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TECHNICAL REPORT
TR-2333-ENV

COST AND PERFORMANCE REPORT FOR PERSULFATE TREATABILITY STUDIES

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Prepared for
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14. ABSTRACT

Five persulfate application projects at four Navy sites and one Marine Corps site provide useful information on the performance of in situ chemical oxidation (ISCO) under different site conditions. The lessons learned from these early applications serve as a good guide for future users. The sites included in this review are located at the following installations: Naval Air Station (NAS) North Island, Alleghany Ballistics Laboratory (ABL), NAS Alameda, Washington Yard, and Marine Corps Base Quantico (MCBQ). The site at Washington Yard is in progress, so final conclusions cannot be made for this site at this time.

Performance data from these sites indicate that persulfate application was successful at reducing contaminants of concern (COCs) at all four sites; however, reductions were not uniform across the sites, which may be the direct result of not being able to evenly distribute the reagent throughout the target treatment areas. Typically, the greatest reductions were observed in areas near injection locations and/or those areas known to have been exposed to a relatively large mass of oxidant. Specific conclusions pertaining to the reduction of COCs at the four sites where testing has been completed include: (1) Operable Unit (OU) 20 North Island; (2) Site 1 ABL; (3) Solid Waste Management Unit (SWMU) 13 Quantico; and (4) Installation Restoration (IR) Site 14 Alameda.

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EXECUTIVE SUMMARY

Five persulfate application projects at four Navy sites and one Marine Corps site provide useful information on the performance of in situ chemical oxidation (ISCO) under different site conditions. The lessons learned from these early applications serve as a good guide for future users. The sites included in this review are located at the following installations: Naval Air Station (NAS) North Island, Alleghany Ballistics Laboratory (ABL), NAS Alameda, Washington Yard, and Marine Corps Base Quantico (MCBQ). The site at Washington Yard is in progress, so final conclusions cannot be made for this site at this time.

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- **Operable Unit (OU) 20 North Island –** Reduction of trichloroethylene (TCE) and dichloroethylene (DCE) were noted in all of the performance-monitoring wells. The sharpest reduction was noted in the monitoring wells located closest to the injection point. Rebound was noted after approximately 1 month of completing the injections, which may be attributed to the influx of contaminated groundwater from the upgradient portion of the aquifer into the treatment area or back diffusion from contamination adsorbed onto soil.

- **Site 1 ABL –** Three weeks after completing the ISCO injections, the average reduction of TCE was approximately 45%. TCE decreased in six of the eight monitoring wells and increase in the remaining two wells. Concentrations had rebounded by the six-week event, possibly due to infiltration from the surrounding untreated aquifer. Based on samples collected 5 months after completing ISCO, the average TCE concentration had rebounded to about 67% of its baseline value.

- **Solid Waste Management Unit (SWMU) 13 Quantico –** Although the application at this site was discontinued after only 13% of the design volume of reagent was injected, reductions of TCE and trichlorobenzene (TCB) were observed. Reduction of TCE (50% to 96%) was greater than that of 1,2,4-TCB (12% to 61%) in wells that had good contact with the oxidant.

- **Installation Restoration (IR) Site 14 Alameda –** The average concentration of vinyl chloride (VC) calculated using results of samples collected from wells located within or immediately adjacent to the treatment area decreased from about 44 to about 13 µg/L, a 70% reduction. Similarly, the mass of VC within the treatment areas was calculated to decrease from 0.69 to 0.21 pounds, also about a 70% reduction. Based on the first monitoring event performed after the final polishing application, only five of the 25 site monitoring wells contained VC at a concentration greater than the 15 µg/L remedial goal (RG) after the third ISCO application.

Specific lessons learned from this review are summarized as follows:

- A reduction of COCs was observed at all four sites at which persulfate was injected; however, reductions were not uniform across the sites, which likely is the direct result of not being able to

evenly distribute the reagent throughout the target treatment areas. Typically, the greatest reductions were observed in areas near injection locations and/or those areas known to have been exposed to a relatively large mass of oxidant. Results indicate that multiple rounds of ISCO injections are necessary to significantly reduce the levels of contaminants at a site. However, it should not be assumed that injecting reagents multiple times at a site will guarantee compliance with RGs. ISCO should be considered as part of a treatment train approach. The practicability of applying additional rounds of ISCO must be compared against the cost (and time required) to implement an alternative treatment technology to achieve the final RGs for the site.

- Direct injection and recirculation of the ISCO reagents are both effective means to reduce the concentration of COCs. However, both methods of application have advantages and disadvantages. Recirculation may be better suited at sites where greater control over the destination of the reagents is required such as sites located near potential receptors (i.e., surface water); sites where surfacing may be more problematic, since recirculation should, in theory, minimize the potential for surfacing; sites with low groundwater velocity; and possibly sites with relatively impermeable soils. Since the application method is dependent on many site-specific factors, pilot testing should be performed to compare the different injection methods to optimize the injection strategy and to achieve good distribution of chemicals, while minimizing the amount of chemicals used. Different injection methods should be evaluated as part of pilot testing, which should be conducted at any site prior to full-scale implementation. The pilot test should focus on optimizing the injection strategy to ensure a good distribution of chemicals, the results of which will maximize the sustainability of the full-scale system.
- Various configurations can be used for the injection layout for a recirculation system. Capture modeling is useful to optimize the configuration of injection and extraction wells.
- Real-time measurements are a useful component to process monitoring during application of ISCO. Groundwater-quality indicators, such as conductivity, pH, oxidation-reduction potential (ORP), and temperature, should be measured and used to assess the distribution of oxidant. In addition, field test kits to measure persulfate are a cost-effective method to evaluate the distribution of oxidant.
- If an activating agent is used (i.e., iron, heat, alkaline, etc.), monitoring should be performed to gauge the distribution of the activating agent to ensure that the persulfate is being activated according to design. Residual persulfate was measured in samples that also contained COCs at two of the sites reviewed, which may indicate that sufficient activation agent was not present to initiate oxidation reactions responsible for contaminant destruction.
- Multiple applications separated by several weeks/months to allow the site to begin reestablishing equilibrium between the dissolved and adsorbed phases may be necessary to achieve RGs. However, the typical cost-benefit tradeoff between the costs of longer time in the field and greater chemical usage versus the benefit of additional chlorinated volatile organic compounds (CVOCs) removal and transition to another less costly technology such as monitored natural attenuation (MNA) should be evaluated.
- Reaction byproducts are generated as sodium persulfate reacts with COCs, natural organic matter (NOM), and reduced metal species. Byproducts can include sulfuric acid, chloride and sulfate ions, ketones such as acetone and 1,2-butanone, and disinfection byproducts such as methylene chloride and trihalomethanes (THMs). Some of these byproducts, such as chloride and sulfate ions, can be monitored and tracked to help assess ISCO performance. However, others can be detrimental to the aquifer and pose risk to human health and the environment. For instance, if sufficient alkalinity is not naturally occurring, produced sulfuric acid can lower the pH of the aquifer as was observed in two monitoring wells at Alameda. Some byproducts are recalcitrant and have drinking-water maximum contaminant levels (MCLs) associated with them, such as

methylene chloride (5 µg/L) and total THMs (80 µg/L). Also, sulfate has a secondary drinking-water standard of 250 mg/L.

- ISCO appears to elevate the concentration of some metals in groundwater. Concentration of these metals may remain elevated, even after the geochemical properties of the groundwater return to baseline conditions. Some of these metals, such as arsenic or chromium (VI), can have both human health and environmental impacts; others, such as iron and manganese, have secondary drinking-water standards associated with them. Hence, longer-term monitoring is necessary to evaluate the potential for migration of these metals.
- Subsurface utilities and infrastructure must be accounted for during the design. For example, subsurface utilities can act as a conduit to transport the oxidant and other reaction products from the treatment area to potential receptors.
- Bench-scale tests are useful tools to determine required oxidant concentration, oxidant demand, and theoretical reductions of COC prior to designing and implementing ISCO at either the pilot- or full-scale level. Soil oxidant demand (SOD) values are site-specific, increasing with increased contact time and oxidant concentration.
- Persulfate persists in the subsurface for weeks, which indicates that the natural oxidant demand (NOD) of the soil for persulfate is low. This also indicates that the performance-monitoring program should include multiple rounds of post-ISCO sampling to better evaluate changes that occur as residual persulfate is consumed.
- It may not always be necessary to add an activating agent depending on site-specific conditions. Substantial declines in TCE and DCE were noted at the North Island site, where application of persulfate was performed at groundwater temperatures of 20 to 24 °C without the addition of a specific activation agent (heat, sodium hydroxide, or iron).
- Rebound observed at North Island and ABL may largely have been due to influx of contaminated groundwater from the upgradient portion of the aquifer, which demonstrates the difficulty of selecting and evaluating the results obtained from a pilot test. It is best to locate the pilot test plot in an area to the side of a plume, which is less likely to be impacted by contaminated groundwater outside the treatment area. Modeling of mass flux downgradient of the treatment area is a useful tool to estimate the impact of the pilot test on downgradient receptors.
- Since the success of this technology appears to hinge on achieving adequate contact between the contaminants and the reagents, ISCO using persulfate will be more successful (i.e., greater overall contaminant reduction, lower cost) at sites that consist of more permeable materials, such as sands, as opposed to impermeable silts and clays. Heterogeneous matrices are much more difficult to treat because it is difficult to distribute the reagents and achieve contact in the low-permeability areas where a significant portion of the contaminants may reside. The vertical extent of contamination and depth of the contamination also will significantly impact cost and ease of application, since it will be more difficult to inject the reagents and achieve uniform distribution across larger vertical horizons. Sites that have a significant mass of contaminants adsorbed to soil in the unsaturated zone also may not be well-suited for this technology, since it may be difficult to achieve adequate contact between the reagents and the contaminated soil for extended periods.

CONTENTS

FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

ABL	Alleghany Ballistics Laboratory
AOC	Areas of Concern
As	arsenic
AST	aboveground storage tank
bgs	below ground surface
BSU	Bay Sediment Unit
COC	contaminants of concern
Cr	chromium
CVOC	chlorinated volatile organic compound
DBP	disinfection byproduct
DCE	dichloroethylene
DNAPL	dense, non-aqueous phase liquid
DO	dissolved oxygen
DoD	U.S. Department of Defense
DPT	direct push technology
EDTA	ethylene diamine tetracetic acid
ESTCP	Environmental Security Technology Certification Program
FWBZ	first water-bearing zone
GAP	generator accumulation point
gpm	gallons per minute
GWETS	groundwater extraction and treatment system
GWTP	groundwater treatment plant
IR	Installation Restoration
I-RACR	Interim Remedial Action Completion Report
ISB	in situ bioremediation
ISCO	in situ chemical oxidation
ITRC	Interstate Technology Regulatory Council
ITSI	Innovative Technical Solutions, Inc.
IWP	industrial wastewater plant
LNAPL	light non-aqueous phase liquid
MCBQ	Marine Corps Base Quantico
MCL	Maximum Contaminant Level
Mn	manganese
MNA	monitored natural attenuation
NAPL	non-aqueous phase liquid
NAS	Naval Air Station
NOM	natural organic matter
NOD	natural oxidant demand

ORP	oxidation-reduction potential
OU	Operable Unit
PCE	perchloroethylene
PLFA	phospholipid fatty acids
psi	per square inch
PVC	polyvinyl chloride
RG	remedial goal
RI	Remedial Investigation
ROI	radius of influence
RPM	Remedial Project Manager
SCFM	standard cubic feet per minute
SOD	soil oxidant demand
SWMU	Solid Waste Management Unit
TCA	1,1,1-trichloroethane
TCB	1,2,4-trichlorobenzene
TCE	trichloroethylene
THM	trihalomethane
TOC	total organic carbon
TPH	total petroleum hydrocarbons
U.S. EPA	U.S. Environmental Protection Agency
UST	underground storage tank
VC	vinyl chloride
VOC	volatile organic compound
WD	washdown
WNY	Washington Naval Yard

Section 1.0: INTRODUCTION

In situ chemical oxidation (ISCO) is a technique used to remediate subsurface contaminants using strong chemical oxidants, such as persulfate, hydrogen peroxide, permanganate, and ozone. The most common contaminants targeted for ISCO treatment are sites with chlorinated solvents and petroleum-related chemicals. The effectiveness of ISCO depends on the geology, the residence time of the oxidant, the amount of oxidant used, and the effective contact the oxidant has with the contaminant(s). This cost and performance report is a critical review of technical and performance data from four Navy projects and two Marine Corps projects involving the use of ISCO utilizing sodium persulfate as the oxidant.

As of the writing of this report, projects at three of the sites were completed; three projects were in process. The sites include:

- Naval Air Station (NAS) North Island, San Diego, California (completed): The report reviewed was *Persulfate Pilot Test Summary Report: Naval Air Station North Island Operable Unit 20, San Diego, California* (Shaw, 2007).

- Alleghany Ballistics Laboratory (ABL), Rocket Center, West Virginia (completed): The report reviewed was *In Situ Chemical Oxidation Pilot Study at the Solvent Disposal Pit Area of Site 1, Alleghany Ballistics Laboratory, Rocket Center, West Virginia* (CH2MHILL, 2008).

- Marine Corps Base Quantico (MCBQ), Quantico, Virginia (completed): The report reviewed was *ISCO Pilot Remediation Results SWMU M-13, Marine Corps Base Quantico* (AGVIQ-CH2MHILL, 2008).

- NAS Alameda, Alameda, California (interim report): The documents reviewed were the *Final Remedial Design/Remedial Action Work Plan Installation Restoration Site 14, Alameda Point, Alameda, California* (Battelle, 2008) and the *Workplan for Data Gap Sampling Investigation, Installation Restoration Site 14, Alameda Point, California* (Innovative Technical Solutions, Inc. [ITSI], 2007). Project files were also available to the authors.
- Washington Navy Yard, Washington, DC (in process): The work plan reviewed was *Work Plan for ISCO Pilot Test Injection at Building 71 UST Case Site, Washington Navy Yard, Washington, D.C.* (CH2MHILL, 2009).

The current document is intended to be a synopsis of the results of these technology applications and a consolidation of the lessons learned for future applications. It is anticipated that this report will be updated once the persulfate applications at all sites have been completed.

1.1 Report Organization

This report is organized into the following sections:

1.0 Introduction. This section provides the report framework, an introduction to the persulfate application, and the variations of this technology that were demonstrated or are currently being demonstrated.

2.0 Persulfate Application at North Island

3.0 Persulfate Application at Alleghany Ballistics Laboratory

4.0 Persulfate Application at Marine Corps Base Quantico

5.0 Persulfate Application at Alameda

6.0 Persulfate Application at Washington Yard

7.0 Summary of Conclusions. This section summarizes the conclusions and lessons learned from the persulfate application at these five sites.

8.0 References. This section lists the references used to prepare this report.

1.2 In Situ Chemical Oxidation Using Persulfate – Technology Description

ISCO involves the introduction of oxidants into the source zone and/or downgradient plume to react with contaminants of concern (COCs) to generate innocuous products such as water, carbon dioxide, and chloride.[1] Historically, strong oxidants such as hydrogen peroxide, ozone, and permanganate have been used. More recently, persulfate has been tested and proven to be an effective oxidant for treating contamination such as chlorinated ethenes.

Persulfate is applied in the form of a salt, which dissociates in water to form the sulfate anion, $S_2O_8^{2-}$. The persulfate salts are available as ammonium persulfate, sodium persulfate, and potassium persulfate. However, ammonium persulfate is typically not applied in environmental applications due to the formation of ammonia and potassium persulfate and because of its low solubility in groundwater.

Sodium persulfate is a yellow crystal having a solubility of about 40% in water at room temperature. It is more stable than hydrogen peroxide and has a high oxidation potential.[2] The oxidation-reduction reaction of persulfate is:

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad (1)$$

Although highly oxidizing, this reaction is kinetically slow. The reaction of persulfate with trichloroethylene (TCE) is:

$$3NaS_2O_8 + C_2HCl_3 + 4H_2O \rightarrow 9H^+ + 2CO_2 + 3Na + 3Cl^- + 6SO_4^{2-} \qquad (2)$$

A number of methods are available to “activate” the persulfate to form the sulfate radical, $SO_4^{-}\bullet$, which has a much higher oxidation potential (2.6 V) than the sulfate anion, is kinetically fast, and is much more stable than the hydroxyl radical, allowing it to migrate greater distances in the aquifer. Methods commonly employed at environmental sites include the application of heat via steam, raising the pH of the aquifer through adding a base such as sodium hydroxide, adding peroxides such as calcium peroxide or hydrogen peroxide, and the addition of a ferrous salt to catalyze the reaction. The reaction mechanisms are complex and involve a number of chain-initiating, -propagating, and -terminating reactions.

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[1] Chloride is generated during the oxidation of chlorinated ethenes, which historically have been the primary COCs treated using ISCO.

[2] The sulfate anion has an oxidation potential of 2.1 V compared to 1.8 V for hydrogen peroxide.

Three principal types of methods have been used to introduce the reagents into the ground:

- **Direct Injection:** The reagents are injected directly from an external source into the subsurface in a specified volume of water, displacing groundwater corresponding to the volume of reagent injected.
- **Pull-Push:** A set volume of groundwater is extracted, amended with reagents aboveground, and then reinjected into the subsurface through the same well and well screen from which it was extracted.
- **Recirculation:** In a closed system, groundwater is extracted from a set of extraction wells, amended with the reagents, and then reinjected into a different series of injection wells.

Direct injection is a common approach for target areas with stationary contaminants, which are usually attached to soils or in the non-aqueous phase liquid (NAPL) phase, so that the natural groundwater can be displaced with the reagent solution to establish contact between the reagents and the contaminants. Direct injection can be used to treat aqueous-phase contamination if steps are taken to establish contact between the reagents and the contaminants. Both pull-push and recirculation strategies tend to be more costly than direct injection and are used to treat both aqueous and more stationary-phase contamination. The advantage of each approach is that contact between the reagents and aqueous-phase contamination is established aboveground, thus ensuring contact. The reagent solution is then injected into the subsurface where it can contact contamination in groundwater, including groundwater in low-permeability zones, as well as soil that still resides in the subsurface. Of these three methods, direct injection historically has been the most common approach utilized at sites.

ISCO using persulfate can be a very effective method to provide in situ destruction of contaminants, such as chlorinated ethenes in groundwater; however, several concerns associated with persulfate application must be considered. Some of the more common concerns are:

- There is potential to mobilize metals within the treatment area due to changes in pH and the oxidation state of the aquifer.
- As with all oxidants, the natural oxidant demand (NOD) must be considered when designing the system.
- Some materials, such as soft metals, may be degraded by a concentrated solution of persulfate.

Section 2.0: PERSULFATE APPLICATION AT NORTH ISLAND

2.1 Introduction

This section summarizes the results, reviews the performance, and cites lessons learned from the persulfate injection pilot test conducted at the Building C-40 site, Operable Unit (OU) 20, NAS North Island, San Diego, California. The report reviewed was *Persulfate Pilot Test Summary Report: Naval Air Station North Island Operable Unit 20, San Diego, California* (Shaw, 2007). The pilot test field activities were conducted between November 2006 and June 2007. The treatment was targeted in an area containing groundwater contaminated with chlorinated volatile organic compounds (CVOCs), primarily TCE. The field pilot tests were conducted after site-specific bench-scale tests showed that persulfate would be effective at this site. Generation of the highly reactive sulfate radical at this site was reportedly initiated by low-temperature heat activation at groundwater temperatures of 20 to 24°C.[3]

2.2 Geology and Hydrogeology

Site lithology identified during installation of the monitoring wells indicates that the unconfined surficial aquifer at this site consists of interbedded layers of poorly graded fine to very fine sand and silty sand. Shell fragments were identified in the majority of the well borings. These soils are part of the Bay Point Formation. The depth to groundwater measured in March 2007 ranged from 19.3 to 20.3 feet below ground surface (bgs).

Regional groundwater flow is toward the northeast, with a relatively flat hydraulic gradient of 0.001 foot/ foot. Accessibility (absence of aboveground buildings, minimum disruption of traffic, etc.) was a major factor in selecting the pilot site at the intersection of Quentin Roosevelt Boulevard and 1st Street (see Figure 2-1).

2.3 Contaminant Distribution

The primary CVOCs detected in direct-push groundwater samples and their maximum concentrations are TCE, cis-1,2-dichloroethene (DCE), and 1,1-DCE at 6,800 μg/L, 2,300 μg/L, and 160 μg/L, respectively.

The highest TCE concentration in the direct-push groundwater sampling occurred in OU 20-DB-06 (see Figure 2-1). The highest detected TCE soil concentration (220 μg/kg) was observed at OU 20-PEW-6 at 49.5 feet bgs. The highest groundwater baseline (pre-treatment) TCE concentration in the monitoring wells occurred in OU20-PMW-9 (16,500 μg/L). In Figure 2-1, a north/south-oriented oval area encompassing these points of high TCE concentration was the targeted treatment area. The highest TCE concentration of 16,500 μg/L, which is about 1.5% of its solubility in groundwater, is higher than the threshold concentration (1% of solubility) and is generally accepted as indicative of dense non-aqueous phase liquid (DNAPL). Elevated concentrations of TCE are present both upgradient and downgradient of the target treatment area, thus indicating the potential presence of additional DNAPL sources in the surrounding aquifer.

