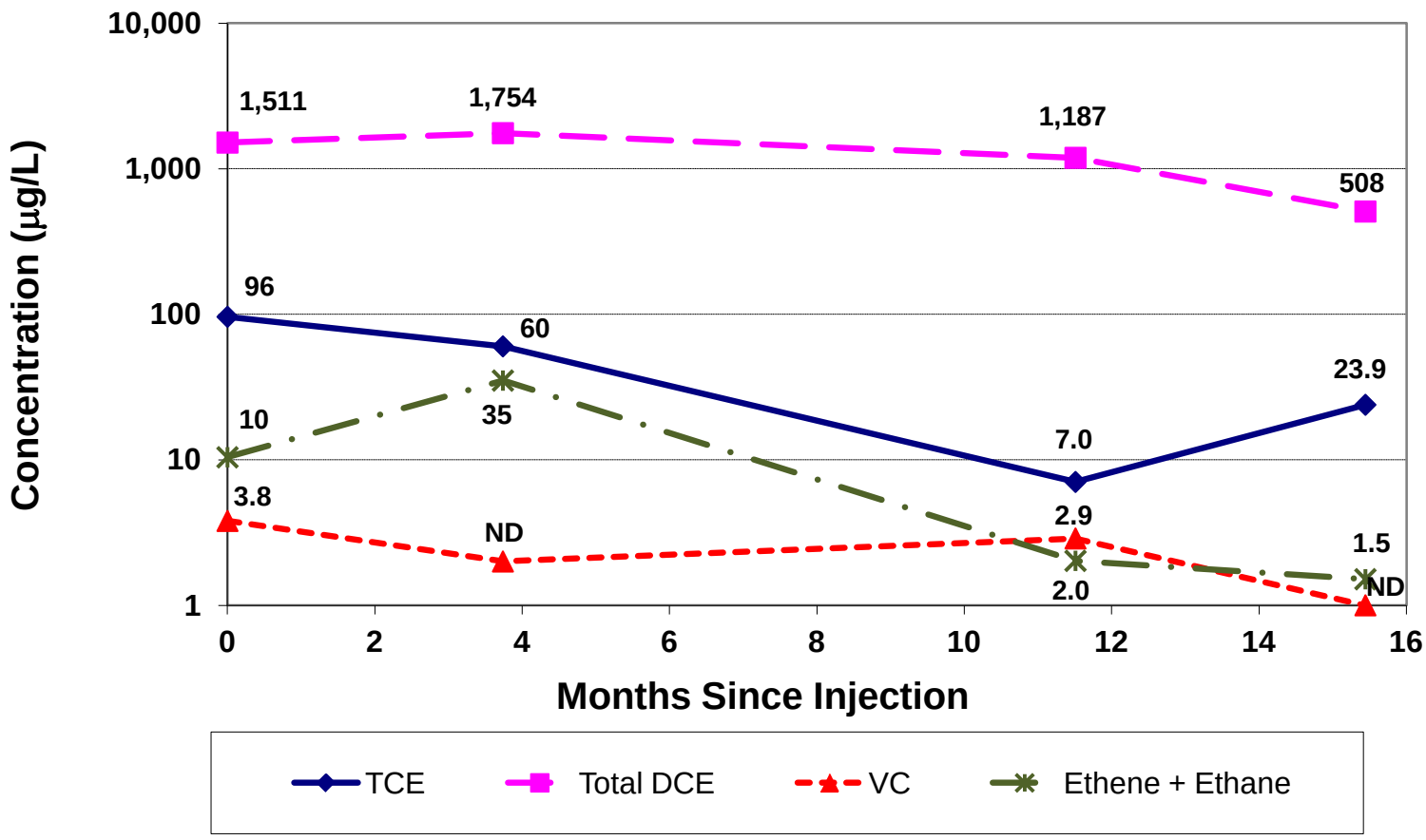


FIGURE A.8A - CONCENTRATIONS OF CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MP08



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.8B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MP08