The pilot-scale treatment was targeted at a 10-foot-thick depth interval ranging from 44 to 54 feet bgs, where much of the contamination is reported to be sequestered. The aquifer continues several feet deeper

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[3] For purposes of this report, no activation is assumed since the groundwater temperature was not augmented via an external source (steam, resistive heating, etc.)

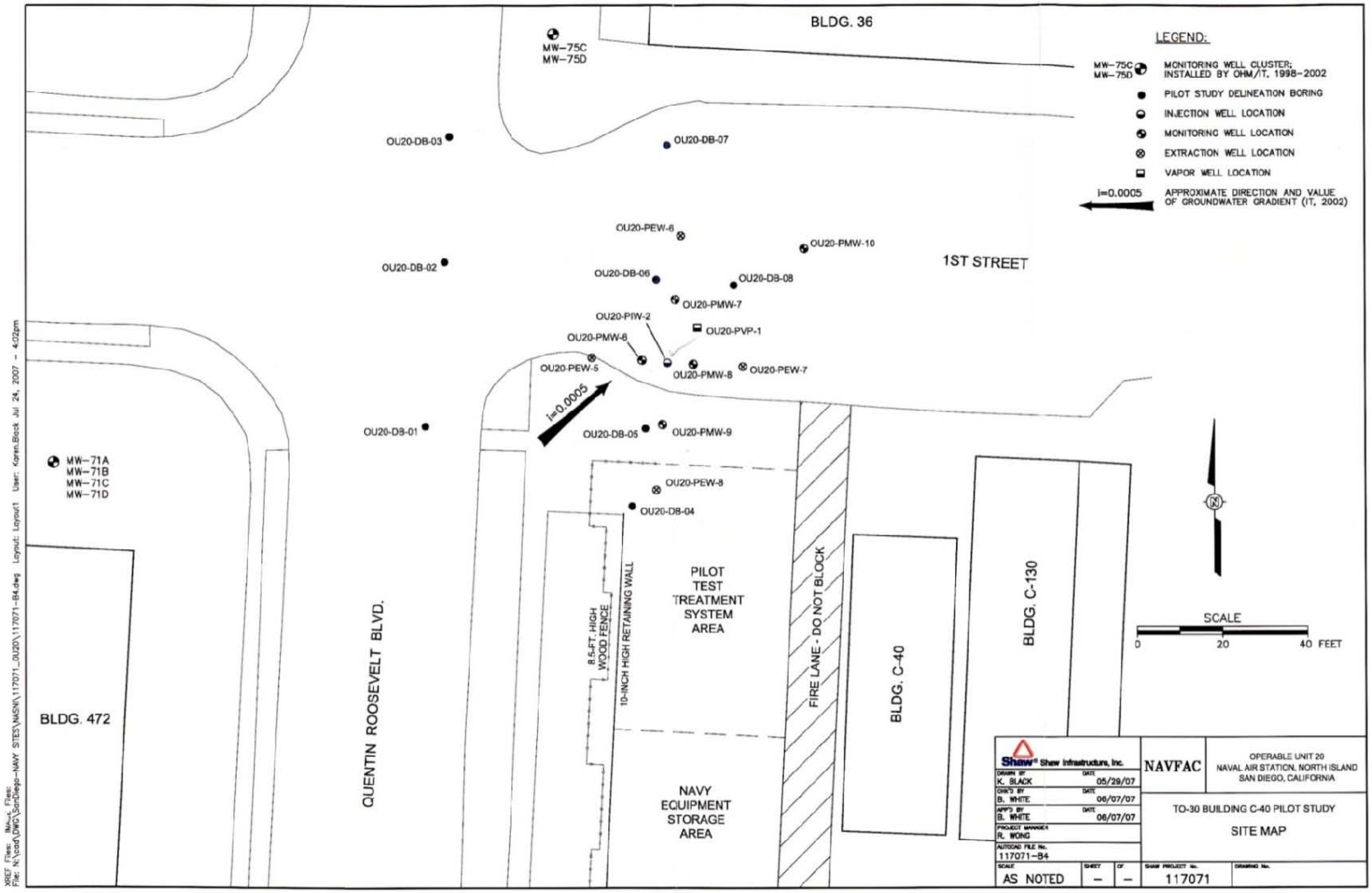


Figure 2-1. NAS North Island Site Layout

below the target treatment zone. It is believed that a freshwater-saltwater interface is present about 54 feet bgs as evidenced by sharp spikes in conductivity that were measured during the membrane interface probe investigation (Shaw, 2007). It is hypothesized that the density gradient at the interface may be preventing further downward migration of the contaminated groundwater.

2.4 Technology Implementation

Persulfate was introduced into the target aquifer zone using a recirculation system consisting of four extraction wells (OU 20-PEW-5, OU 20-PEW-6, OU 20-PEW-7, and OU 20-PEW-8) located at the approximate corners of a diamond-shaped area. The northern and southern extraction wells were located farther apart than the eastern and western extraction wells. These wells have 10-foot-long screens targeted at the 44- to 54-feet bgs interval. The target treatment volume was estimated to be about 40 feet wide (between eastern and western extraction wells), 60 feet long (between northern and southern extraction wells), and 10 feet thick. At an estimated porosity of 28%, this equates to a pore volume of about 50,300 gallons.

The primary components of the injection system consisted of transfer pumps, a system manifold to receive the extracted groundwater, a pre-filtration element to remove sediment from the water, a mixer to mix the persulfate with the extracted water, and a post-filtration element to remove particulates from the injected fluids. Based on bench-scale results, a 3% to 6% solution of persulfate was determined to be desirable, and a 4.5% solution was targeted for the field application. A total of 22,600 pounds of sodium persulfate well mixed with 60,000 gallons of groundwater were extracted from the edges of the treatment zone and injected back in the aquifer.

The oxidant was injected continuously from January 26 to February 1, 2007. The initial groundwater extraction rates were 3 gallons per minute (gpm) per well (from the northern and southern extraction wells) and 2 gpm per well (from the eastern and western extraction wells) for a total injection rate of 10 gpm. Each batch of treated groundwater consisted of approximately 1,020 gallons of groundwater mixed with 386 pounds of oxidant. Potassium iodide starch paper was used to gauge how far persulfate had traveled in the aquifer from the central injection well.

2.5 Performance Evaluation Approach

Four performance-monitoring wells (OU 20-PMW-06 to -09) were installed between the central injection well and each of the extraction wells. A soil vapor probe was installed at OU 20-PVP-1. An additional monitoring well (OU 20-PMW-10) was installed just beyond the downgradient edge of the array to determine any downgradient migration of contaminants or oxidant. All monitoring wells have 10-foot-long screens at the target treatment interval. Aquifer slug tests were conducted before and after treatment in injection and extraction wells. Water-level measurements were conducted on March 19, 2007.

Following a baseline (pre-treatment) groundwater sampling event conducted from January 9 through 11, 2007, post-treatment monitoring was conducted 7, 19, 30, 60, and 90 days after the final injection of persulfate (February 8, February 20, March 5, April 4, and May 2). In addition to the CVOCs, groundwater samples were analyzed for field parameters (dissolved oxygen [DO], oxidation-reduction potential [ORP], pH, conductivity) and geochemical parameters (including trace metals).

2.6 Technology Performance

Figure 2-2 shows the TCE and cis-1,2 DCE trends in the performance-monitoring wells. TCE levels showed a sharp decline, especially in the 7-day and 19-day post-treatment events, following

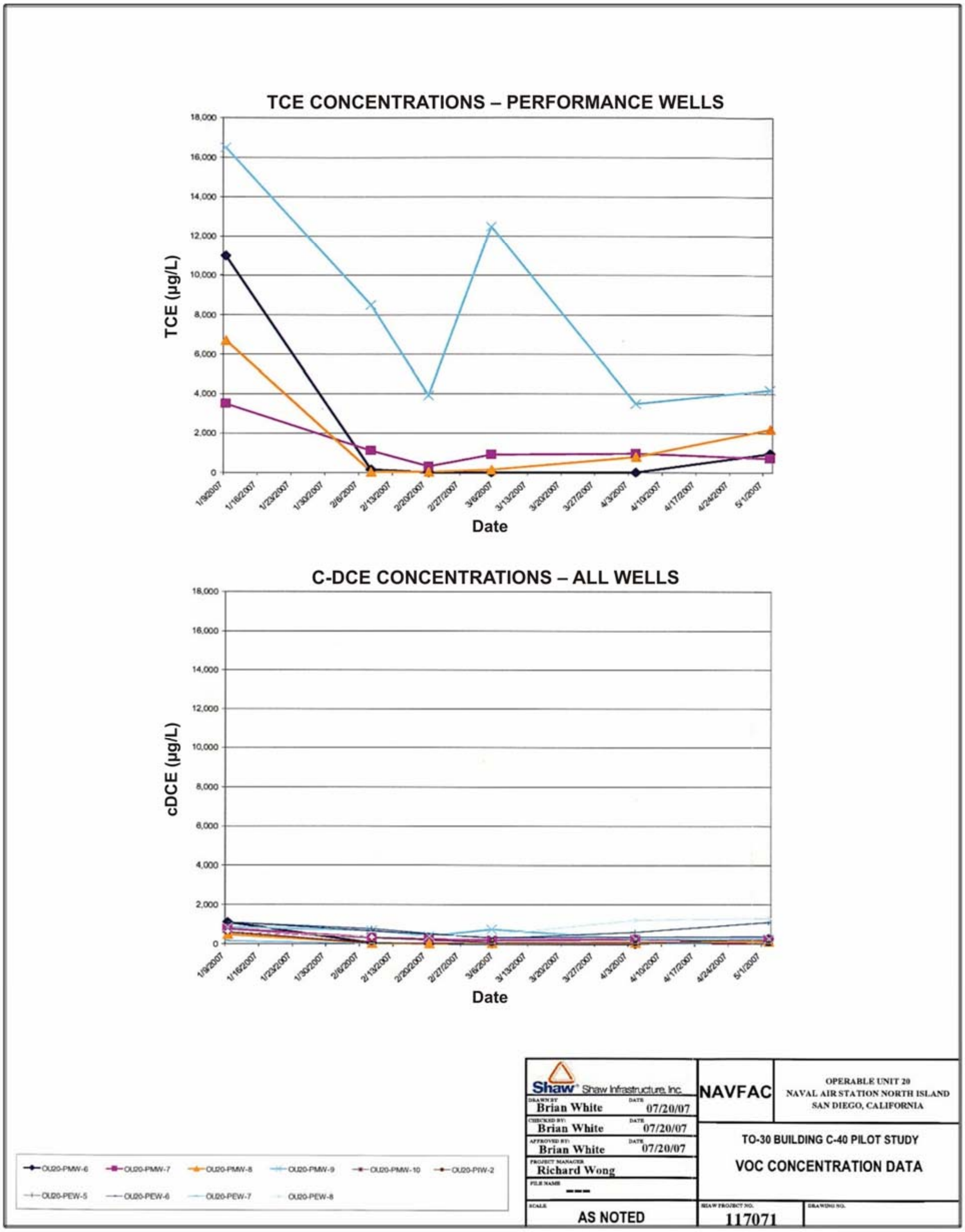


Figure 2-2. TCE and cis-1,2 DCE in Treatment Area Wells

which the wells showed varying degrees of rebound. This sharp decline in TCE levels immediately following oxidant injection, along with other indicators, showed that the oxidant distribution was successful. The subsequent rebound appears to be largely due to influx of contaminated groundwater from the upgradient portion of the aquifer. PMW-6 and PMW-8 exhibited the sharpest decline in both TCE and cis-1,2 DCE. These are the two wells located closest to the central injection point (approximately 10 feet). PMW-7 and PMW-9, which are located farther away (approximately 20 feet) from the injection point, did not show as sharp a decline, although TCE concentrations continued to decline into the 60- and 90-day post-treatment periods in these wells. This indicates that oxidant persisted in the aquifer for a considerable time. As expected, TCE and cis-1,2 DCE levels declined sharply in injection well PIW-2, often to non-detect levels.

Figure 2-3 shows the residual persulfate concentrations in the wells at different times. The persulfate data are congruent with the TCE data. The wells with the highest persulfate residuals (PIW-2, PMW-6, and PMW-8) also show the greatest TCE declines and are closest to the injection well. More distant wells, such as PMW-7 and PMW-9, as well as eventually PMW-10, indicate arrival of the residual persulfate front. At the end of 90 days, residual persulfate remained in all treatment-area wells. The fact that residual persulfate co-exists with stable or increasing TCE levels in several wells, such as PEW-5, may indicate that a certain threshold level of persulfate may be required to initiate oxidation reactions responsible for TCE destruction. PEW-5 was the only well that did not show any substantial TCE post-treatment decline, indicating that persulfate distribution in this region may have been limited. On the other hand, TCE levels declined initially in PMW-8, but rebounded sharply during later monitoring events, despite high levels of residual persulfate reaching this well.

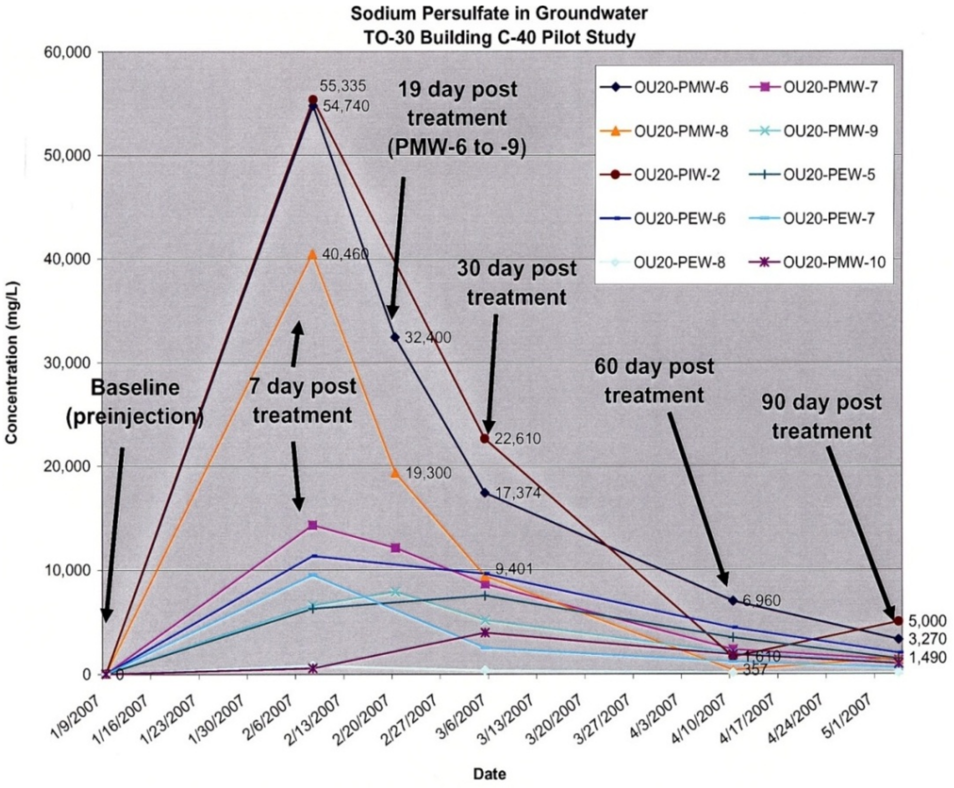


Figure 2-3. Residual Persulfate Levels in Treatment Area Wells

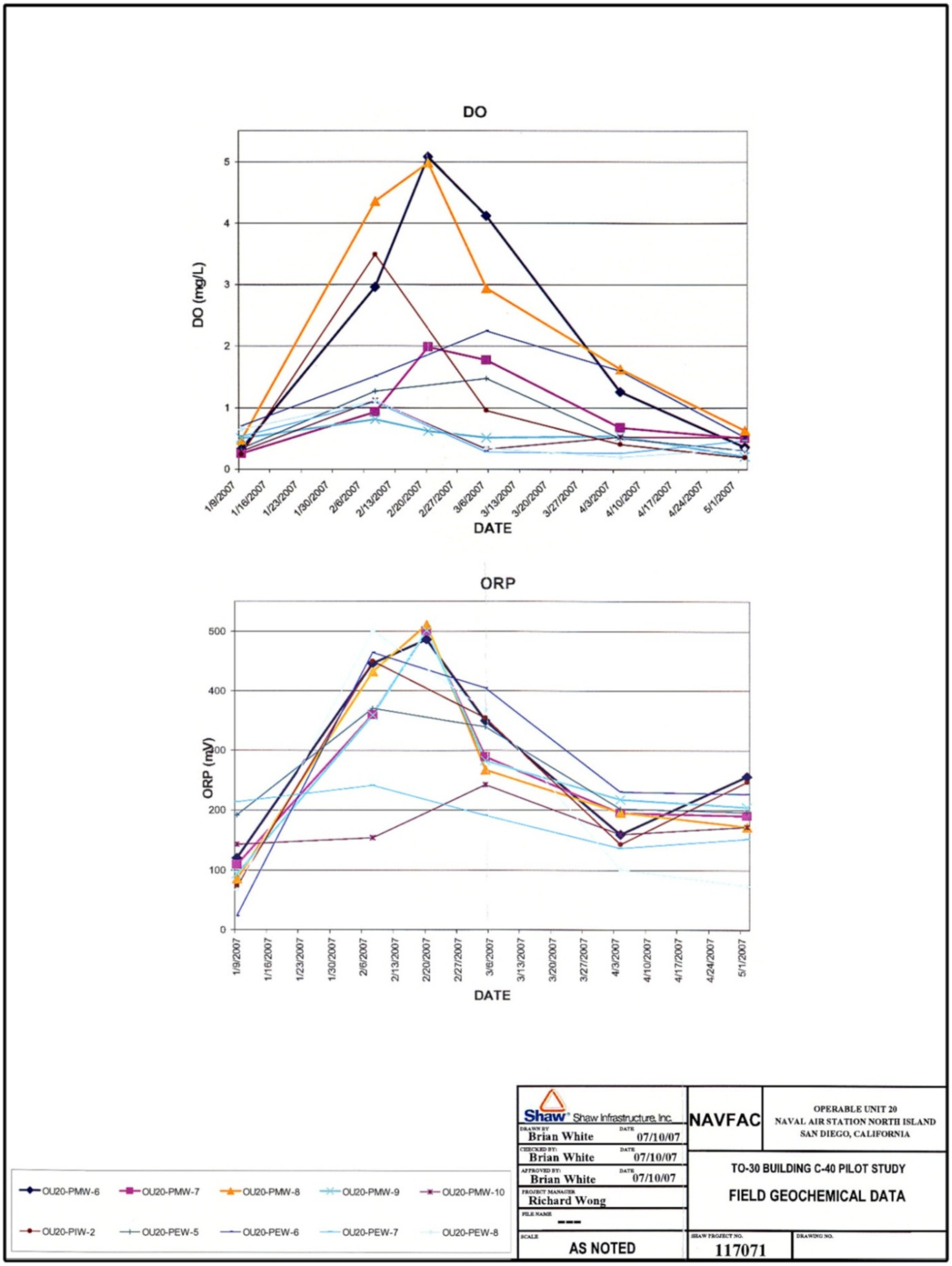
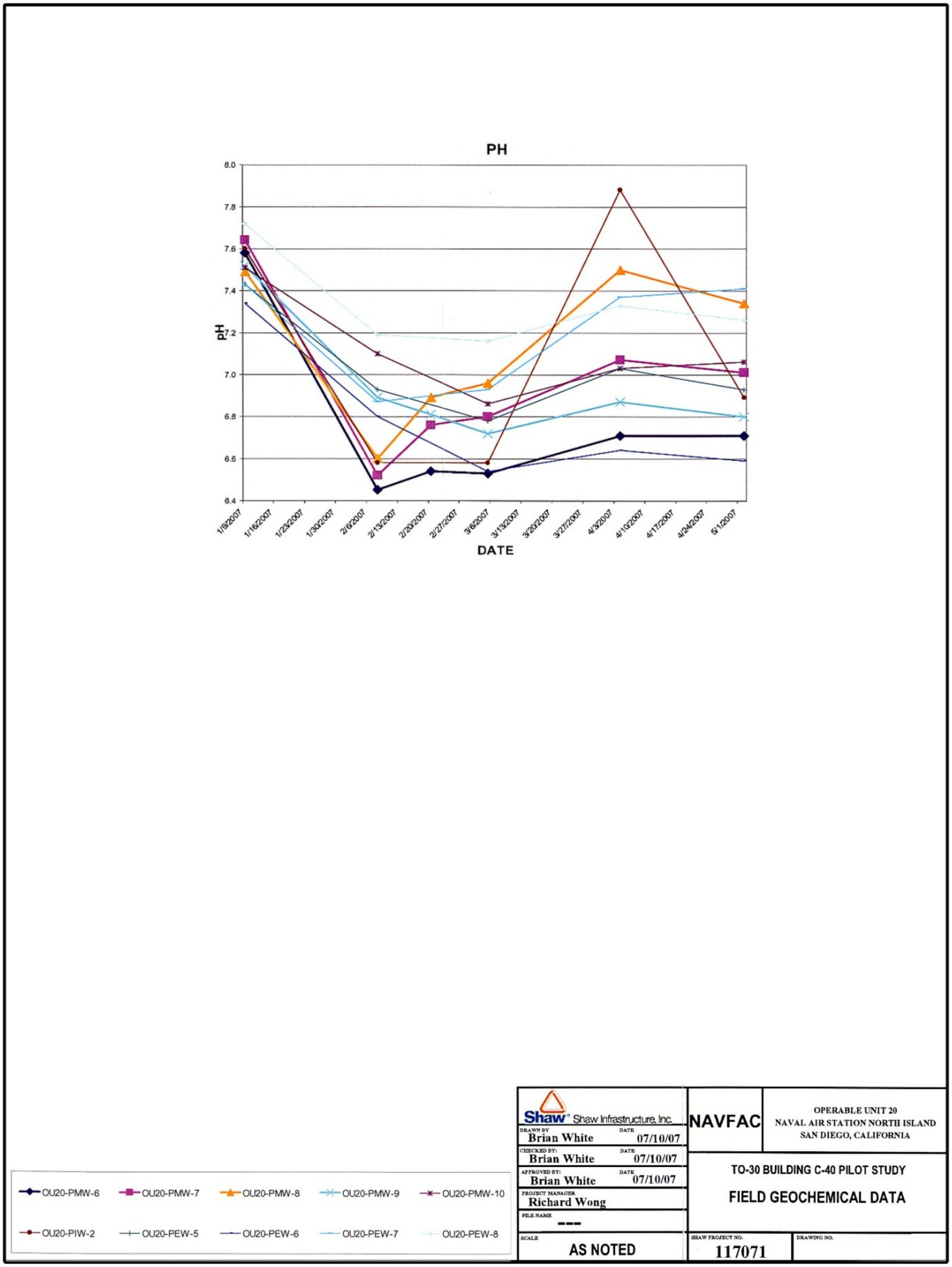


Figure 2-4. DO and ORP



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OPERABLE UNIT 20
NAVAL AIR STATION NORTH ISLAND
SAN DIEGO, CALIFORNIA

TO-30 BUILDING C-40 PILOT STUDY
FIELD GEOCHEMICAL DATA

SHAW PROJECT NO. 117071
DRAWING NO.