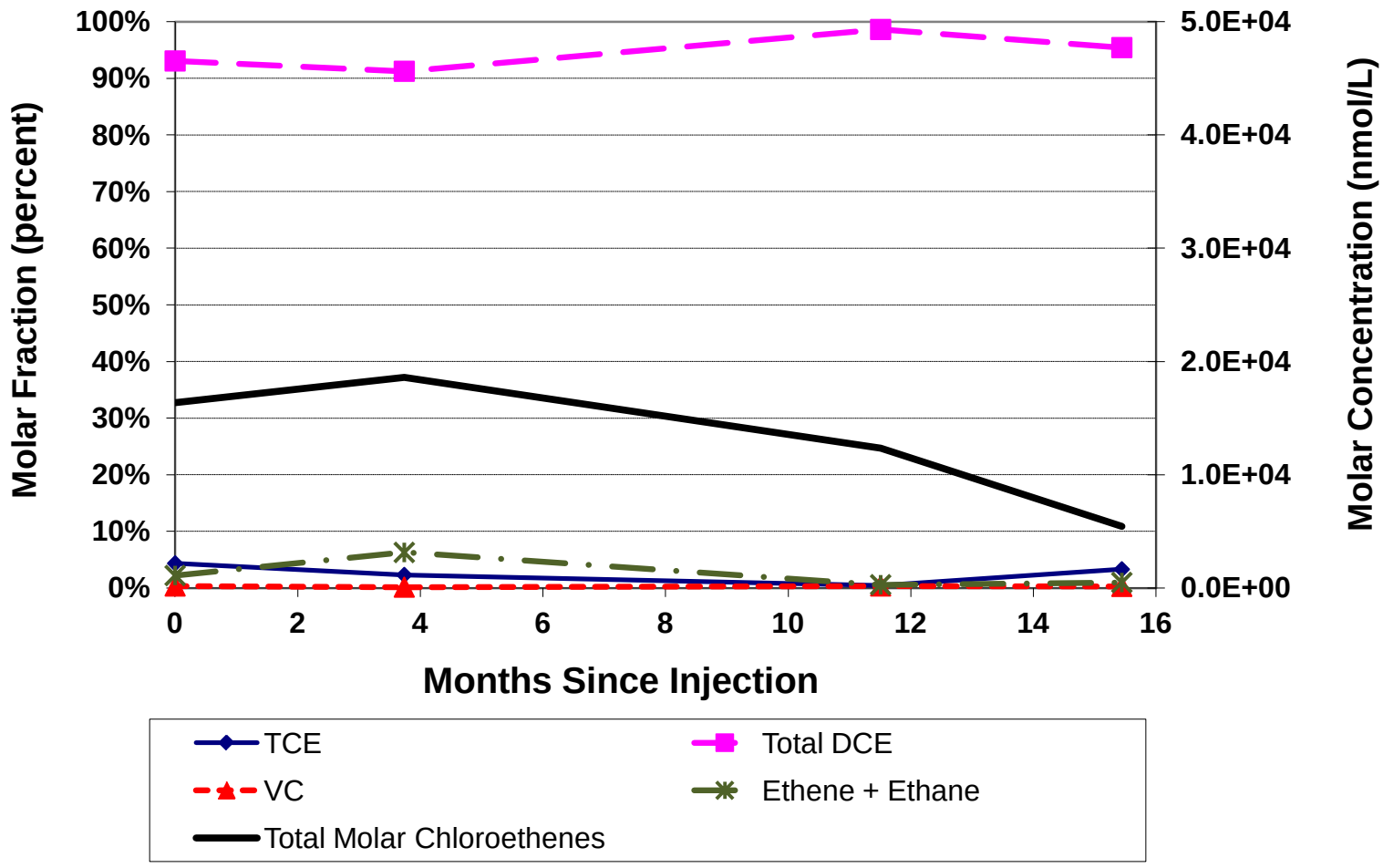
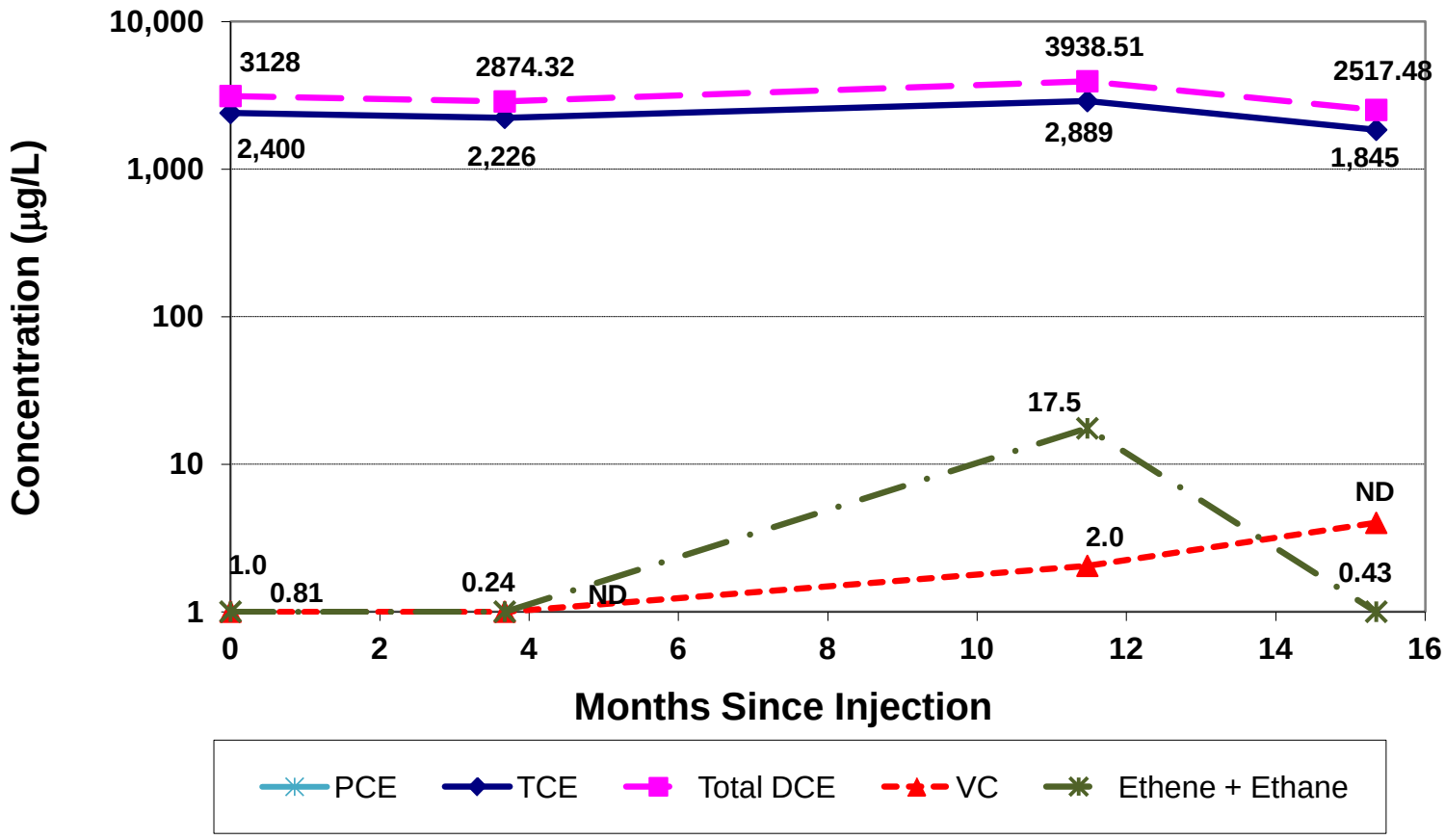


FIGURE A.9A - CONCENTRATIONS OF CHLOROETHENES AT UPGRADIENT LOCATION DP98MW04



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.9B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT UPGRADIENT LOCATION DP98MW04