Figure 2-5. Groundwater pH

ORP, DO, and pH (see Figures 2-4 and 2-5) responded sharply to the persulfate injection. ORP rose sharply in several wells, whereas pH declined sharply. These trends are along the expected lines for generation of strongly oxidizing conditions in the aquifer. However, it is difficult to correlate TCE treatment performance with residual persulfate, ORP, or pH levels in individual wells.

Chloride and sulfate (see Figure 2-6) rose sharply in several wells. The sharp increase in sulfate levels is accounted for by the fact that persulfate reacts with reduced organic matter (and CVOCs) to form sulfate. The sharp increase in chloride levels in some wells, such as PMW-10, PEW-8, and PIW-2, is harder to explain. Pre-treatment CVOC concentrations are in the few tens of mg/L, whereas pre-treatment chloride concentrations ranged from 220 to 1,520 mg/L. It would be difficult for any chloride generated from CVOC degradation to have a noticeable impact on native chloride levels.

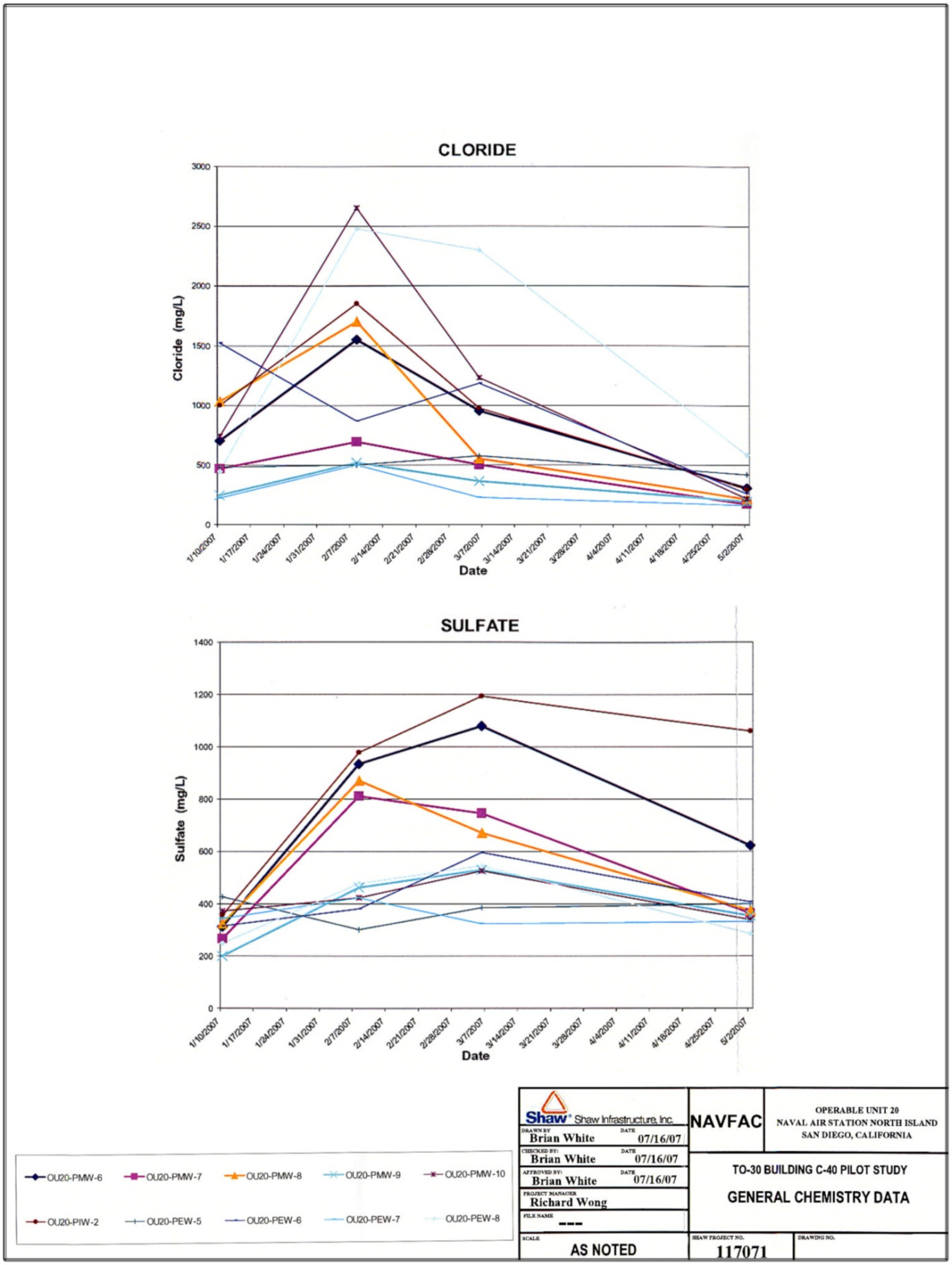
Figures 2-7, 2-8, and 2-9 show the metals concentrations in the groundwater. Dissolved iron rose sharply in some wells, and manganese (Mn) levels declined sharply in all wells. The sharp drop in manganese is another indication of the strongly oxidizing conditions that convert Mn (II) to Mn (IV), which precipitates out as manganese dioxide. Typically, native dissolved iron is expected to precipitate out (decline) under strongly oxidizing conditions, but in this case, the source of iron might be mineral in origin. Dissolution of reduced mineral species (e.g., pyrite and other ores) under strongly oxidizing conditions may contribute to increases in both dissolved iron and sulfate, as well as increased arsenic (As), vanadium, and chromium (Cr). Although the geochemical environment (pH, ORP, and DO levels) has rebounded to pre-treatment conditions, many of these metals continue to remain substantially elevated. The fate of these metals needs to be tracked during additional monitoring in the treatment-zone wells, and perhaps in wells that are further downgradient.

As shown in Table 2-1, slug tests conducted in the treatment-zone wells before and after persulfate treatment showed that the hydraulic conductivity did not change much, except in PEW-07; the reason for this is unclear. Slug tests were conducted only in the injection and extraction wells. Water entering the injection well had been filtered twice, once before and once after the persulfate mixing tank; hence, any suspended solids would have been removed during the recirculation. Bench-scale tests that indicated the possibility that calcium sulfate solids generated when persulfate reacted with native alkalinity (calcium carbonate) in the groundwater could be significant. However, in this recirculation-filtration mode, this does not appear to have been a problem. It would have been interesting to analyze the solids deposited on the filters for calcium. It also would have been interesting to see slug test results for some of the performance-monitoring wells, especially PMW-6 and PMW-8, which are close to the injection well and probably received the strongest dose of persulfate.

Table 2-1. Slug Test Results

Well	Date*	Average Hydraulic Conductivity (ft/day)
PIW-02	Jan-07	0.58
	Mar-07	0.69
PEW-05	Jan-07	22.44
	Mar-07	25.24
PEW-06	Jan-07	22.85
	Mar-07	26.11
PEW-07	Jan-07	73.99
	Mar-07	14.83
PEW-08	Jan-07	31.47
	Mar-07	30.20

*Pre-treatment (January) and post-treatment (March).



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TO-30 BUILDING C-40 PILOT STUDY
GENERAL CHEMISTRY DATA

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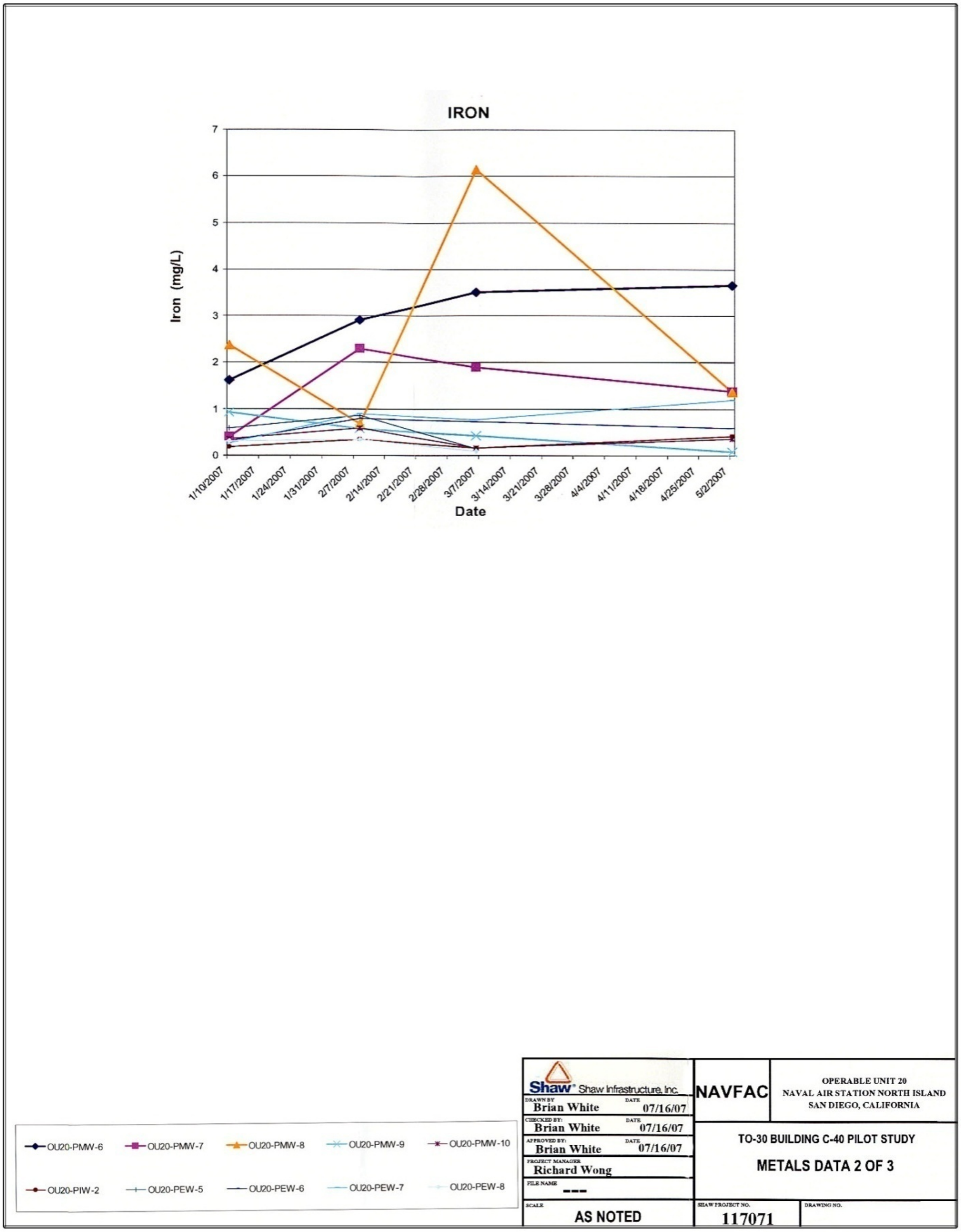
Figure 2-6. Chloride and Sulfate



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METALS DATA 2 OF 3

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Figure 2-7. Dissolved Iron

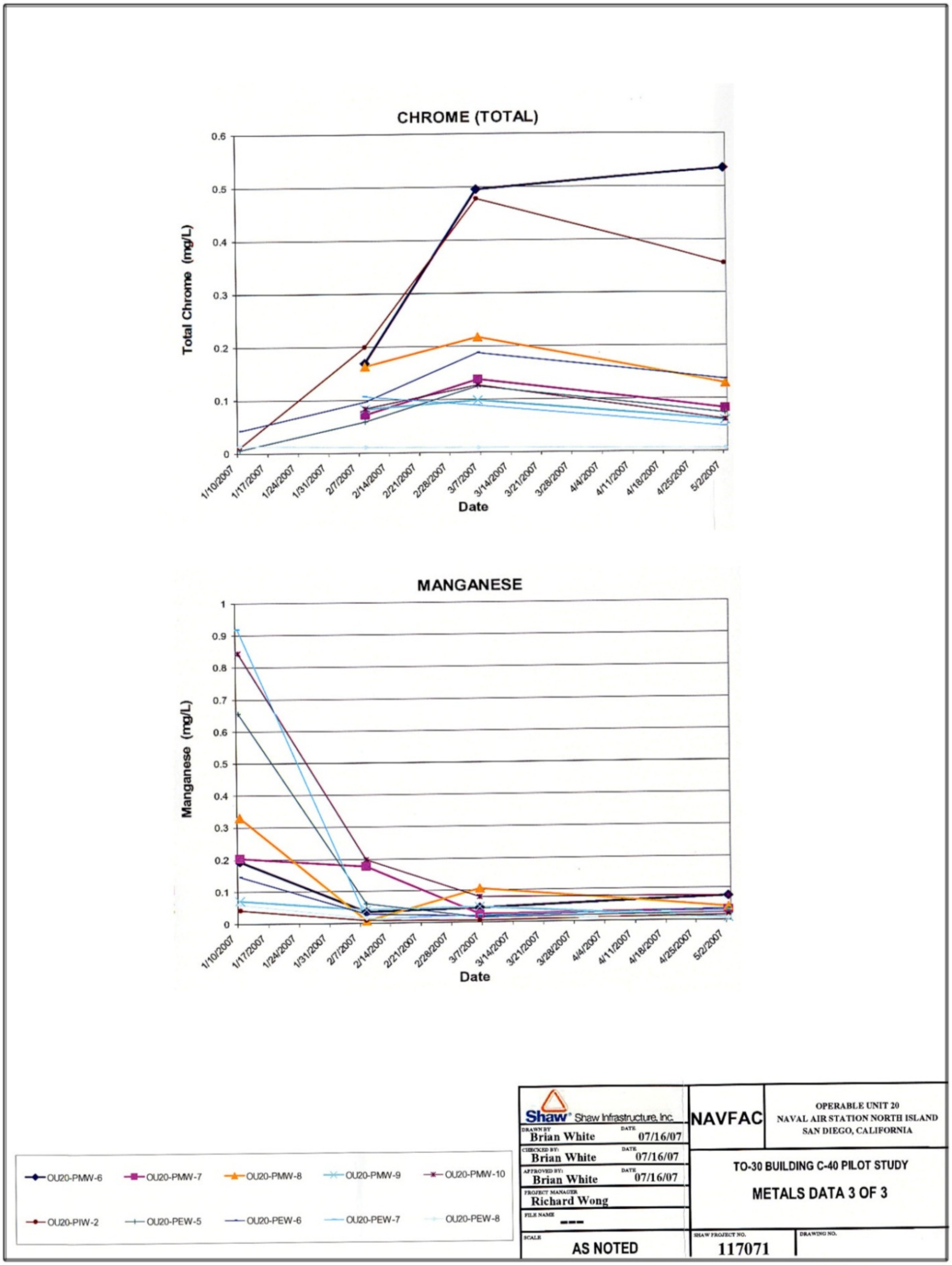

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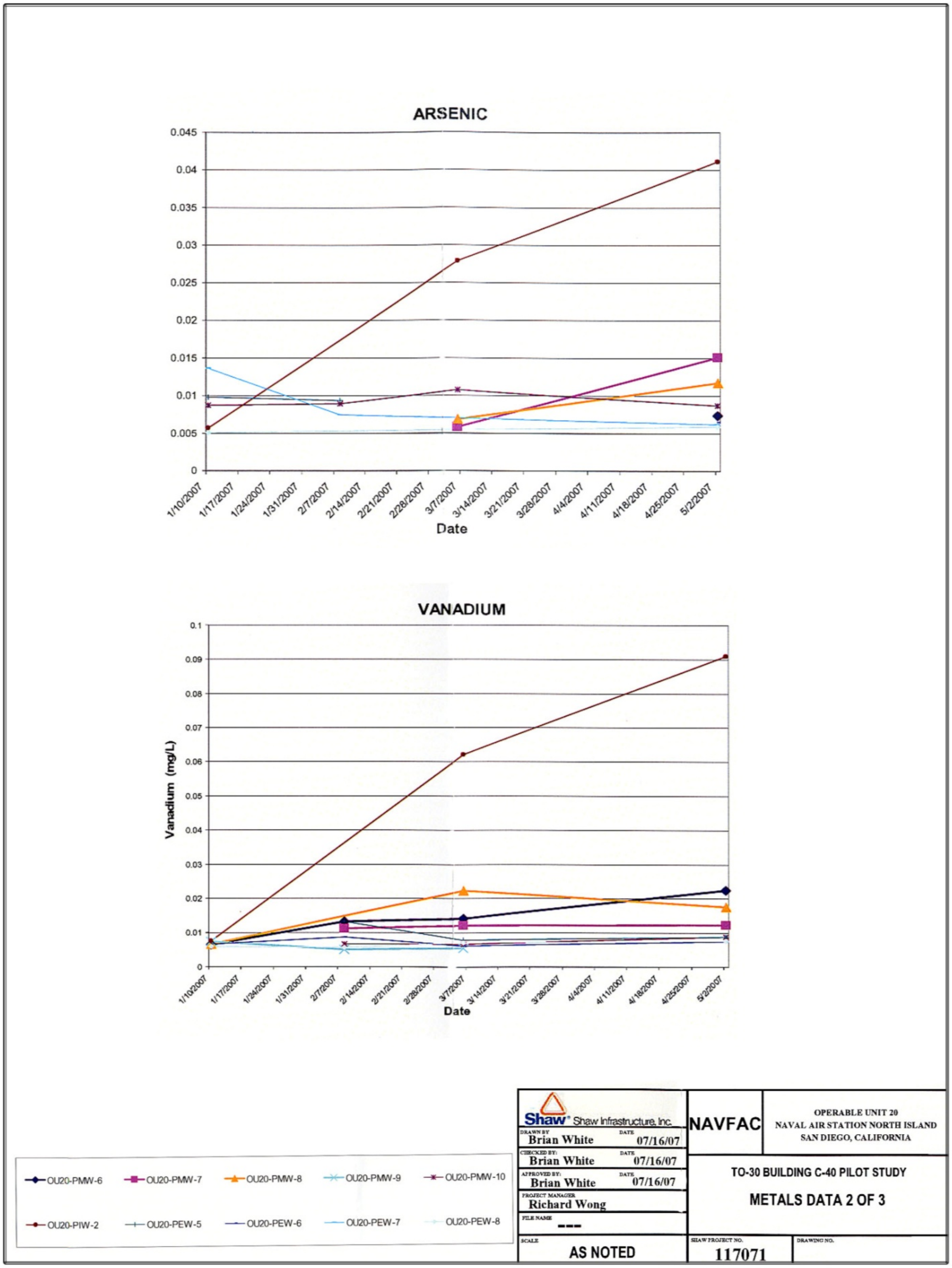
Figure 2-8. Chromium and Manganese



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METALS DATA 2 OF 3

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Figure 2-9. Arsenic and Vanadium

2.7 Cost

The objective of the cost summary shown in Table 2-2 is to compare costs for different technologies on an equivalent basis. Therefore, site-specific or situation-specific costs, such as work plan preparation, design, planning, permitting, and monitoring, have been excluded from this evaluation and for evaluations presented in subsequent sections of this report. The focus is on the cost required to mobilize to the site, conduct the treatment, and demobilize. Total treatment cost for the project is estimated by adding the capital investment and operating cost. Next, a unit cost of treatment is estimated based on the volume of aquifer targeted for treatment. This is based on two assumptions driven by past experience with such projects. One is that most, if not all, treatments seek to create conditions conducive to removing contamination in a given volume of aquifer and that this volume is a bigger driver of the treatment cost than the contaminant mass (which can be subject to poor initial estimates, different degrees of post-treatment residuals, etc.). Second, the assumption is that the volume targeted for treatment is more relevant than the volume actually claimed to be treated. Often, the reagent injected migrates beyond the boundaries of the target treatment zone, but this extra volume is not included. Finally, the maximum depth of treatment and the site geology are qualitative/semi-quantitative measures that drive degree of difficulty, so treatment costs should be calibrated against these measures.

Table 2-2 shows that the total cost of the project was $170,173. For the 889 cubic yards of aquifer targeted, the unit cost of treatment is approximately $191/cubic yard, which is cost-competitive with most other in situ treatment technologies involving injection of a reagent into the subsurface. With a maximum treatment depth of 54 feet bgs in moderately permeable soils, this site may present a moderate challenge for reagent distribution remediation in comparison to other sites. Site preparation and mobilization were the largest components of the total cost.

2.8 Discussion

The field pilot test was well designed and well implemented, with performance monitoring that was comprehensive in evaluating various important aspects of the persulfate application. There is a fair amount of evidence from the pilot test that the persulfate application succeeded in substantially treating the primary CVOCs, TCE, and cis-DCE present in the target aquifer zone at this site:

- The sharp decline in TCE and cis-DCE levels can most likely be attributed to reaction with the persulfate.
- Residual persulfate levels were highest in the injection well (PIW-2) and in the two monitoring wells closest to the injection well (PMW-6 and PMW-8). The degree of decline in groundwater TCE levels exactly matches this persulfate distribution, with the greatest declines occurring in PIW-2, followed by PMW-6 and PMW-8.
- Residual persulfate did not reach as high a level in wells PMW-7, PMW-9, PEW-5, and PEW-7, which are farther away (along the longer axis of the elongated oval treatment area). Presumably, the more concentrated core of the persulfate front had not reached these locations in the 90-day period, perhaps retarded by CVOCs and natural organic matter (NOM) in the soil. The TCE and cis-DCE declines in these wells are substantial, but not as much as in the closest wells. This is to be expected and follows the typical cost-benefit tradeoff between the costs of longer time in the field and greater chemical use versus the benefit of additional CVOC removal. A distant well (PMW-10), which is located approximately 50 feet downgradient from the injection well, also showed a substantial decline in CVOC concentrations, thus indicating that the oxidant was distributing laterally and downgradient.

Table 2-2. Cost of Persulfate Application at NAS North Island

No.	Item	Unit	No. of Units	Unit Cost	Cost
CAPITAL INVESTMENT (Fixed Cost)					
1	Site preparation (utility lines, concrete pad, etc.)	Dollar	1.00	$88,481	$88,481
2	Mobilization/demobilization (transportation to site, storage, fabrication, assembly, setup, dismantle)	Dollar	1.00	$18,646	$18,646
3	Equipment purchase (total cost if one-time use; amortized cost used at multiple sites)	Dollar	1.00	$14,454	$14,454
4	Labor (for transportation, on-site setup, unless included in mobilization)	Hr	150.00	$38	$5,682
5	Other				$0
				TOTAL CAPITAL COST:	$127,263
OPERATING COST (Variable Cost)					
6	Equipment leasing (e.g., storage tanks, pumps)	Dollar	1	$5,492	$5,492
7	Chemicals/reagents	Pound	1.16	$15,125	$17,485
8	Other consumables (estimated)			$500	$500
9	Power (Base provided)				$0
10	Other utilities (Base provided)				$0
11	Waste disposal (taken to Base industrial wastewater plant [IWP])	Gallon	275	$0.10	$28
12	Labor (for operating the system)	Dollar	1	$19,406	$19,406
13	Other				$0
				TOTAL OPERATING COST:	$42,910
TOTAL TREATMENT COST FOR PROJECT (Capital + Operating)					$170,173
Volume of aquifer targeted for treatment				Cubic yard	889
Unit cost of treatment				$/Cubic yard	$191
Maximum depth of treatment				Feet bgs	54
Site Geology: Site lithology in the pilot test area consists primarily of interbedded layers of poorly graded fine to very fine grained sand and silty sand. The depth to groundwater is approximately 20 feet bgs. The aquifer is unconfined.					

- Geochemical indicators are congruent with the achievement of good oxidant distribution. Substantially elevated ORP, DO, sulfate, and dissolved iron levels and substantially depressed pH and dissolved manganese levels all point to the creation of a strongly oxidizing environment.

The continued co-existence of both TCE and residual persulfate in many of the treatment-area wells (and in many cases, rebound of TCE levels) toward the end of the 60-day and 90-day post-treatment monitoring periods may indicate that, in addition to a stoichiometric presence of persulfate in the groundwater, some threshold concentration of persulfate may be required to initiate CVOC-persulfate reactions or at least drive the kinetics of the reactions to a level where further declines in TCE are noticeable. In other words, below a certain threshold persulfate concentration, the ability of any remaining persulfate in the aquifer to drive additional CVOC treatment may be minimal.

Chloride is theoretically the best indicator of CVOC treatment because generation of chloride attributable to CVOC destruction can help eliminate the possibility that the observed decline in CVOC may be due to dilution from influx of cleaner water from the surrounding aquifer. However, in many field situations where native chloride levels are already relatively high, the impact on chloride levels attributable to CVOC destruction is difficult to gauge. This may be the case at this site. Chloride levels increased in some wells, declined in others, and remained approximately the same in some wells. This may simply indicate a redistribution of chloride due to the pumping and recirculation of the groundwater among the wells. Extraction wells PEW-6 (4,100 µg/L) and PEW-7 (2,600 µg/L) had much lower baseline (pre-treatment) TCE levels compared with PEW-5 (11,000 µg/L) and PEW-8 (10,000 µg/L). No data were available on TCE levels in these wells or in the manifold, which combines the extracted water from these wells and leads it to the persulfate mixing tank during persulfate injection. In the post-treatment sampling, TCE levels in PEW-5 and PEW-6 did not change considerably. In PEW-8, there is some post-treatment decline in TCE levels, and in PEW-7, there is a sharper decline in TCE. Again, it is difficult to attribute the decline in TCE in these extraction wells along the edge of the treatment zone to either dilution or treatment. If data were available on the TCE levels at the inlet to the persulfate mixing tank and at the inlet of PIW-2 during the injection, they would better address the TCE dilution-versus-treatment issue.

The trace metal levels in the treatment zone groundwater may be worth tracking for a few more quarters. The fate of these metals is unclear. At the end of 90 days post-treatment, other geochemical parameters, such as DO, pH, and ORP have returned close to their pre-treatment equilibrium levels. However, trace metals, such as chromium, arsenic, and vanadium continue to remain at substantially elevated levels. The level of these metals needs to be tracked on a quarterly basis in the treatment-area wells and in downgradient wells (e.g., PMW-10).

Section 3.0: PERSULFATE APPLICATION AT ALLEGHANY BALLISTICS LABORATORY

3.1 Introduction

This section summarizes the results, reviews the performance, and draws lessons learned for future applications from the persulfate injection pilot study conducted at ABL, Rocket Center, West Virginia. The report reviewed was *In Situ Chemical Oxidation Pilot Study at the Solvent Disposal Pit Area of Site 1, Allegany Ballistics Laboratory, Rocket Center, West Virginia* (CH2M HILL, 2008), as well as project documentation provided by the site Remedial Project Manager (RPM). The pilot test field activities were conducted between April and October 2005. The primary objective of the pilot study was to evaluate the effectiveness of in situ source treatment to reduce contaminant mass in the alluvial and bedrock aquifers of the Solvent Disposal Pit Area of Site 1 (see Figure 3-1). The ultimate goal for the pilot study was to evaluate whether the technology could be implemented full scale to cost-effectively reduce contaminant mass near Site 1 groundwater that may contain DNAPLs. If successful, remediation may be expedited and/or life-cycle cost of the existing groundwater extraction and treatment system (GWETS) reduced. The pilot study activities included installing 11 alluvial wells and two bedrock wells; conducting a baseline assessment of groundwater conditions; injecting sodium persulfate in the alluvial aquifer; injecting potassium permanganate in the bedrock aquifer; and performing four post-injection groundwater sampling events to monitor the effectiveness of the in situ treatment. The focus of this report is on the pilot test that used sodium persulfate in the alluvial aquifer.

3.2 Geology and Hydrogeology

Site 1 is an 11-acre area (Figure 3-1), consisting of several disposal units, which include an active 8-acre, fenced burning ground for reactive wastes, propellants, and explosive wastes; three former disposal pits for spent solvents and acids, a former storage area for drums containing hazardous wastes, a former open-burning area and associated dump, and a former inert-burning area and associated dump. The three disposal pits have been backfilled, all drums have been removed from the drum storage area, and both former burning areas and associated dumps are overgrown with vegetation. The three former solvent disposal pits at Site 1 are believed to be the primary source of volatile organic compound (VOC) contamination detected in groundwater across the site.

The site is underlain by two distinct lithologies: unconsolidated alluvial deposits of clay, silt, sand, and gravel and predominantly shale bedrock. The alluvial deposits that overlie the bedrock can generally be divided into two distinct layers. The upper layer extends from ground surface to depths of 10 to 15 feet bgs; it consists of silt and clay and is considered floodplain deposits from the North Branch Potomac River. The bottom alluvial layer consists of poorly sorted sand, gravel, and pebbles that generally become coarser with depth and are regarded as alluvial deposits from the North Branch Potomac River. This lower alluvial layer has an average thickness of 14.5 feet bgs beneath Site 1.
In many locations, a layer of cobbles with varying amounts of sand, silt, and clay is found at the base of the alluvium. The groundwater table is estimated to range from about 16 to 21 feet bgs.

Bedrock below the alluvium consists mainly of calcareous shale and limestone of Silurian age. The bedrock is predominantly shale, with limestone becoming increasingly prevalent in the western half of the site. The average depth to bedrock at Site 1 is 26.5 feet bgs, and the bedrock is fractured to depths of at least 100 feet bgs.

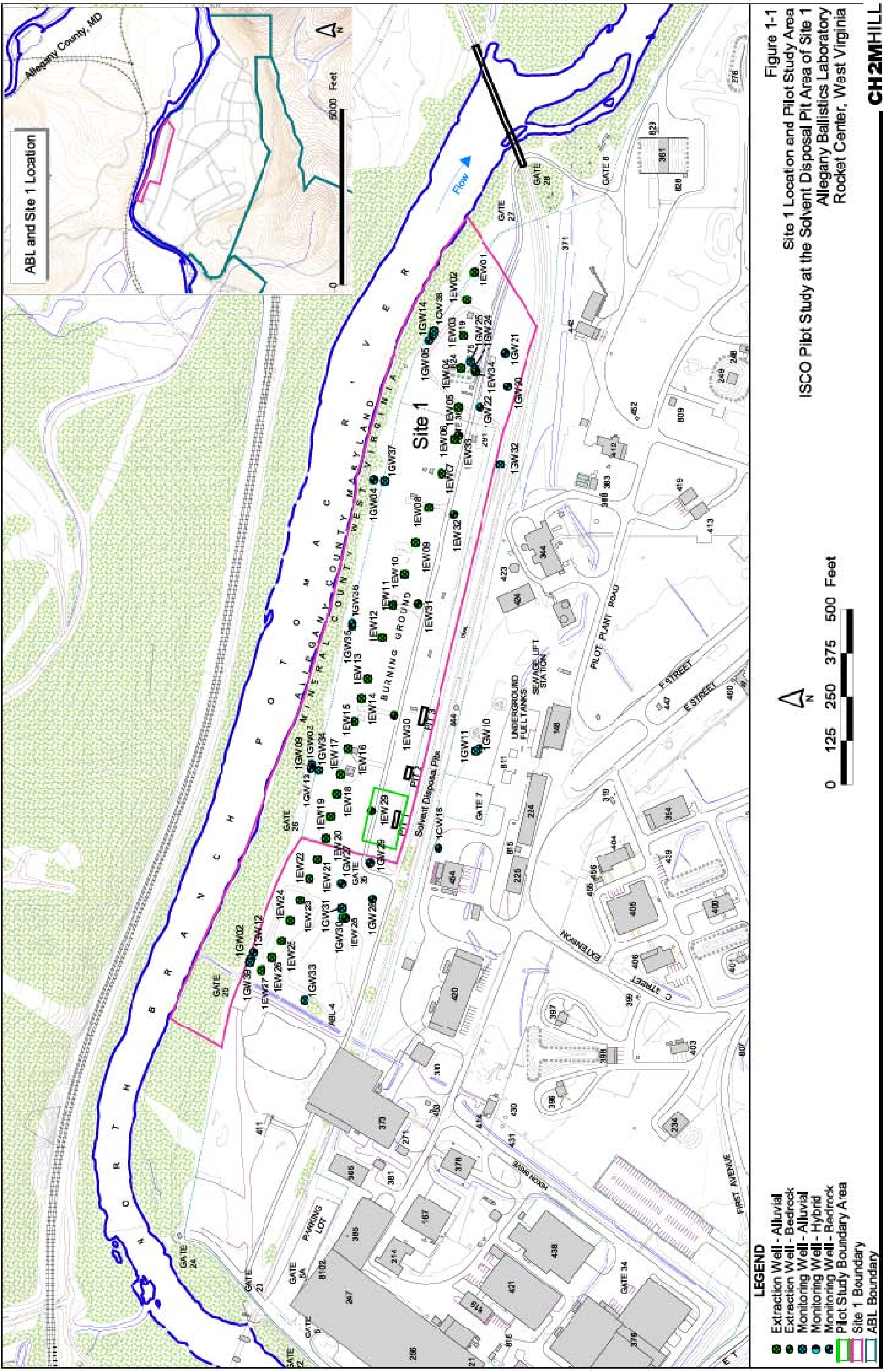

Figure 3-1. Alleghany Ballistics Laboratory, Rocket Center, West Virginia - Site 1

Two distinct aquifers have been identified at Site 1: an upper aquifer consisting of the saturated portion of the alluvium and a lower bedrock aquifer. The alluvial aquifer is typically 10 to 20 feet thick. Groundwater flow in the bedrock takes place in the fractures and bedding planes of the shale. The hydraulic behavior in the bedrock of the extraction wells and monitoring wells suggests that the fractures are numerous, well distributed, and interconnected. It is assumed that fracture apertures and bedding-plane partings are reduced with depth because of the increasing pressure of overburden, and that the majority of groundwater flow occurs in the upper 100 feet of bedrock. However, the maximum depth to which flow persists in the bedrock aquifer is unknown due to the limited depth to which bedrock wells are completed.

The alluvial and bedrock aquifers are in direct contact with the absence of a distinct confining unit between them. Groundwater flow is generally toward the north/northeast in both the alluvial and bedrock aquifers; the North Branch Potomac River is a discharge boundary to groundwater flow within both the alluvium and the bedrock aquifers on the north and west sides of Site 1. The majority of groundwater flow in both the alluvial and bedrock aquifers is believed to be the result of direct infiltration of precipitation, although some groundwater inflow may occur through the bedrock.

3.3 Contaminant Distribution

Site 1 has been part of a number of investigations conducted at ABL. Between 1970 and 1978, approximately 1,000 pounds per month of TCE were disposed in three unlined pits. Analysis of groundwater samples collected from alluvial wells indicates 17 VOCs have been detected in the alluvial aquifer at Site 1. Of the 17 VOCs detected, TCE is the most prevalent, detected above the Maximum Contamination Level (MCL) in all but two of the extraction and monitoring wells. The maximum TCE concentration reported was 52,000 μg/L in extraction well 1EW18. The highest TCE concentrations are concentrated in the western portion of the site, between extraction wells 1EW17 and 1EW20. Elevated TCE concentrations also are present in the eastern portion of the site near extraction wells 1EW02 and 1EW03. It should be noted that elevated cis-1,2-DCE concentrations also exist in the areas of elevated TCE concentrations, indicating the potential for biodegradation of TCE.

Information gathered during the Remedial Investigation (RI) and Focused RI indicated that, in addition to TCE, 1,2-DCE, 1,1,1-trichloroethane [1,1,1-TCA], methylene chloride, and acetone were constituents of potential concern detected at Site 1 in soil, alluvial and bedrock groundwater, surface water, and sediment.

3.4 Technology Implementation

A pilot test was performed to evaluate the effectiveness of ISCO in reducing the mass of TCE in the alluvial and bedrock aquifers. The test involved using sodium persulfate to treat the alluvial aquifer and using potassium permanganate to treat the bedrock aquifer.[4]

Direct injection of sodium persulfate was performed in seven alluvial wells space approximately 20 feet apart. Four injection wells (1IW05 through 1IW08) were installed in the alluvial aquifer before the test. The other three wells, including 1IW01 through 1IW03, had been installed previously during the site characterization phase. The injection wells were installed within and downgradient of the solvent pit area. Figure 3-2 shows the injection locations. The wells were constructed of 2-inch-diameter, stainless-steel casing and screen. They were screened to a depth of about 28 to 30 feet bgs. All of the wells were constructed using 10-foot-long screens with the exception of Well 1IW02, which was equipped with a 15-foot-long screen.

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[4] This cost and performance report does not include the results of the permanganate application.

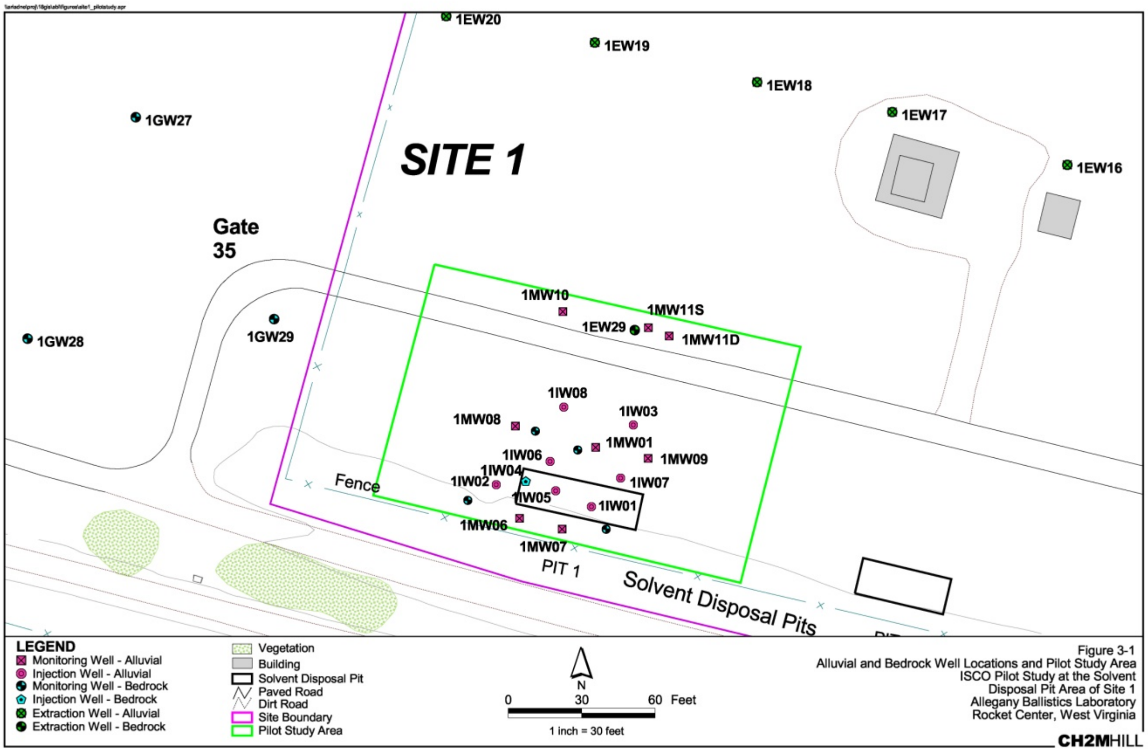

Figure 3-2. Pilot Study Area Well Locations

The target treatment area was approximately 13,500 square feet (150 feet long by 90 feet wide). Assuming an average saturated thickness of 14 feet, an aquifer volume of approximately 189,000 cubic feet was targeted.