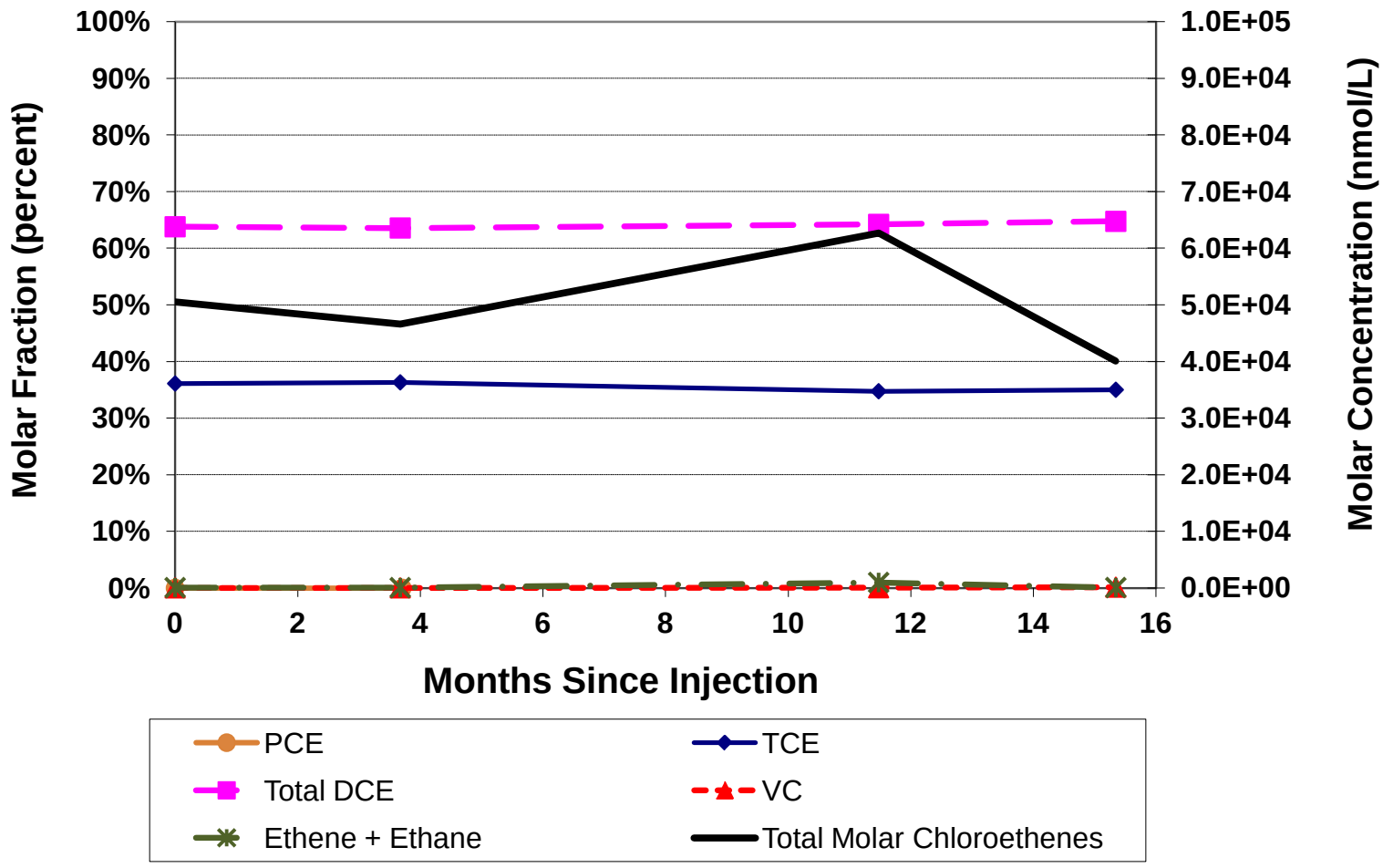
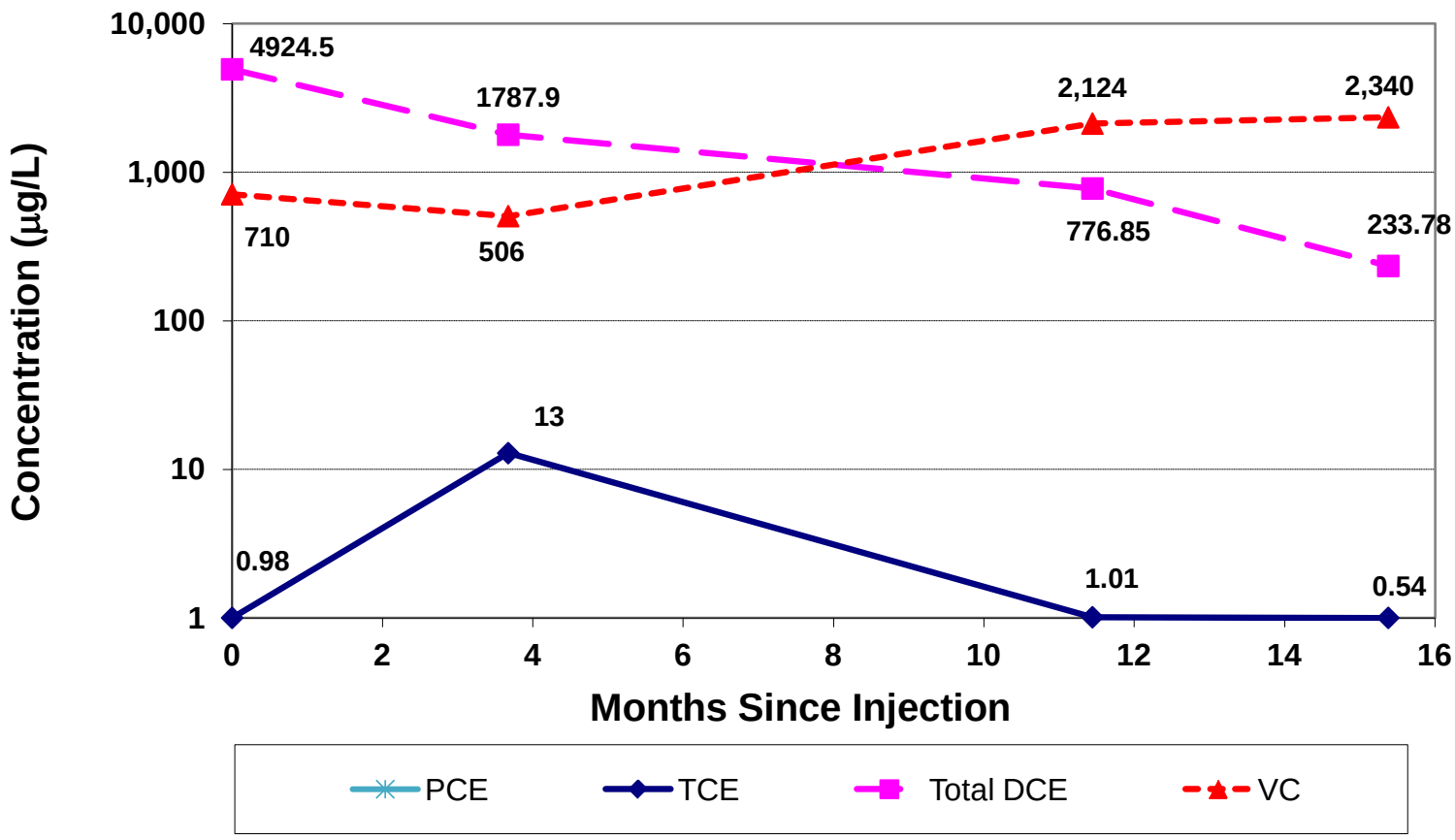