A combination of heat- and iron-activated persulfate was used. Batches of reagent were made by mixing 990 pounds of sodium persulfate with iron ethylene diamine tetracetic acid (EDTA), 15 pounds of lime, and 400 gallons of water, resulting in a concentration of about 297 g/L. Injection of the persulfate began on May 17, 2005. A total of 6,930 pounds of sodium persulfate, 105 pounds of lime, and 49 pounds of EDTA were injected into the seven alluvial injection wells. The reagents were injected at about 10 gpm at pressures between 10 and 30 pounds per square inch (psi).

Following injection of sodium persulfate solution, steam was used as a heat catalyst to activate the persulfate, making it more reactive. Steam was injected into the seven alluvial injection wells from May 17 through June 2, 2005, to achieve an optimum groundwater temperature of approximately 40 to 45ºC. Steam was injected into two to four injection wells at a time for approximately 9 to 12 hours each day.

3.5 Performance Evaluation Approach

Performance monitoring was conducted using eight monitoring wells, which included one previously existing alluvial monitoring well (1MW01) and seven new wells: 1MW06 through 1MW10, 1MW11S, and 1MW11D. The new wells were constructed similarly to the injection wells, using 2-inch-diameter, stainless-steel casing and screen. With the exception of Wells 1MW11S and 1MW11D, each well was equipped with a 10-foot-long section of screen terminating at the bedrock layer located about 28 to 30 feet bgs. Wells 1MW11S and 1MW11D were installed to monitor the expected downward flow immediately downgradient of the injection wells. Well 1MW11S was screened 12.3 to 23.3 feet bgs and Well 1MW11D was screened from 22.3 to 32.3 feet bgs.

Baseline sampling was performed from May 11 through May 15, 2005, prior to injection of the ISCO reagents. The four newly installed injection wells and the seven newly installed monitoring wells were sampled and analyzed for VOCs, total organic carbon (TOC), sulfate, chloride, and alkalinity. Groundwater quality parameters, including DO, temperature, ORP, conductivity, turbidity, and pH, also were measured.

Post-injection monitoring was performed at 3 weeks (June 14, 2005), 6 weeks (July 5), 3 months (August 31), and 5 months (November 8) to document contaminant concentrations after applying ISCO, evaluate rebound of contamination (if any), and evaluate if contamination migrated back into the area from an upgradient location. Samples were collected from the same locations and, with the exception of DO, were analyzed for the same parameters as those of the baseline event. DO was not analyzed because of concerns that residual persulfate could damage the DO probe.

In addition to monitoring wells installed for the pilot study, the ISCO effects on the groundwater extraction-and-treatment system were monitored weekly for the first 4 weeks and again at 6 weeks after injection in alluvial extraction wells 1EW17, 1EW18, and 1EW19, bedrock extraction well 1EW29, and the effluent of the groundwater treatment plant (GWTP). The extraction wells and the GWTP were monitored for potential biofouling of the air-stripper unit and mobilization of inorganics to ensure that GWTP discharge did not exceed regulatory limits for metals. The extraction wells and the GWTP groundwater samples were analyzed for Cr, Mn, and nickel (Ni). In addition, the 1EW29 sample was analyzed for sulfate.

3.6 Technology Performance

Groundwater monitoring data indicate that application of the ISCO reagents resulted in a modest reduction of VOCs in the test area. Changes in TCE concentrations are summarized graphically in Figures 3-3 and 3-4. The greatest reduction of TCE was noted 3 weeks after completing injection of the reagents. In some wells, a significant amount of rebound was observed in subsequent monitoring events, resulting in concentrations near or at even greater levels than baseline (i.e., Well 1MW09). The size of the plume appeared to return to near baseline conditions 5 months after completing the injections. The average concentration of TCE calculated for each sampling event further demonstrates this trend (Figure 3-5). Although a 45% reduction was noted 3 weeks after injecting the reagents, by 5 months the average concentration had rebounded to about 72% of the baseline concentration. Although some reduction was observed, the concentrations of TCE were sufficiently reduced to MCLs or to levels that would not require further treatment. Hence, these data indicate that additional injections of oxidant or an alternate technology would be required.

Similar trends were observed with respect to 1,2-DCE. However, results were much more variable with respect to TCA reduction. Three wells exhibited increases immediately after treatment, and five exhibited decreases in TCA levels. Longer-term monitoring results for TCA indicated continued decreases in some wells and rebound in others. The average concentration was reduced by only 17% when the baseline data were compared to the three-week post-ISCO data.

Changes in the concentration of TCA after the application followed the same trend as TCE (Figure 3-3), which is unexpected, since TCA is much more recalcitrant than TCE. Although the reduction of TCE appears to be slightly greater than TCA immediately after ISCO, concentrations

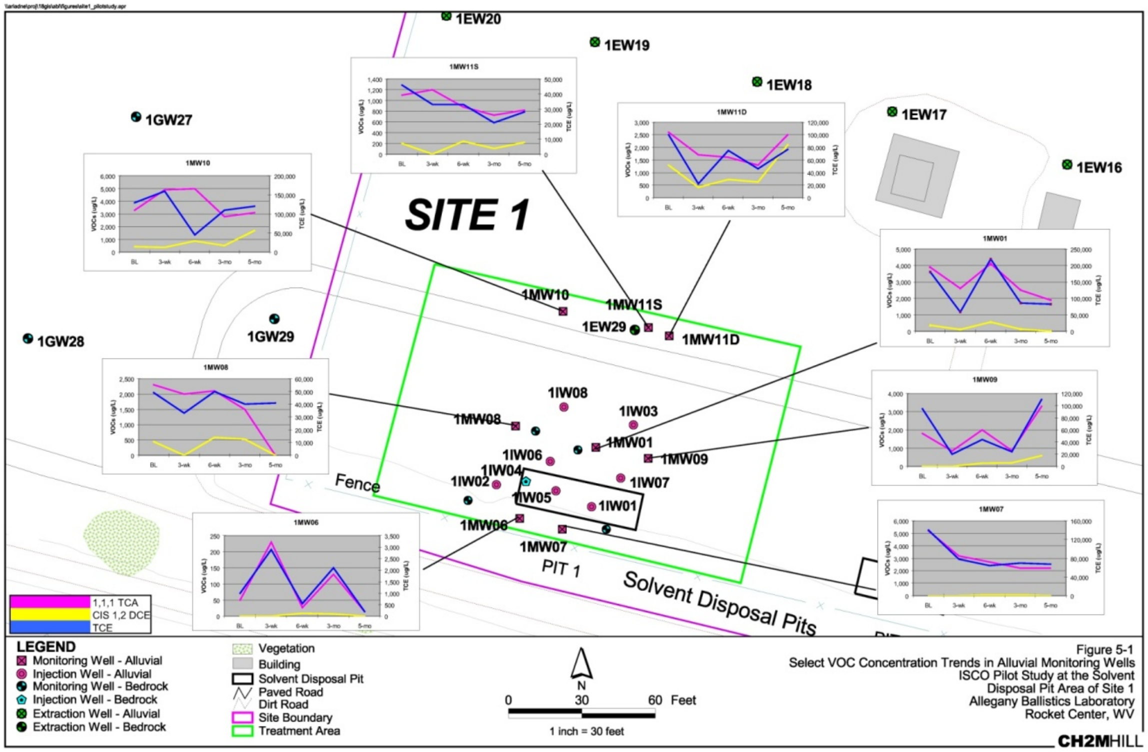

Figure 3-3. Changes in VOC Concentrations in Alluvial Monitoring Wells

measured during subsequent events indicate that these two COCs are following similar trends. These data may indicate that the changes in concentration observed are a result of natural fluctuations in groundwater concentrations as opposed to a reduction through chemical oxidation; the changes could even indicate that recontamination is occurring from an upgradient source.

To better assess the effectiveness of the pilot study, baseline data and post-ISCO monitoring data were compared to the mass flux of TCE through the aquifer downgradient of the pilot test area. Numerical simulations of the groundwater flowrate were performed using a groundwater flow model developed for the facility (CH2M Hill, 2001). Figure 3-6 presents the results. An initial decrease in the mass flux (about 27%) from the test area was calculated at 6 weeks after completing the ISCO injections; however, the flux had increased to 15% greater than the baseline value 3 months post-injection. The increasing trend may be attributed in part to the rebound of TCE concentrations in groundwater. However, it also is likely it occurred because the GWETS extraction Well EW-29, located within the pilot test area, was turned off shortly after concluding the pilot test (May 18). Turning off this well resulted in an increased horizontal groundwater flow, which contributed to the higher mass flux observed in post-injection monitoring events. The fact that the mass flux indicated a 27% decrease shortly after completing the ISCO injection, despite the increased groundwater flow, further indicates that the ISCO injections did have at least a short-term positive impact on the site.

Sulfate and chloride levels were measured during the baseline and post-injection monitoring events and are plotted in Figure 3-7 and 3-8, respectively. Maximum sulfate concentrations were measured during the three-week post-ISCO event and then gradually decreased during subsequent events, possibly due to dilution as fresh groundwater infiltrated the test area. Concentrations of chlorine did not appear to change during and subsequent to the ISCO injections, which could be expected to occur if

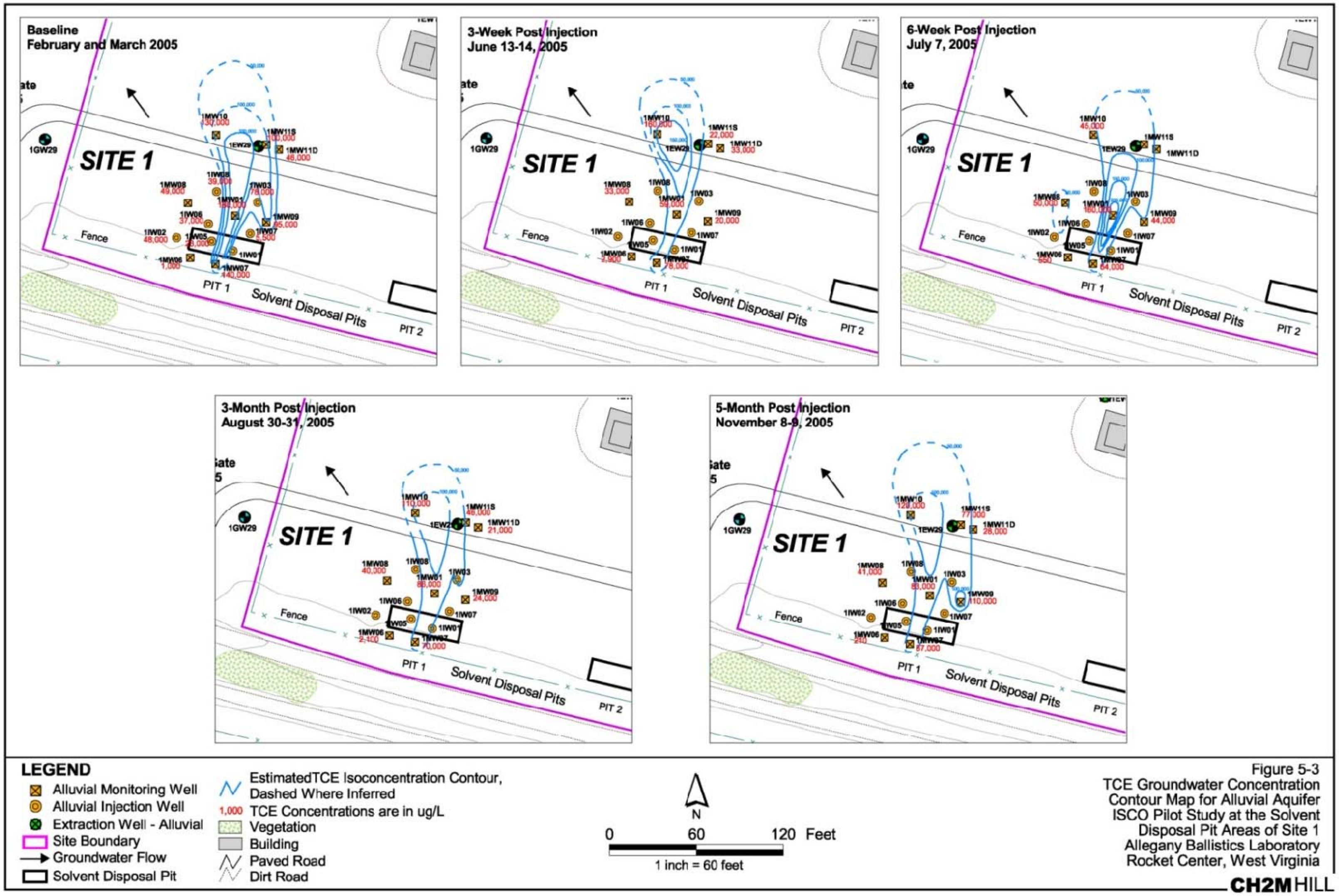

Figure 3-4. TCE Groundwater Concentration Contours

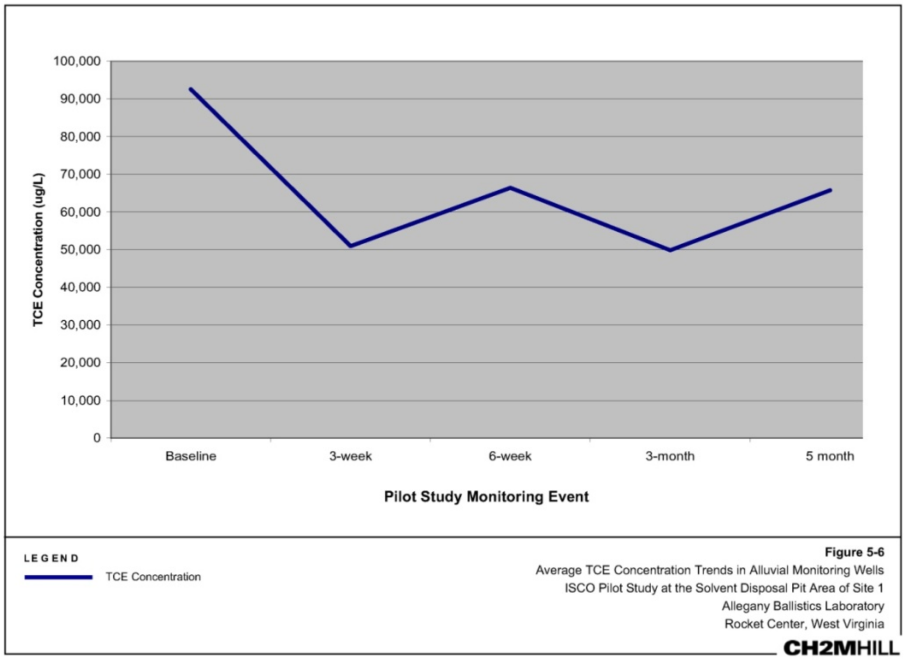

Figure 3-5. Average TCE Concentration Measured in Alluvial Monitoring Wells

extensive oxidation of the chlorinated CVOCs were occurring, given the relatively high concentration of CVOCs and low concentrations of naturally occurring chlorine in groundwater. Hence, it is possible that the reduction in TCE and TCA was partly a result of dilution and/or redistribution, as opposed to reaction with the ISCO reagents. As discussed above, the fact that the changes in the concentrations of TCE and TCA follow the same trend is another line of evidence that the contaminants may have been redistributed, as opposed to being oxidized.

ORP was measured during injection of the oxidants and during each subsequent post-injection sampling event. The average value was calculated for each sampling event (Figure 3-9). An increase in ORP compared to baseline was observed during injection, which indicates distribution of oxidant through the aquifer to the monitoring wells. The ORP decreased to near baseline values between the time of injection and 6 weeks after injections. This is consistent with the decrease in sulfate level, indicating that the sodium persulfate was consumed quickly or that the flow of fresh groundwater through the test area diluted any residual persulfate. However, a spike in the ORP was observed at the three-month post-ISCO monitoring event. Levels greater than those measured during injection of the persulfate were observed. Although not specifically discussed in the reviewed literature, it is possible that this spike in ORP is a result of transport of groundwater containing permanganate[5] into the alluvial aquifer. This could have resulted from natural groundwater fluctuations or from operating the nearby GWETS. The concentration of TCE was observed to decrease in wells 1MW01, 1MW06, 1MW09, 1MW11S, and 1MW11D, which is also an indicator that additional oxidant (permanganate or persulfate) came into contact with the groundwater in these wells. Unfortunately, the ORP measured in each well was not

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[5] A separate pilot test was performed in the bedrock aquifer, into which potassium permanganate was introduced as the oxidant.