FIGURE A.10A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ01



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.10B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ01

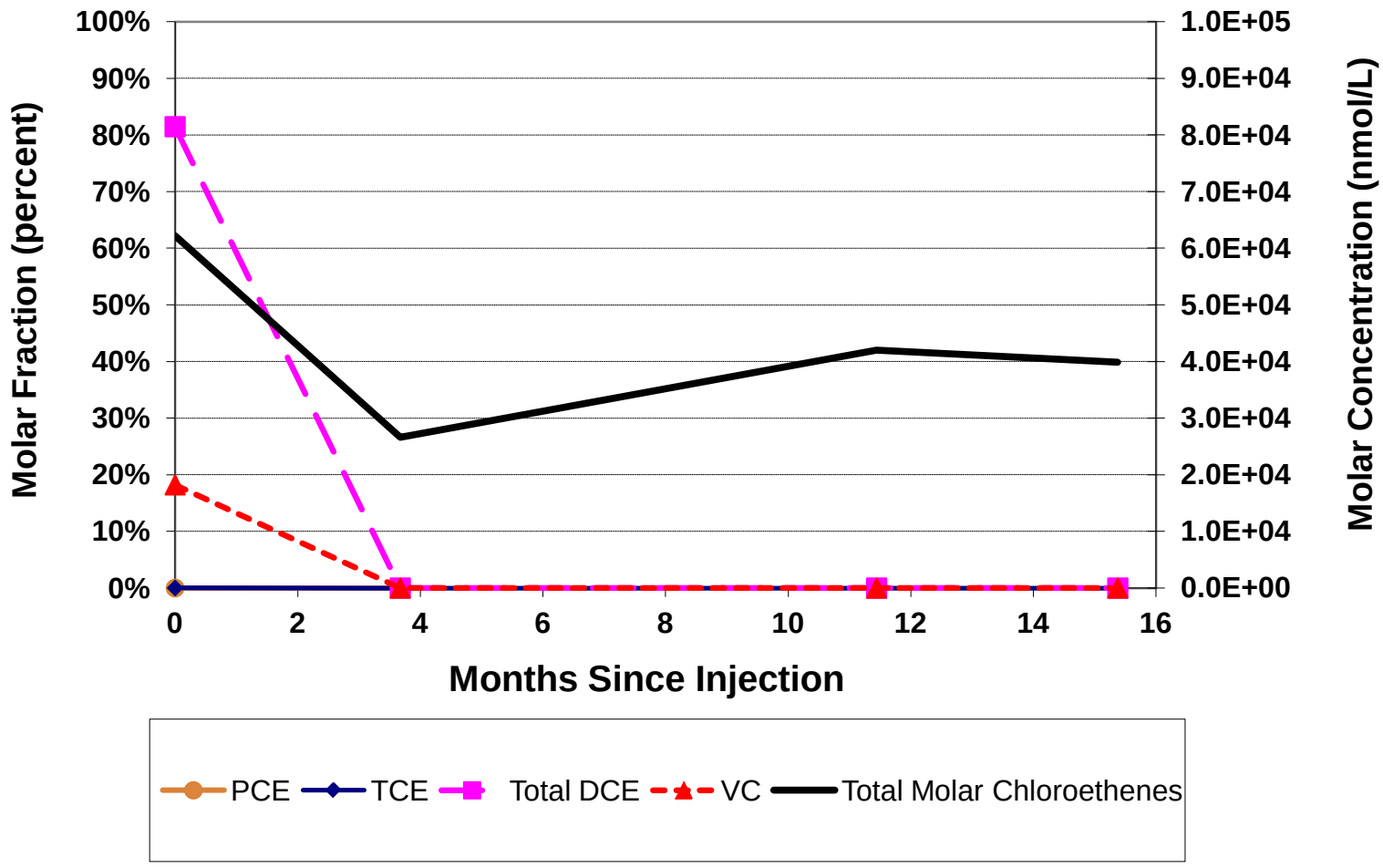


FIGURE A.11A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ02