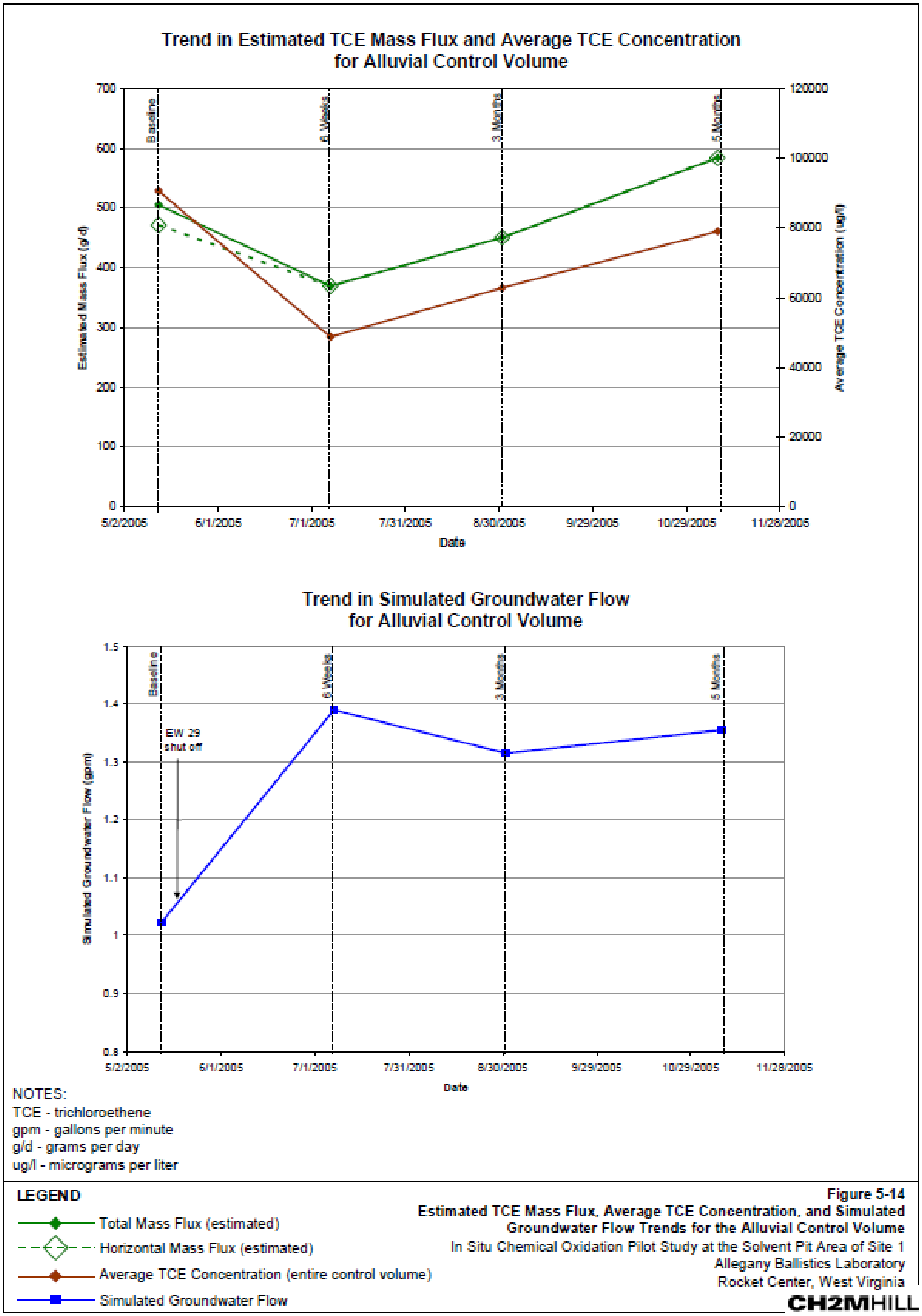

Figure 3-6. TCE Mass Flux Results

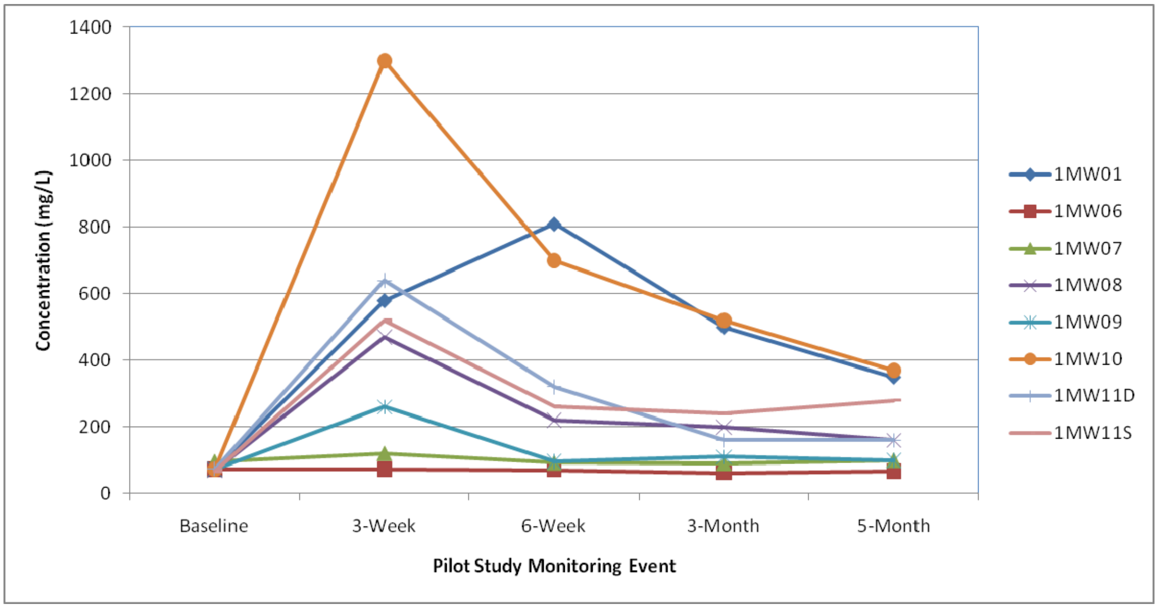

Figure 3-7. Changes in Sulfate Concentrations

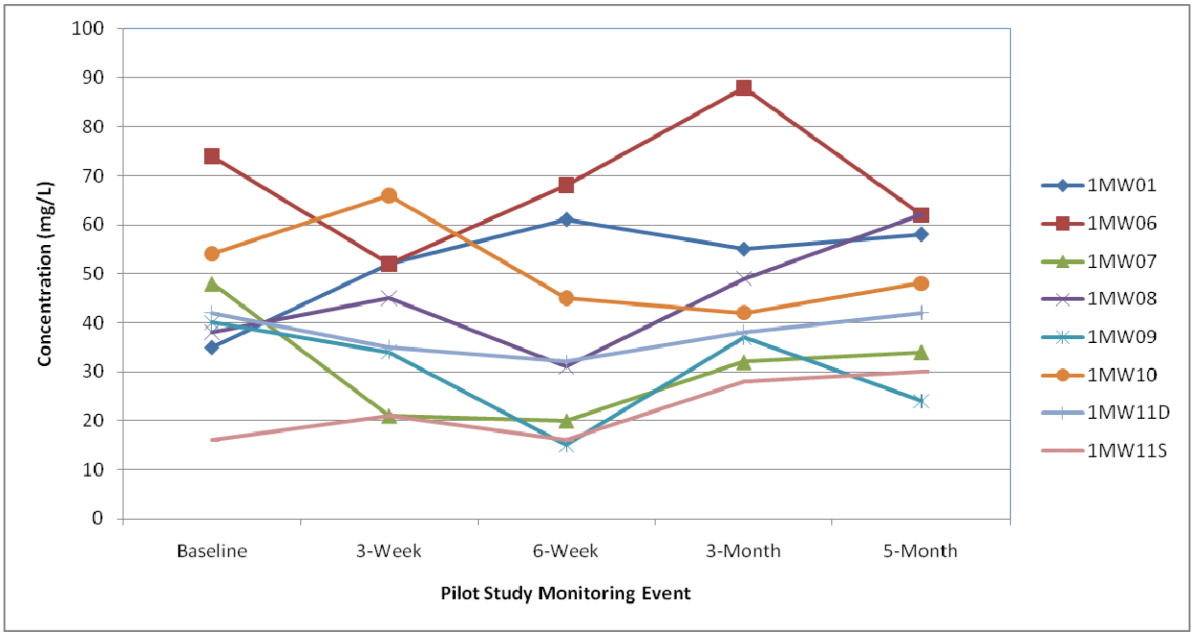

Figure 3-8. Changes in Chloride Concentrations

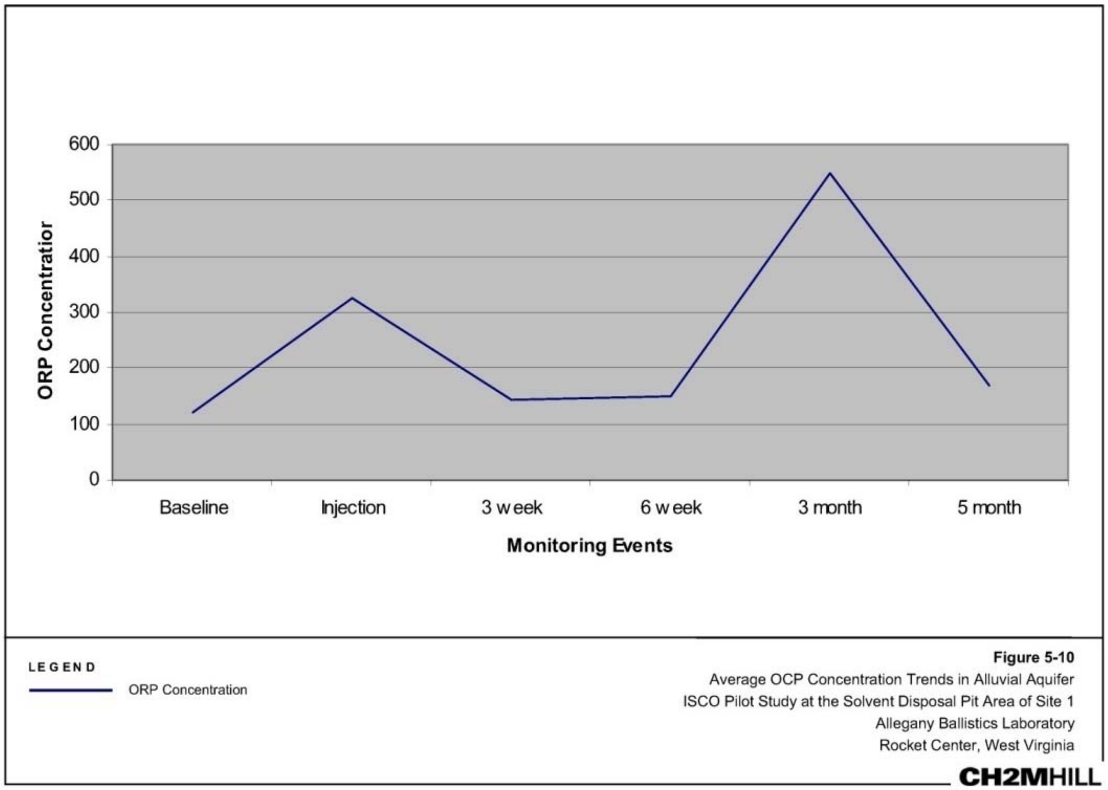

Figure 3-9. Average ORP Values

reported, nor were other parameters reported, such as changes in the concentration of manganese and conductivity that could corroborate this hypothesis.

A review of the data indicates that trihalomethanes (THMs) and may be forming at low levels. However, of the four THMs (bromoform, chloroform, bromodichloromethane, dibromochloromethane), analytical results were only reported for chloroform and bromodichloromethane. In addition, the detection limits during baseline sampling and post-ISCO monitoring events were high; hence, it is difficult to determine if the low levels observed in a few wells are a result of applying the ISCO reagents. Also, methylene chloride, which is a precursor to chloroform, is a potential COC at the site. Baseline values for methylene chloride were elevated in several monitoring points. Hence, it is not possible to evaluate the extent to which this precursor was formed during ISCO, if at all.

Concentrations of metals in the monitoring wells were not analyzed during and subsequent to treatment. Hence, it is not possible to evaluate potential dissolution and migration of metals that may have occurred as a result of applying the ISCO reagents.

Temperatures in monitoring wells were measured every 2 feet while steam was introduced into the seven alluvial injection wells. With the exception of well 1MW09, all of the monitoring wells exhibited only a slight increase in temperature (about 2ºC). The groundwater temperature in well 1MW09 increased from 11.4 to 56.3ºC. A temperature profile for well 1MW09 is shown as Figure 3-10. As shown in this figure, the highest temperature in this well was achieved between 20 to 25 feet bgs, which may indicate a more conductive layer in this region. Two important conclusions can be drawn from this result: (1) since the majority of the monitoring wells did not exhibit a temperature increase, heat

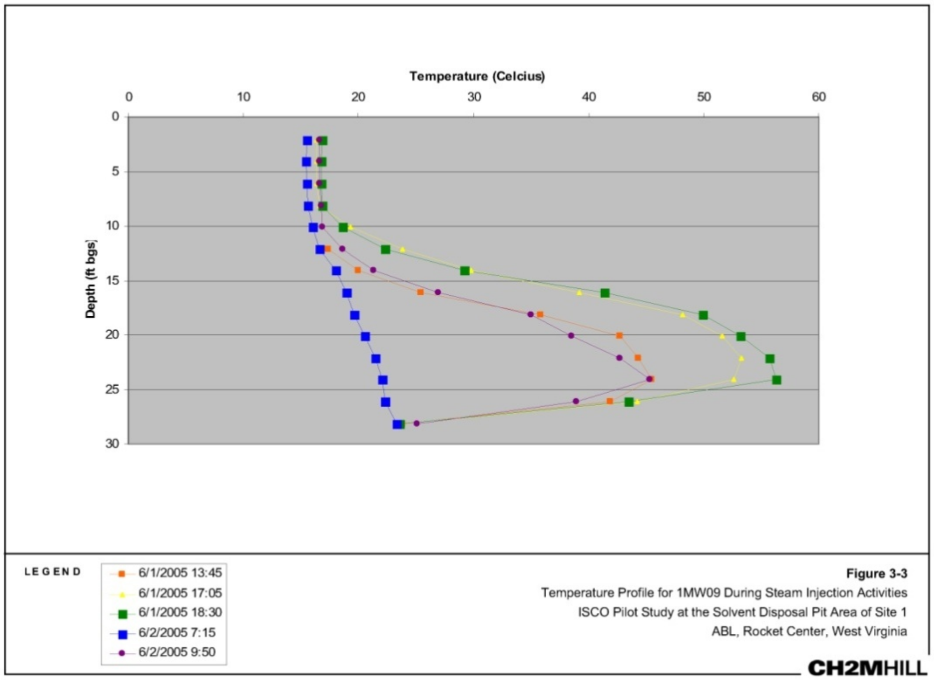

Figure 3-10. Temperature Profile for Well 1MW09 During Steam Application

activation of the persulfate did not occur and (2) as is typical at many sites, uniform distribution of the steam (and likely ISCO reagents) was not achieved.

3.7 Cost

The objective of the cost summary shown in Table 3-1 is to compare costs for different technologies on an equivalent basis. Similar to the cost table provided in Section 2.7, costs that are site-specific or situation-specific, such as work plan preparation, design, planning, permitting, and monitoring, have been excluded. The focus is on the cost of mobilization to the site, conduct of the treatment, and demobilization.

The total cost of the project is estimated to be about $407,000. For the 7,000 cubic yards of aquifer targeted, the unit cost of treatment with a maximum treatment depth of 90 feet bgs was approximately $58/cubic yard. The costs associated with well installation, chemical purchase and injection, and post-injection sampling were the largest components of the total cost.

3.8 Discussion

Based on the analysis results of groundwater samples, reduction of the CVOCs in the alluvial aquifer was limited. Based on the concentration of TCE measured in monitoring wells during the three-week monitoring event, the average reduction of TCE was about 45%. However, in general, the concentration of TCE exhibited considerable rebound during subsequent monitoring events. Reduction of TCA, which is more recalcitrant than TCE, was determined to be much less (an average of about 17%). The primary mechanisms for the rebound observed are likely to be a combination of (1) migration of dissolved VOCs from upgradient and cross-gradient location; (2) reaction of the oxidant with NOM that, in turn, might release additional COCs into the groundwater (especially compounds that have a relatively high organic carbon partitioning coefficient, $K_{o,c}$ such as TCE and TCA); (3) diffusion from relatively tighter zones or layers that were not sufficiently contacted by the oxidants; and (4) insufficient contact of the oxidant and groundwater during the application.

Table 3-1. Cost of Persulfate Application at Alleghany Ballistics Laboratory

No.	Item	Unit	No. of Units	Unit Cost	Cost
CAPITAL INVESTMENT (Fixed Cost)					
1	Work planning (direct-push sampling, work plan writing)	Dollar	1.00	$18,686	$18,686
2	Well installation (labor, other direct costs, travel, utility clearance, drilling, surveying, etc.)	Dollar	1.00	$74,443	$74,443
3	Baseline sampling (labor, lab, data validator, equipment rental, etc.)	Dollar	1.00	$49,628	$49,628
4	Injection of sodium persulfate and potassium permanganate (labor, injection vendor, Investigative derived waste [IDW])	Dollar	1.00	$79,061	$79,061
5	Post-injection sampling (labor, lab, data validation, equipment rental, etc.)	Dollar	1.00	$71,575	$71,575
6	Reporting	Dollar	1.00	$29,748	$29,748
				TOTAL CAPITAL COST:	$323,141
OPERATING COST (Variable Cost)					
7	Equipment leasing (e.g., storage tanks, pumps)				$0
8	Chemicals/reagents	Dollar	1.00	$70,759	$70,759
9	Other consumables (estimated)				$0
10	Power (Base provided)				$0
11	Other utilities (Base provided)				$0
12	Waste disposal (water IDW taken to Base IWP)	Dollar			$0
13	Labor (for operating the system)	Dollar	1.00	$12,690	$12,690
14	Other				$0
				TOTAL OPERATING COST:	$83,449
				TOTAL TREATMENT COST FOR PROJECT:	406,590
			Volume of Aquifer Targeted for Treatment	Cubic yard	7,000
			Unit Cost of Treatment	$/Cubic yard	$58
			Max. Depth of Treatment	Feet bgs	90
Site Geology: Site 1 is an 11-acre area consisting of several disposal units, including an active 8-acre fenced burning ground for reactive wastes, propellants, and explosive wastes. The subsurface geology at Site 1 is quite complex, comprising an alluvial aquifer (in which sodium persulfate was injected as part of the pilot study) and a fractured bedrock aquifer (in which potassium permanganate was injected as part of the pilot study).					

Since DNAPL is reportedly present at the site, and since the principal COCs are known to have relatively high partitioning coefficients, it may have been useful to evaluate removal efficiency by measuring concentrations of the COCs in both soil and groundwater. It is possible that removal efficiency achieved by the pilot test was underreported, based solely on analytical results of groundwater samples. A significant reduction of TCE and TCA may have occurred on soil, without exhibiting much of a reduction in groundwater.

It is unclear how well the oxidant was distributed in the aquifer. The average ORP indicated that the reagent was distributed to some extent in the aquifer, as demonstrated by an increase measured during the three-week post-ISCO sampling. However, values for individual wells were not reported in the reviewed literature. Hence, it is possible that the increased average value was a result of substantial increases in only a few of the wells at the site, as opposed to a uniform increase across the site, which would indicate a uniform distribution. In addition, other parameters, such as pH and conductivity, were not reported.

Increases in sulfate concentrations measured 3 weeks after the injections indicate that at least some sulfate (a byproduct of the ISCO reaction) was transported to the groundwater-monitoring wells. Although the presence of sulfate may be a good indicator that persulfate was distributed near the monitoring wells, it may have been distributed and consumed upgradient of the wells, with the sulfate subsequently transported in groundwater to the monitoring well. In general, sulfate concentrations varied significantly from well to well, indicating that the reagent likely was distributed unevenly.

Multiple activation methods were used including steam and iron. However, the effectiveness of either to activate the persulfate to form the peroxide radical is unclear. Only one of the eight monitoring wells exhibited a significant increase in temperature, which likely was a result of short-circuiting through a permeable lens. A permeable cobble zone at the base of the alluvial aquifer reportedly yields relatively high groundwater flowrates, which would have required a large volume of steam to sufficiently heat the formation. In addition, during application, the steam-injection process was slowed due to rapid calcification buildup in the steam lines. This resulted in the lines clogging, which increased pressure and ruptured the steam lines. To alleviate this problem, several calcium-, lime-, and rust-removal water softeners were used to filter the hydrant water before it entered the steam generator, which would slow calcification.

Chelated iron was added to provide a secondary activation mechanism. However, change in the concentration of dissolved iron in groundwater was not reported, nor was any other method reported to evaluate the distribution of the activating agent; hence, it is not possible to determine if the iron was effectively distributed.

Lime also was added to the injected solution, presumably to buffer against a reduction in pH, which can result through the decomposition of persulfate. However, at very high pH (greater than 10 to 11), which could occur in the injected solution as the lime hydrolyzes, the chelated iron could drop out of solution, rendering it ineffective as an activation agent.

Additional conclusions and lessons learned during application and subsequent monitoring include the following:

- Extraction well EW-29, which is used by the existing groundwater pump-and-treat system, was in operation during the pilot test. It was not turned off until May 18, 2005. Mass flux modeling indicated that a vertical influence was exerted by extracting fluids from this well, which may have interfered with distribution of the oxidants in the subsurface.
- A sharp increase in (average) ORP was noted during the three-month monitoring event. Since sulfate levels were observed to decrease during this period and because the ORP increase was large (>500 mV), it likely is a result of something other than persulfate. It is

hypothesized that residual permanganate, which was injected into the bedrock aquifer as part of a separate pilot test, may have been transported to the alluvial aquifer, resulting in the elevated levels. Transport of permanganate-laden water may have been facilitated by turning off GWETS extraction well EW-29, which created a small downward gradient in the test area.

- Concentration of metals should be measured as part of the baseline and subsequent monitoring events, since application of persulfate can cause metals to migrate within and possibly downgradient of the treatment zone.
- Displacement and transport of COCs due to the injections themselves and due to groundwater flow may have occurred. In particular, the large volume of steam injected may have displaced contaminated water and/or volatilized some of the COCs. Discrete sampling points and soil-gas monitoring points could be installed at various locations to confirm that injection of the reagents is not inducing contaminant migration.
- It was not possible to draw a conclusion regarding the formation of disinfection byproducts, including THMs and their precursors (methylene chloride and cloromethane), at this site due to lack of reported data, high analytical detection limits, and the presence of methylene chloride in baseline samples. However, the formation of THMs and their precursors has been noted to occur at other sites. Because there are MCLs associated with these compounds, bench-scale testing and sufficient monitoring during pilot (and full-scale) application should be performed to better understand the formation and transport of these compounds.
- More comprehensive monitoring of the activating agent, alternative dosing, and/or greater concentration of oxidant could enhance the application’s effectiveness.
- Reductions in TCE correlated well with ORP. VOCs were observed to decrease in groundwater samples in which greater ORPs were measured.
- It is useful to use field test kits to evaluate real-time distribution of the persulfate in monitoring wells.

Section 4.0: PERSULFATE APPLICATION AT MARINE CORPS BASE QUANTICO

4.1 Introduction

This section summarizes the results, reviews the performance, and draw lessons learned for future applications from the persulfate injection pilot study conducted at Solid Waste Management Unit (SWMU) M-13 at MCBQ. The report reviewed was *ISCO Pilot Remediation Results SWMU M-13, Marine Corps Base Quantico* (AQVIQ-CH2M HILL, 2008), as well as associated project documentation provided by the site RPM.

SWMU M-13 (see Figure 4-1) comprises a former motor pool and former heating plant, which was operational from 1941 to 1986. Fuel was delivered to the plant through multiple aboveground and underground storage tanks and through a pipeline. The plant burned fuel oils, waste oils, solvents, and thinners. Halogenated hydrocarbons were added to the fuel. The objective of the pilot remediation was to evaluate ISCO's ability to shorten the timeframe for achieving site closure. A two-phased approach was used. During Phase I, data were collected to identify the preferred activation method of persulfate, the site-specific demand of persulfate, and the profile of the contaminant mass within the treatment area. These data were used to design the injection parameters during Phase II. This field implementation phase consisted of the delivery of the activated persulfate into the target subsurface and the associated groundwater monitoring events to assess the technology's performance. The Phase I field activities began in June 2007 and concluded in August 2007. The Phase II field activities began on October 1, 2007 and concluded on April 9, 2008. Activities associated with the implementation phase (Phase II) and relevant conclusions are presented in this section.

4.2 Geology and Hydrogeology

Figure 4-2 presents a cross-section of the soil lithology extending from the southwest to the northeast. The site is underlain by silts and clays from approximately 6 to 24 feet bgs, beneath which are discontinuous layers of sand and silts. Groundwater flow is predominantly to the east toward the Potomac River.