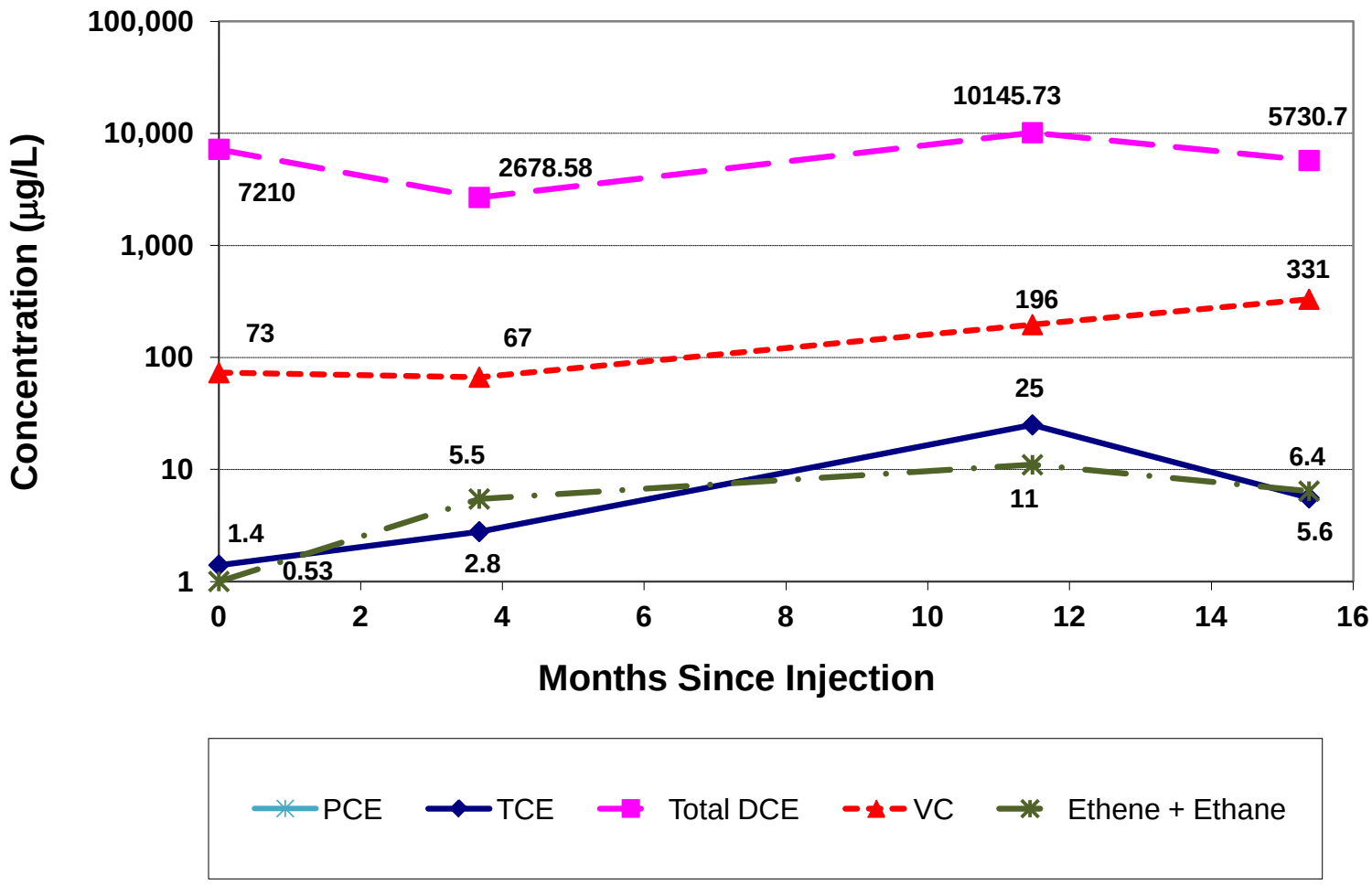


FIGURE A.11B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ02

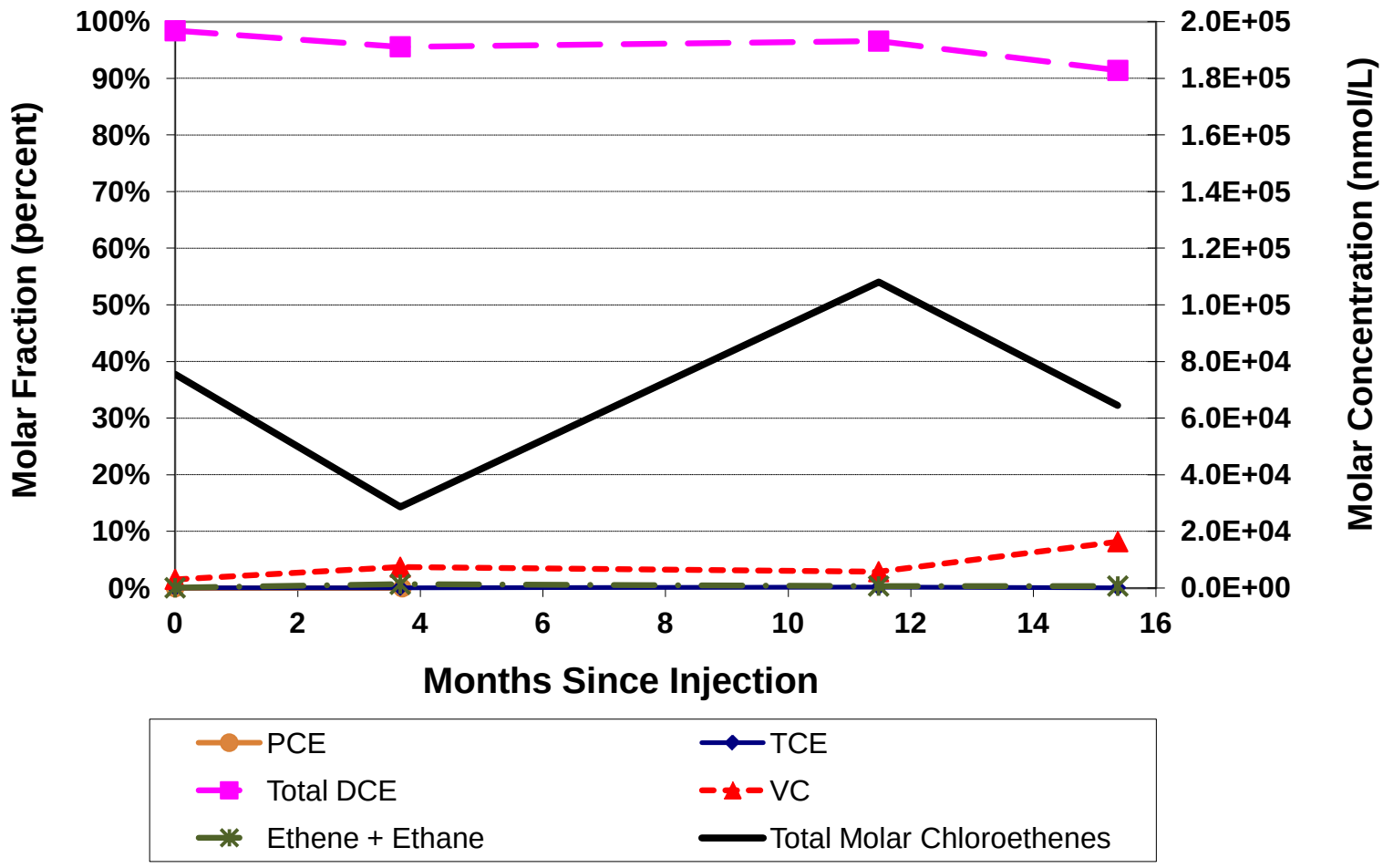


FIGURE A.12A - CONCENTRATIONS OF CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ03

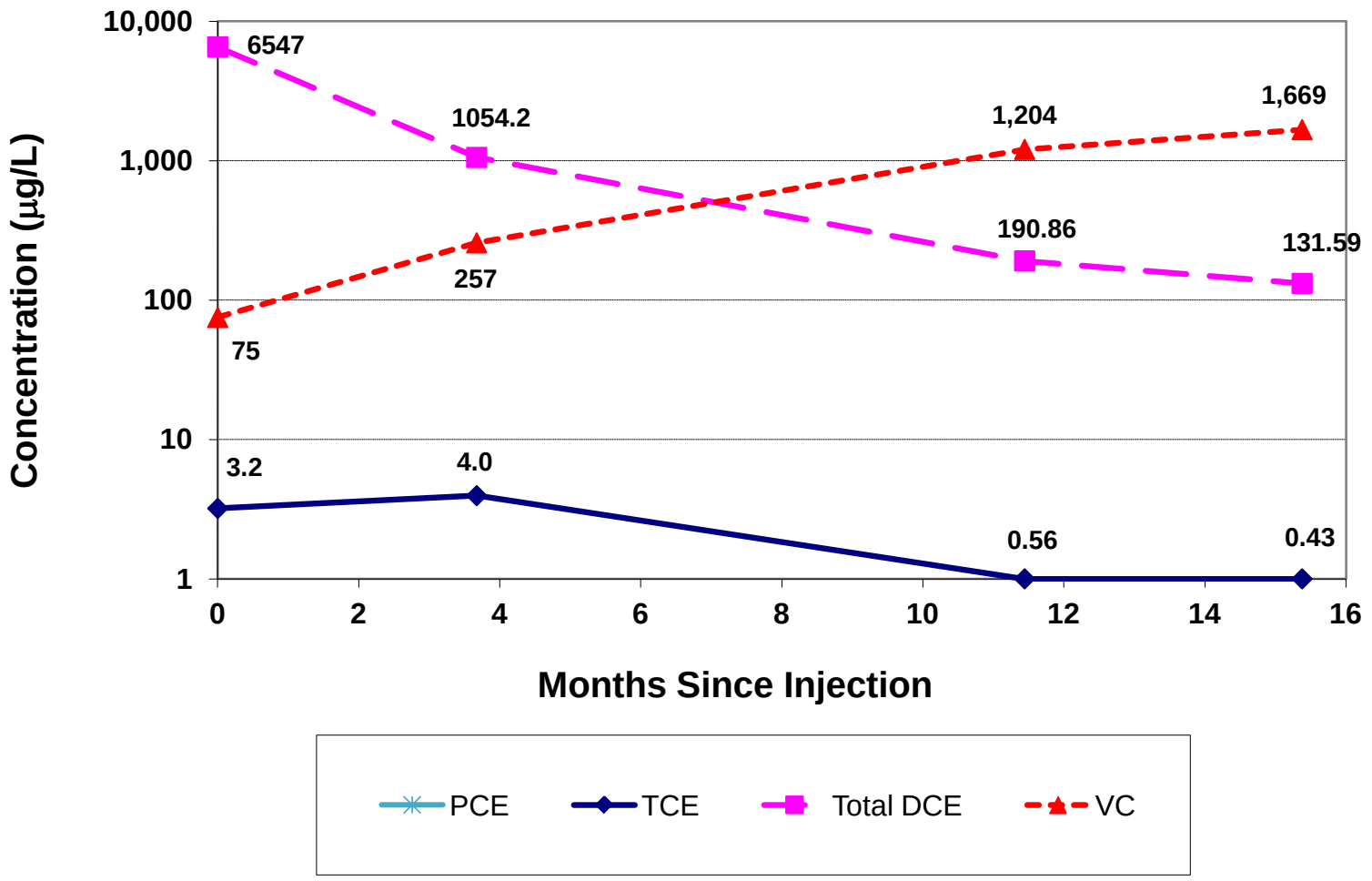


FIGURE A.12B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT REACTION ZONE LOCATION DP98INJ03