The presence of surface features (buildings, retaining wall, steep grade, and numerous manholes) and subsurface utilities (electric, fuel, communication, sewer, and storm drain) constrained the remedial design. There also was limited knowledge about lateral and vertical extent of contamination because sampling was limited to assessable areas.

4.3 Contaminant Distribution

The primary groundwater contaminant at the site was 1,2,4-trichlorobenzene (TCB) at approximately 1,000 µg/L. Other COCs included TCE, PCE, DCE, and vinyl chloride (VC). The target remediation area was about 2,300 square feet, and the interval of contamination extended from approximately 6 to 23 feet bgs. The contaminant mass was estimated to be 7.8 pounds.

4.4 Technology Implementation

The remedial design included injecting iron-activated persulfate at a concentration of 200 g/L through 19 injection points. The solution was directly injected into the aquifer using a Geoprobe 6629 equipped with custom-designed injection tooling. These initial injections, performed on October 22 through October 25, 2007, reportedly failed because of clay and silt clogging in the injection

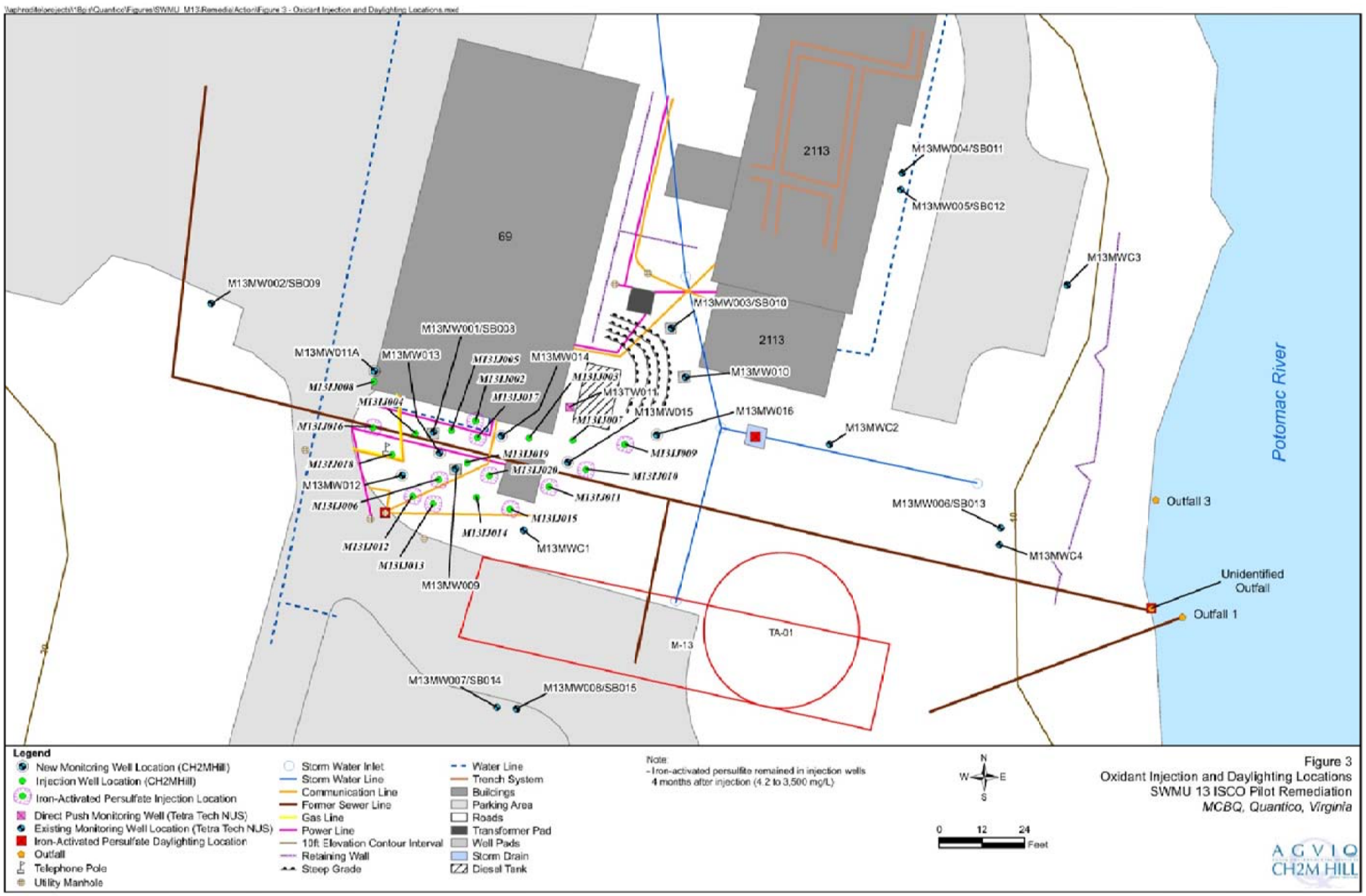

Figure 4-1. SWMU M-13 at Marine Corps Base Quantico, Virginia

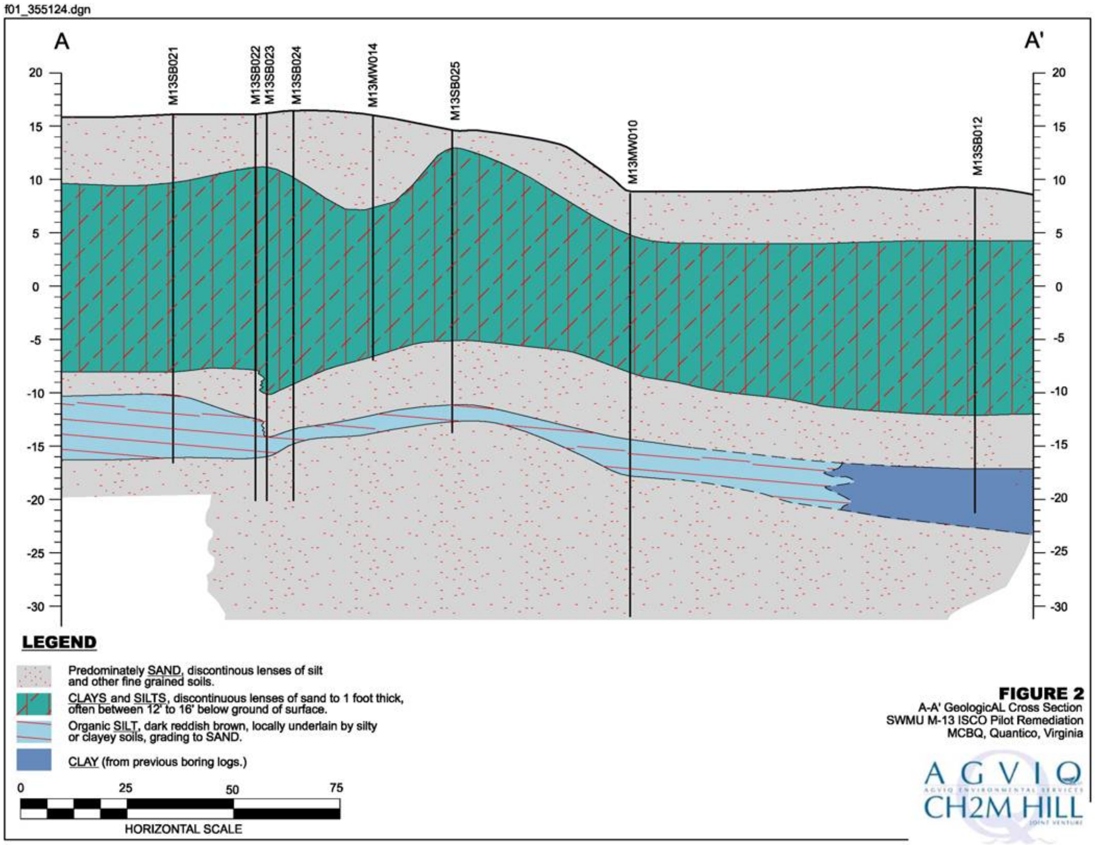

Figure 4-2. Geologic Cross-Section at SWMU M-13, MCBQ

nozzles (Figure 4-3). It was determined that frequent rain caused the clay layer overlaying the sand layer to swell and clog the injection tooling.

The system was modified by converting the injection points into 1-inch-diameter polyvinyl chloride (PVC) wells. The screen interval of each well was determined in the field based on observations of soil lithology. The 19 injection wells were installed from October 25 through November 9, 2007. Installation was performed using a combination of a hollow stem and direct-push technology (DPT) method to prevent collapse of the borehole. The locations of some points were offset from their original design locations, which had been selected based on a design radius of influence of 5 feet, due to the presence of a large number of underground utilities.

Figure 4-3. Clogged Injection Tooling

The components of the batching system consisted of a number of aboveground PVC tanks, inline mixers, and pumps to make up and feed the reagents. The reagent solution was pumped through a Schedule 80 PVC manifold that divided the flow into multiple streams, which were then transported through reinforced polypropylene tubing to the injection wells. Digital flowmeters were used to gauge the volume injected into each well. Figure 4-4 shows the equipment.

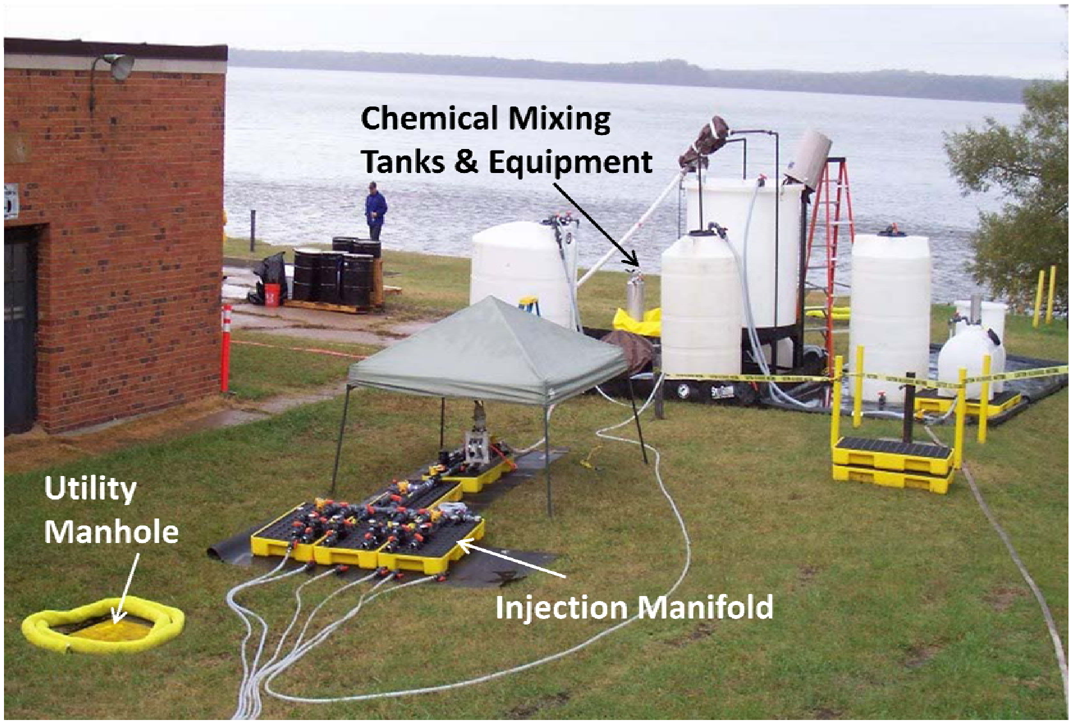

Figure 4-4. Chemical Mixing and Injection Equipment

Table 4-1. Reagent Injection Summary

Well ID	Interval (feet bgs)	Total Volume of Reagent (gallons)
IJ002	11 – 16	193
IJ006	25 – 30	67
IJ009	13 – 18	8
IJ010	10 – 15	164
IJ011	14 – 19	32
IJ012	15 – 20	356
IJ013	10 – 15	12
IJ015	10 – 15	270
IJ016	15 – 20	412
IJ017	23 – 28	70
IJ020	10 – 15	68

Injection into the fixed wells was initiated on November 12, 2007. The vertical target interval was 13 to 23 feet bgs, with the exception of the injection points near well M13MW001,[6] which were 8 to 26 feet bgs. The design called for 21,000 pounds of persulfate to be injected at a concentration of about 200 g/L. However, because surfacing of persulfate and iron solution was observed to occur in a previously unidentified outfall at the Potomac River and in a manhole for a communication line, injection activities stopped prematurely on November 14, 2007. Approximately 2,700 pounds of the 21,000 pounds (about 13%) of the persulfate were introduced into the aquifer. Table 4-1 presents the volume of solution injected[7] into each point, and Figure 4-1 shows the locations of the points, the subsurface utilities that may have acted as a conduit to transport the reagent, and the areas where

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[6] Future references to well identifications will omit the M13 prefix.

[7] The reagent consisted of approximately 1.65 pounds of sodium persulfate per gallon of solution (~200 g/L).

surfacing was observed to occur. Note that because of the short duration of application, reagents were not introduced into eight of the injection wells

4.5 Performance Evaluation Approach

Performance monitoring was performed using 12 dedicated monitoring wells. Six of these wells (MW011 through MW016) were installed from October 1 through 3, 2007, for the purpose of evaluating ISCO performance. The newly installed wells were constructed of 1-inch-diameter Schedule 40 PVC with a pre-packed screen and seal. Wells MW011 through MW014 were screened from 8 to 18 feet bgs, and Wells MW015 and MW016 were screened from 8 to 18 and 6 to 16 feet bgs, respectively, to account for elevation changes in topography.

Previously installed wells, including MW01 through MW03, MWTW11, MWC1, and MWC2 also were monitored during and subsequent to the ISCO injections. The screen intervals of these wells were not available at the time this report was prepared; however, it is assumed that the screens are located roughly in the same interval as the newly installed wells.[8] Figure 4-1 shows the locations of all monitoring wells.

Baseline sampling was performed (October 15 through October 17) prior to injecting the ISCO reagents. Groundwater samples were collected from the 12 performance-monitoring wells described above. Samples were analyzed for VOCs, total metals, dissolved metals, alkalinity, and sulfate. Four samples also were analyzed for nitrate; ferrous iron; methane, ethane, and ethane; and phospholipid fatty acids (PLFA) to assess the impact of ISCO on natural attenuation. Depth to groundwater and groundwater quality measurements, including DO, temperature, ORP, conductivity, and pH, also were measured during the baseline sampling event.

Throughout injection activities, persulfate concentration, field water quality parameters, including DO, ORP, conductivity, temperature, and pH, and flow rates were monitored. Depth to water also was measured in monitoring wells to evaluate mounding of reagents/groundwater near the injection points and to gauge the potential for surfacing of reagents and groundwater. CHEMetrics® test kits were used to periodically take field measurements of the persulfate concentration in groundwater monitoring wells.

Two post-ISCO monitoring events were conducted: one at 1 month after completing injections (January 7 and 8, 2008) and the other at 4 months (April 7 through April 9). Groundwater sampling and analysis during the 1-month post-injection monitoring were identical to the baseline event, with the exception that samples were not analyzed for nitrate, ferrous iron, methane, ethane, ethene, or PLFA. In addition, the concentrations of persulfate in monitoring wells were measured. Field measurements of persulfate also were performed, and depths to water were measured in the 11 extraction wells used during the pilot test. The 4-month post-ISCO sampling was identical to the baseline event, with the exception that persulfate was measured in the monitoring and injection wells.

4.6 Technology Performance

Surfacing of the reagents at various site locations necessitated termination of ISCO after injecting only 2,700 pounds of persulfate, which is only about 13% of the design mass. Table 4-1 summarizes the volume of reagent injected into each well and the injection depth. The concentration of the injected reagent was about 200 g/L.

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[8] Well M13MW001 is reported to have a deeper screen interval than the remaining wells and historically had the highest concentration of 1,2,4-TCB (1,100 micrograms per liter [µg/L]).

Even though the design mass of oxidant could not be injected into the subsurface, the application achieved reductions of 1,2,4-TCB and TCE concentrations in some areas of the site. Figure 4-5 displays the results of the baseline, 1-month, and 4-month monitoring events for the COCs. Figure 4-5 shows a side-by-side comparison of 1,2,4-TCB and TCE reduction in four of the wells.

Reduction of 1,2,4-TCB and/or TCE was noted in wells located closely to injection points that received reagent, such as MW013, MW014, and MW015. Well MW003, located 50 feet or so outside the injection area, also exhibited a significant reduction of COCs, which may be attributed to channeling of the reagent along one of the many subsurface utility corridors at the site (see Figure 4-1).

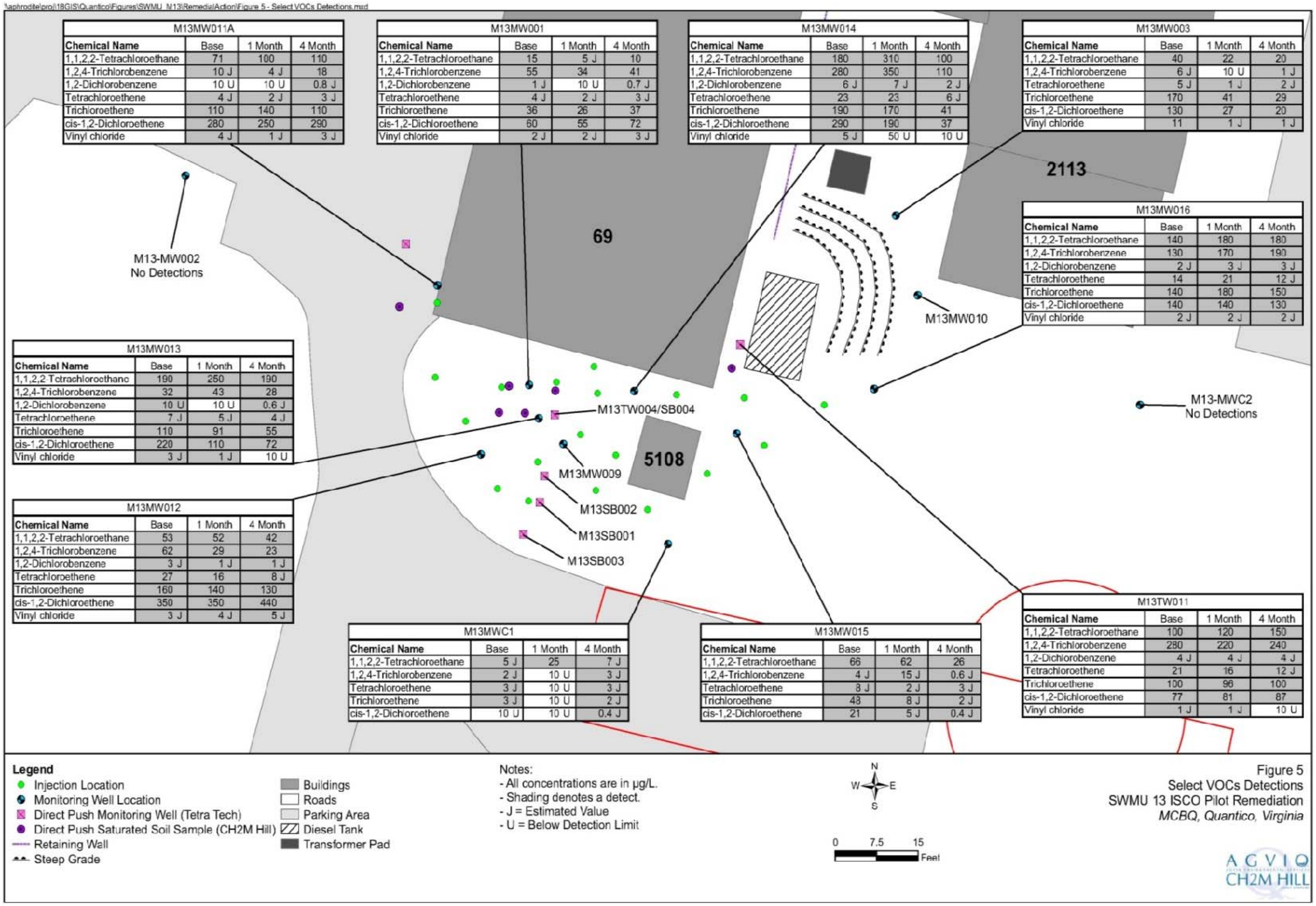
Comparing the 4-month post-ISCO monitoring results to the baseline data, the percent reduction of TCB and TCE ranged from 12 to 61% and from 50 to 96%, respectively, in wells located within 7 feet of points into which reagent was injected. With the exception of Well MW013, which exhibited a decrease in COCs as noted above, the concentration of 1,2,4-TCB and/or TCE remained about the same. Figure 4-7 shows three-dimensional plumes of 1,2,4-TCB and TCE constructed using data from the baseline and 1- and 4-month sampling events.