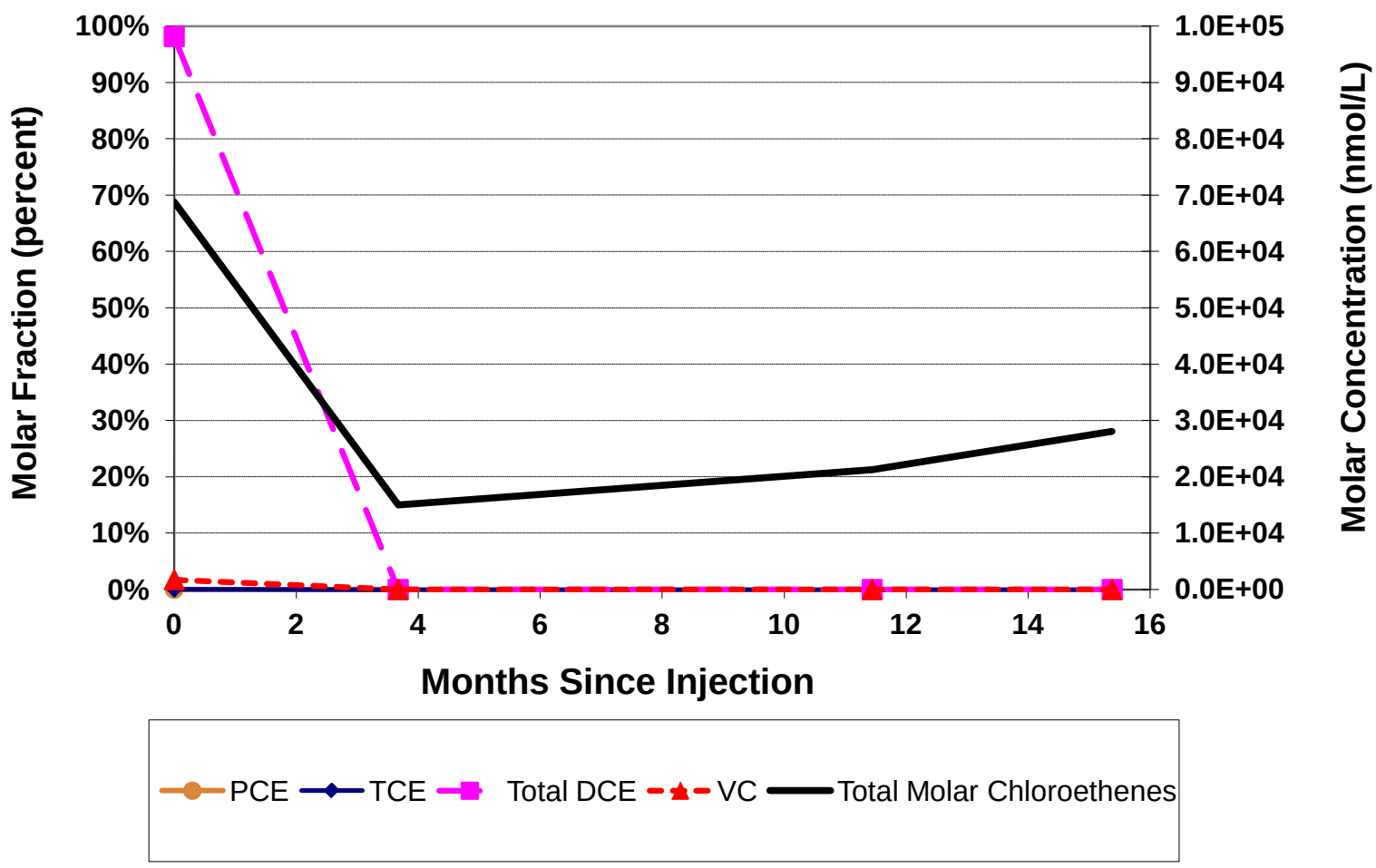
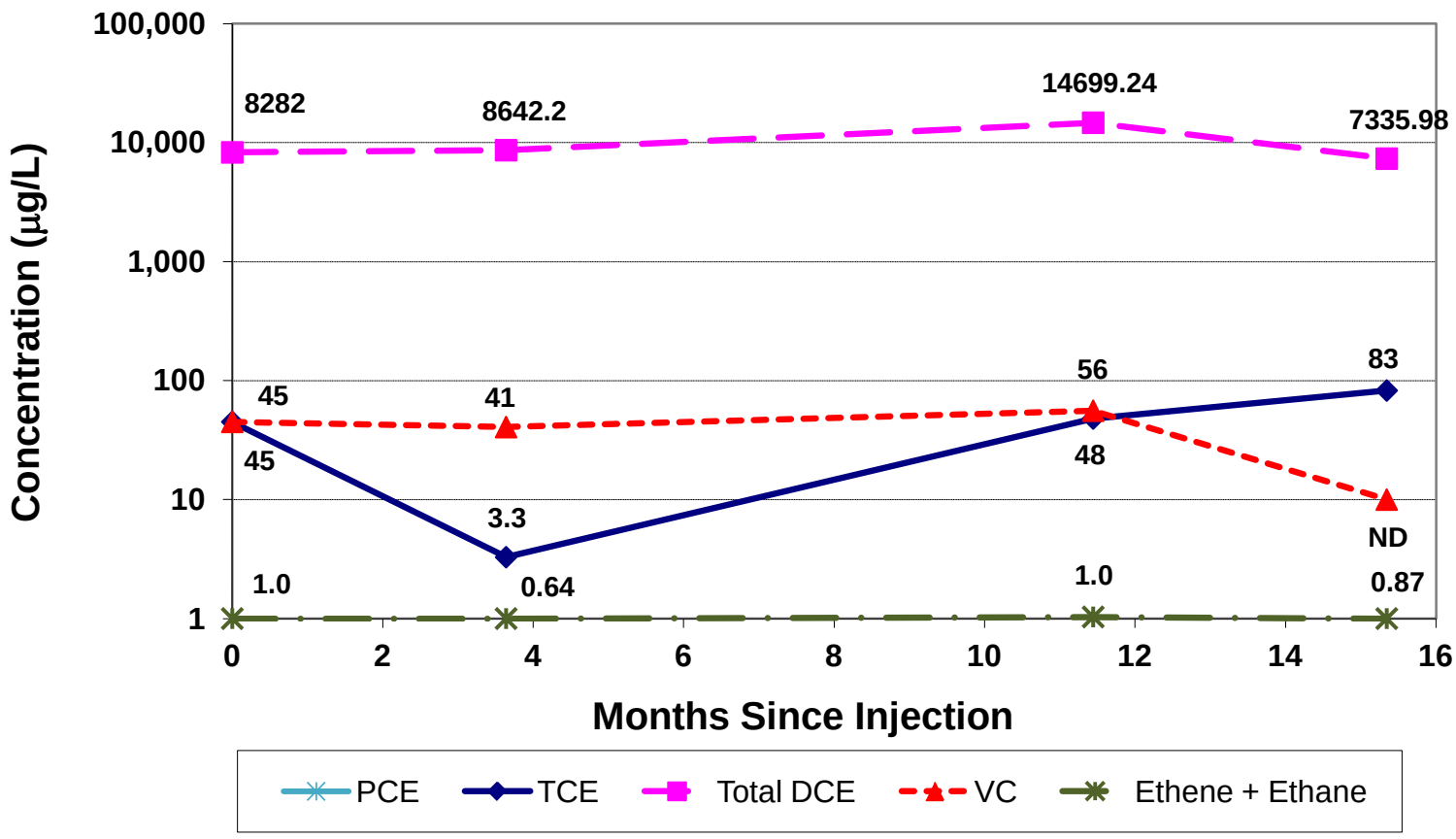


FIGURE A.13A - CONCENTRATIONS OF CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MW05



ND = non-detect. Non-detects were plotted as 1/2 the method detection limit. Values and non-detects less than 1.0 were plotted as 1.0 for the purposes of the graph ical analysis .

FIGURE A.13B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MW05

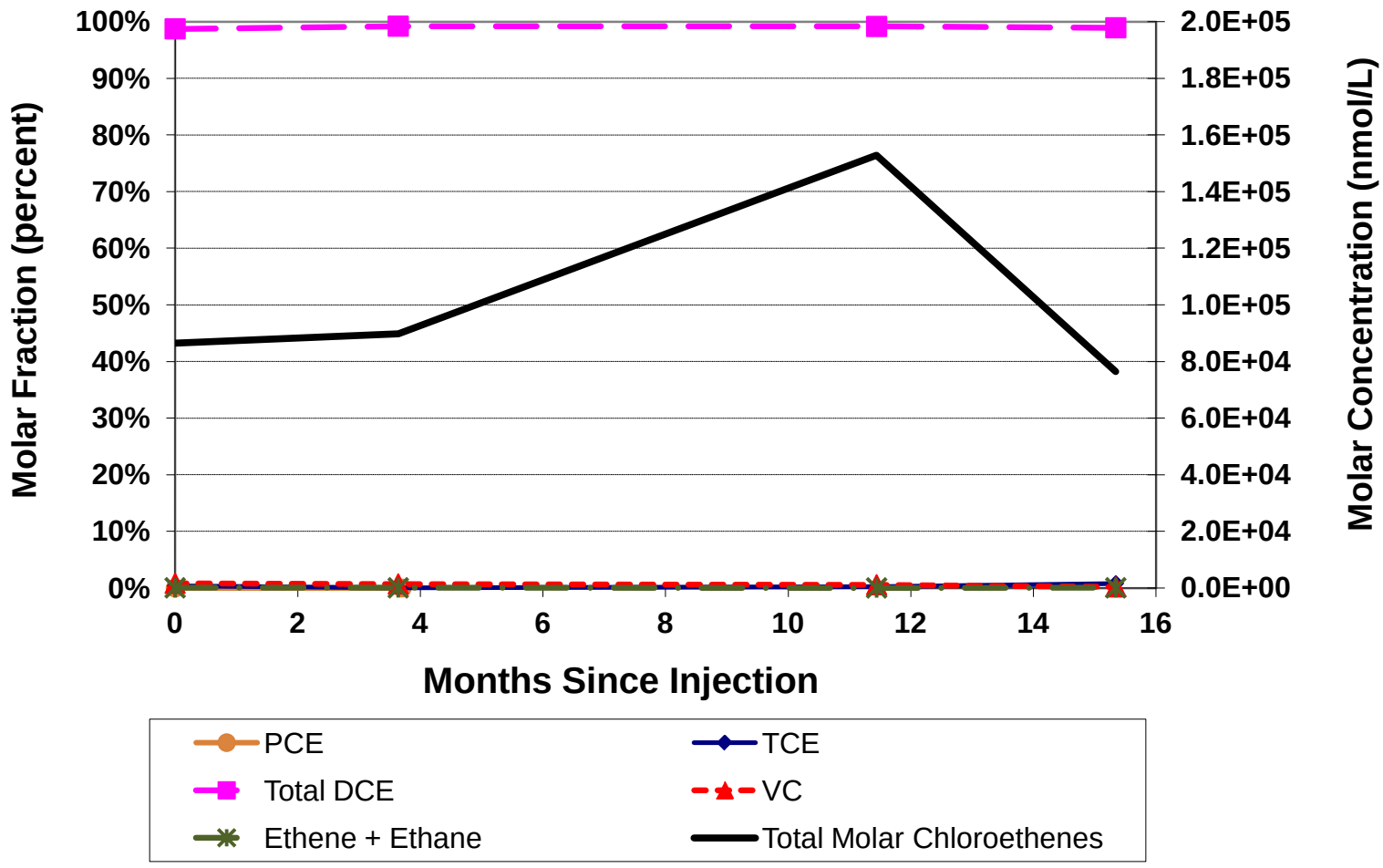


FIGURE A.14A - CONCENTRATIONS OF CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MW06

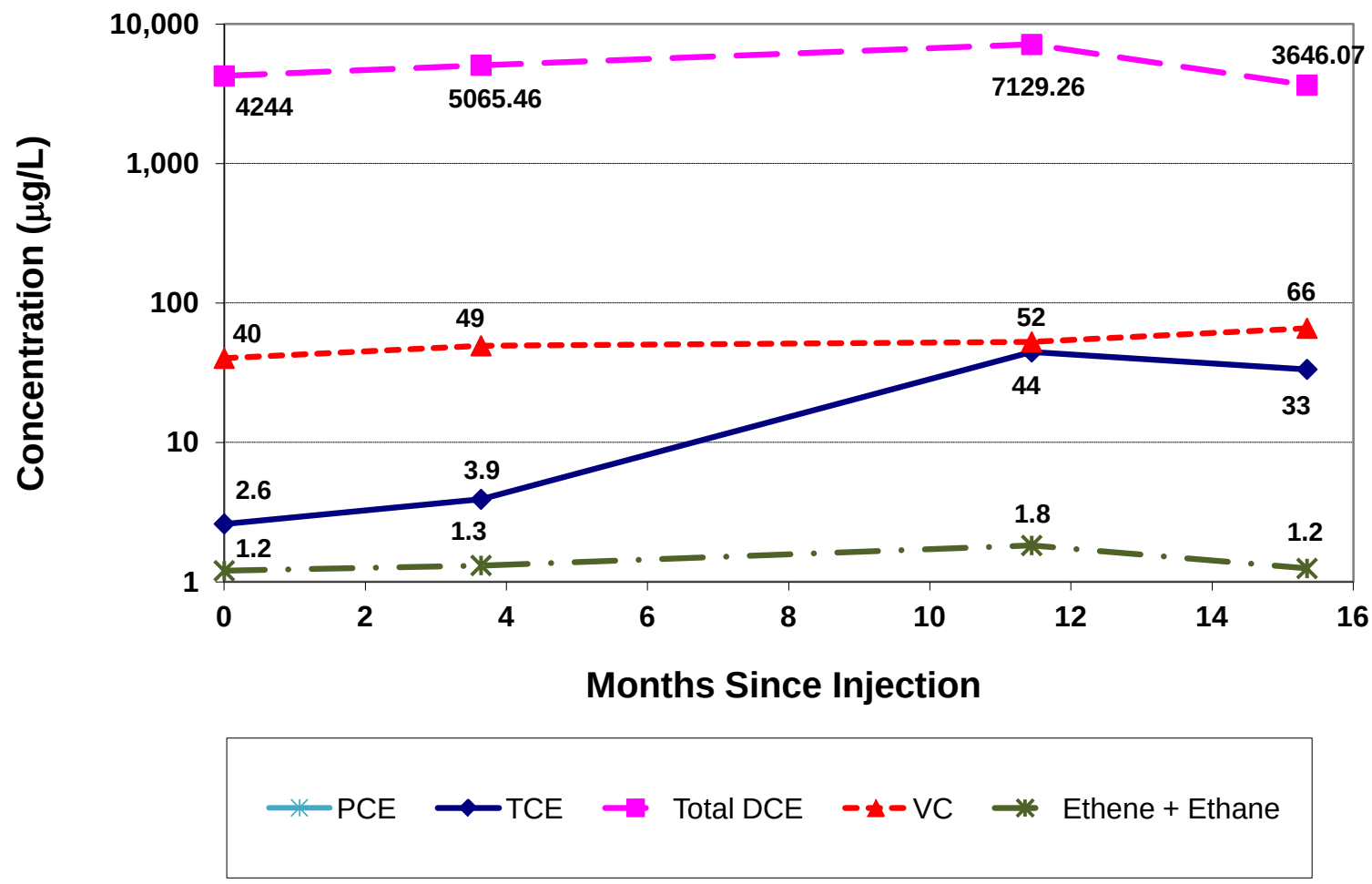


FIGURE A.14B - MOLAR FRACTION AND TOTAL MOLAR CHLOROETHENES AT DOWNGRADIENT LOCATION DP98MW06