The concentration of persulfate in wells MW001 and MW012 through MW016 was measured 1 day after completing the ISCO injections. Detectable levels of persulfate were measured in wells MW013, MW014, and MW016 at concentrations of 6, 35, and 225 mg/L, respectively, indicating some distribution of persuflate. In addition, analyses of persulfate were made during the 1-month and 4-month post-injection sampling events in each injection well. Elevated concentrations of persulfate were present, having mean and maximum concentrations of 5,100 and 14,000 mg/L, respectively, 1 month after injecting the persulfate, and mean and maximum concentrations of 1,900 and 7,000 mg/L, respectively, 4 months after completing the injections.

Laboratory analyses of groundwater samples confirmed elevated levels of sulfate were detected in wells MW013, MW014, MW015, and MWC1 (Figure 4-6). At one month after injection, the sulfate levels in these wells had increased by one to three orders of magnitude above baseline conditions, which is not surprising considering that persulfate had been detected in wells MW013, MW014, and MW015 one day after injection was completed. Note that MWC1 also may have contained persulfate, but a sample had not been collected from this well and analyzed to confirm its presence.

Figure 4-8 graphically compares the baseline values of pH, conductivity, ORP, and DO with the values measured during the 1- and 4-month post-ISCO sampling events. The observed changes are consistent with what one would expect if the oxidant was not distributed uniformly in the subsurface. Some wells displayed a slight decrease in pH, elevated ORP, and conductivity, and an increase in oxygen 1 month after the application, while others did not. Many of the wells had returned to near baseline conditions during the 4-month event, although ORP appeared to remain slightly elevated, possibly due to residual persulfate persisting in the subsurface.

A comparison of total metals measured during baseline sampling with those measured during the 1- and 4-month post-ISCO sampling events indicates increases in concentrations in several wells. Figure 4-9 presents changes in concentrations of four select metals, including arsenic, manganese, iron, and chromium. In general, concentrations were found to be highest during the 1-month sampling event, and decreased substantially 4 months after completing the ISCO injections. The greatest increases correlated well with wells in which high sulfate, conductivity, and ORP were measured. These results indicate that the application of persulfate tends to increase metal levels, but that they may return to near baseline values as the persulfate is consumed and the sulfate levels and redox conditions return to baseline levels.



M13MW011A

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	71	100	110
1,2,4-Trichlorobenzene	10 J	4 J	18
1,2-Dichlorobenzene	10 U	10 U	0.8 J
Tetrachloroethene	4 J	2 J	3 J
Trichloroethene	110	140	110
cis-1,2-Dichloroethene	280	250	290
Vinyl chloride	4 J	1 J	3 J

M13MW001

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	15	5 J	10
1,2,4-Trichlorobenzene	55	34	41
1,2-Dichlorobenzene	1 J	10 U	0.7 J
Tetrachloroethene	4 J	2 J	3 J
Trichloroethene	36	26	37
cis-1,2-Dichloroethene	60	55	72
Vinyl chloride	2 J	2 J	3 J

M13MW014

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	180	310	100
1,2,4-Trichlorobenzene	280	350	110
1,2-Dichlorobenzene	6 J	7 J	2 J
Tetrachloroethene	23	23	6 J
Trichloroethene	190	170	41
cis-1,2-Dichloroethene	290	190	37
Vinyl chloride	5 J	50 U	10 U

M13MW003

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	40	22	20
1,2,4-Trichlorobenzene	6 J	10 U	1 J
Tetrachloroethene	5 J	1 J	2 J
Trichloroethene	170	41	29
cis-1,2-Dichloroethene	130	27	20
Vinyl chloride	11	1 J	1 J

M13MW016

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	140	180	180
1,2,4-Trichlorobenzene	130	170	190
1,2-Dichlorobenzene	2 J	3 J	3 J
Tetrachloroethene	14	21	12 J
Trichloroethene	140	180	150
cis-1,2-Dichloroethene	140	140	130
Vinyl chloride	2 J	2 J	2 J

M13MW013

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	190	250	190
1,2,4-Trichlorobenzene	32	43	28
1,2-Dichlorobenzene	10 U	10 U	0.6 J
Tetrachloroethene	7 J	5 J	4 J
Trichloroethene	110	91	55
cis-1,2-Dichloroethene	220	110	72
Vinyl chloride	3 J	1 J	10 U

M13MW012

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	53	52	42
1,2,4-Trichlorobenzene	62	29	23
1,2-Dichlorobenzene	3 J	1 J	1 J
Tetrachloroethene	27	16	8 J
Trichloroethene	160	140	130
cis-1,2-Dichloroethene	350	350	440
Vinyl chloride	3 J	4 J	5 J

M13MWC1

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	5 J	25	7 J
1,2,4-Trichlorobenzene	2 J	10 U	3 J
Tetrachloroethene	3 J	10 U	3 J
Trichloroethene	3 J	10 U	2 J
cis-1,2-Dichloroethene	10 U	10 U	0.4 J

M13MW015

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	66	62	26
1,2,4-Trichlorobenzene	4 J	15 J	0.6 J
Tetrachloroethene	8 J	2 J	3 J
Trichloroethene	43	8 J	2 J
cis-1,2-Dichloroethene	21	5 J	0.4 J

M13TW011

Chemical Name	Base	1 Month	4 Month
1,1,2,2-Tetrachloroethane	100	120	150
1,2,4-Trichlorobenzene	280	220	240
1,2-Dichlorobenzene	4 J	4 J	4 J
Tetrachloroethene	21	16	12 J
Trichloroethene	100	96	100
cis-1,2-Dichloroethene	77	81	87
Vinyl chloride	1 J	1 J	10 U

Notes:
- All concentrations are in µg/L.
- Shading denotes a detect.
- J = Estimated Value
- U = Below Detection Limit

Figure 4-5. Post-ISCO Monitoring Results for Select VOCs

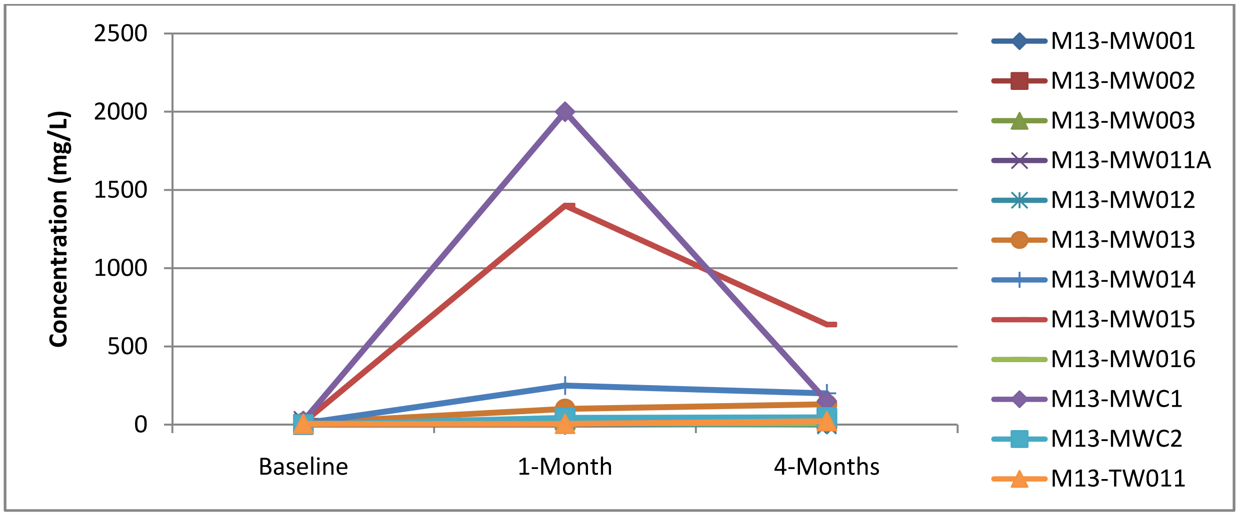


Figure 4-6. Changes in Sulfate Concentration in Groundwater

Changes in natural attenuation parameters were monitored in wells MW001, MW013, and MW016. Conditions in well MW001 remained anaerobic and reducing, which are the conditions necessary for biodegradation via reductive dechlorination. However, MW013 and MW016 were found to be more aerobic and oxidizing compared to baseline values (see Figure 4-8), which is not favorable to reductive dechlorination. In addition, sulfate levels remained high in several of the site wells 4 months after injection, which under certain circumstances can inhibit reductive dechlorination.

Figure 4-10 presents the results of the PLFA analysis performed on groundwater samples collected during the baseline sampling event and during the 4-month post-injection sampling event. MW001 located within the target treatment area and MW002 located upgradient of the treatment area both exhibited increases in viable biomass. However, the level of viable biomass in well MW013, also located within the treatment area, decreased by nearly an order of magnitude. Well MW016 also exhibited a small decrease. Sulfate levels and groundwater parameters measured in wells MW013 and MW016 indicated that the groundwater was impacted by the ISCO reagents, whereas wells MW001 and MW002 did not appear to be affected. In general, the microbial community appeared to be more diverse in wells with high VOC concentrations, as evidenced by increased anaerobic indicator populations, such as Firmicutes, Proteobacteria, anaerobic metal reducers, and sulfate-reducing bacteria, which suggest that the site may support reductive dechlorination.

4.7 Cost

The total cost of the project was $520,816. For the 2,300 square feet of aquifer targeted, the unit cost of treatment with a 5-foot-thick target injection interval[9] and a maximum treatment depth of 23 feet bgs was approximately $1,200 per cubic yard. A breakdown of the costs associated with this project was not available. The high cost per cubic yard of soil is believed to be attributed to the small treatment area, the fact that the application was pilot-scale as opposed to full-scale, and the various operational problems that occurred during application.

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[9] The reviewed documents did not specify a specific target interval. A 5-foot-thick target interval is inferred, based on the screened intervals of the injection wells.

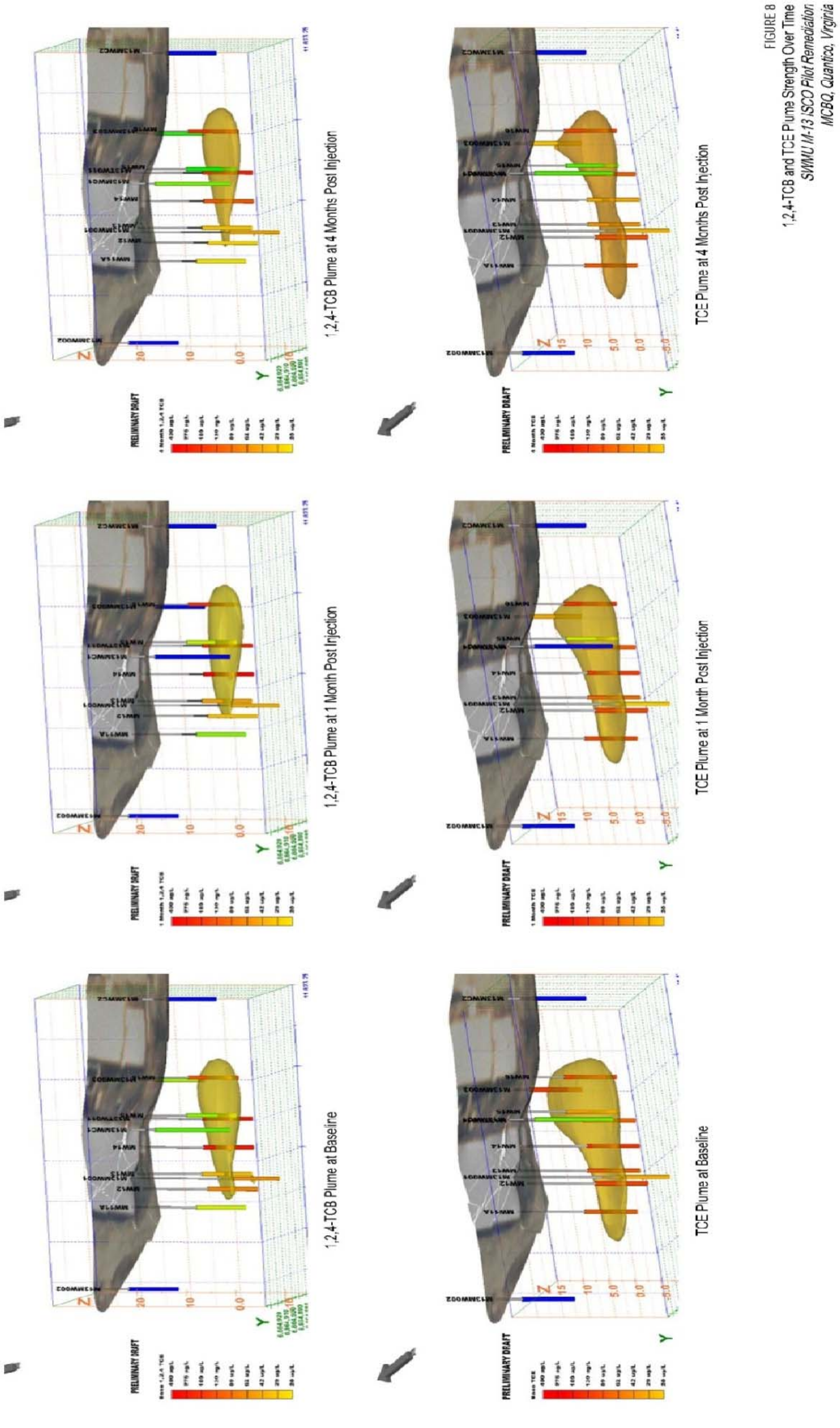

Figure 4-7. 1,2,4-TCB and TCE Plumes

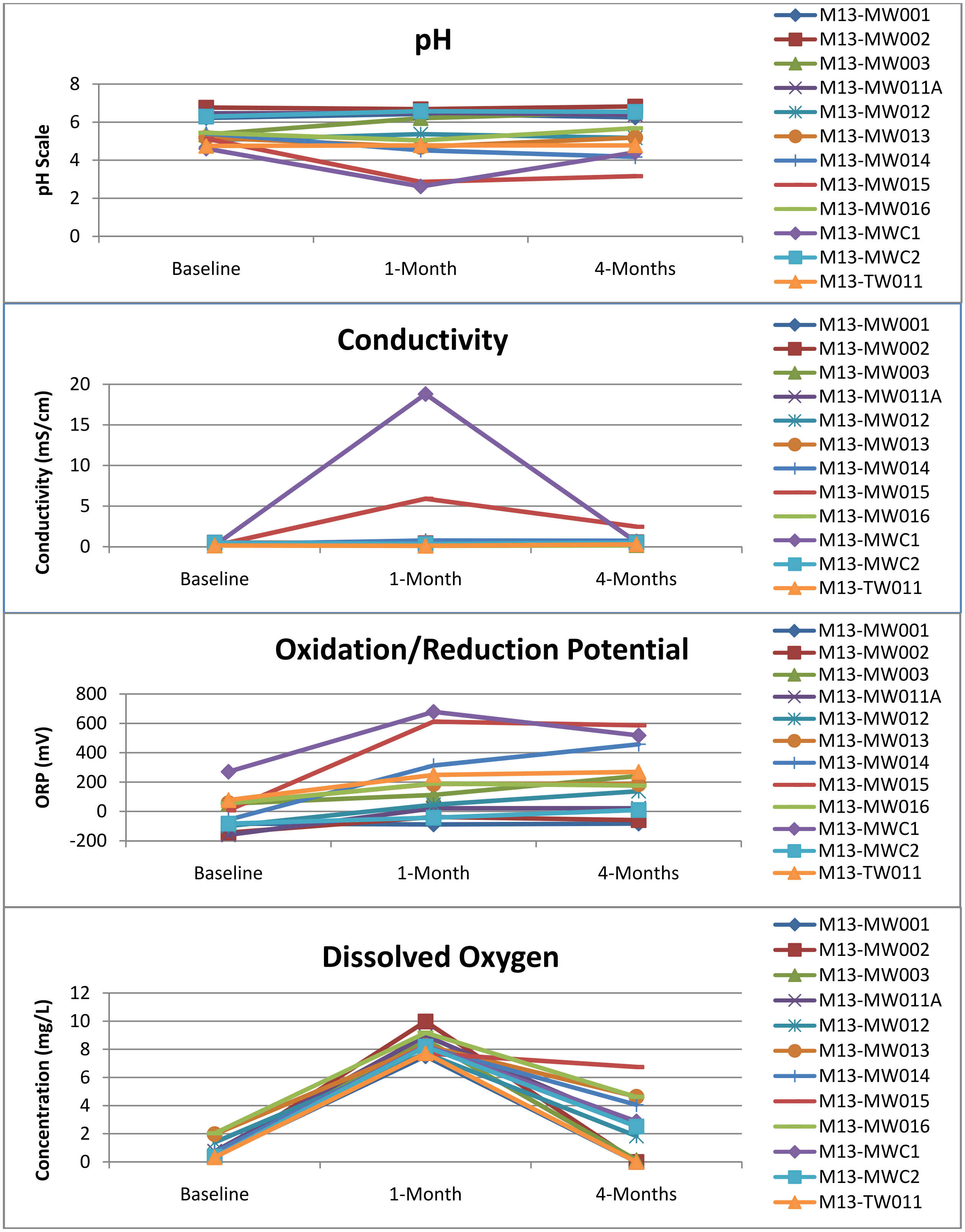

Figure 4-8. Groundwater Quality Parameters

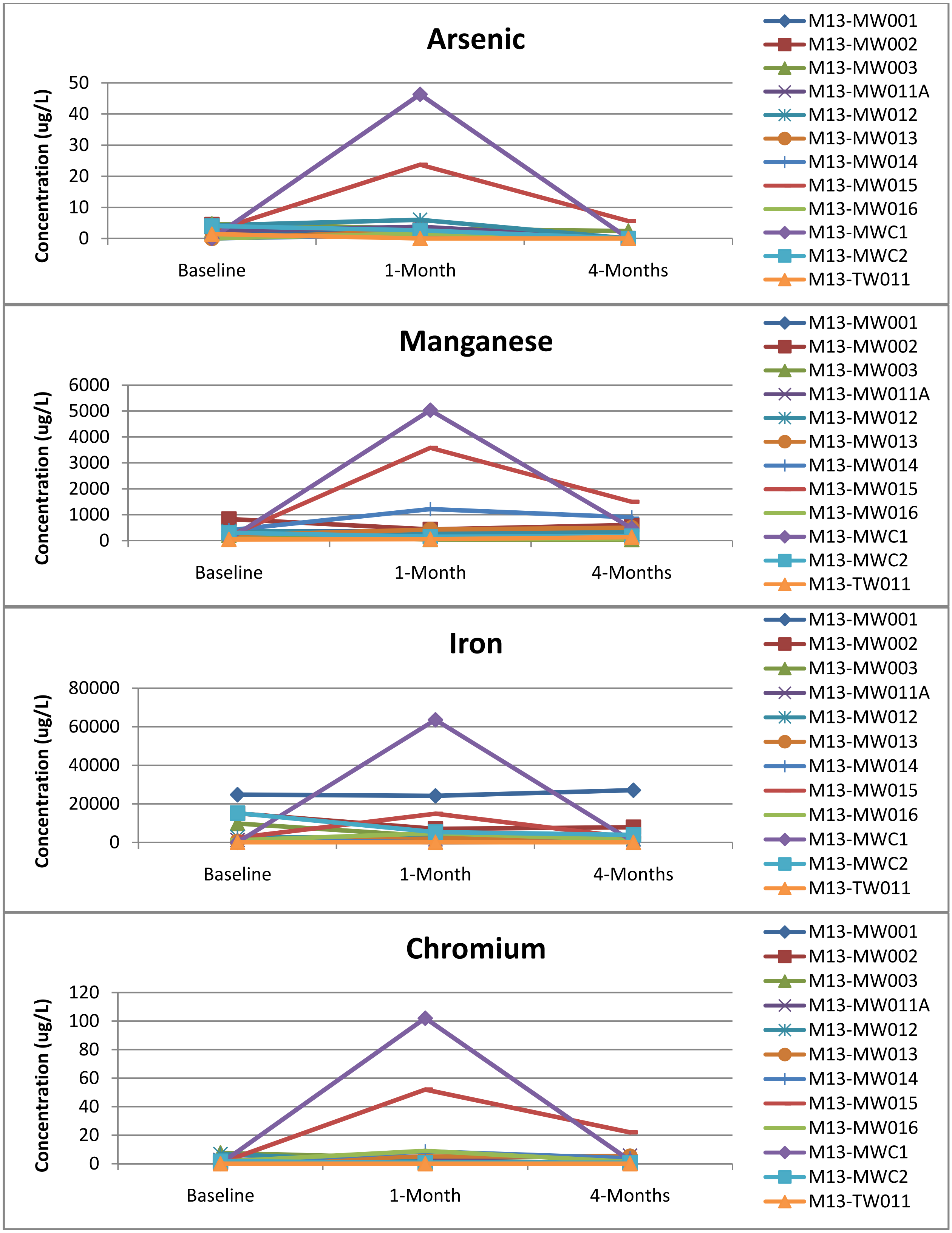

Figure 4-9. Total Metals

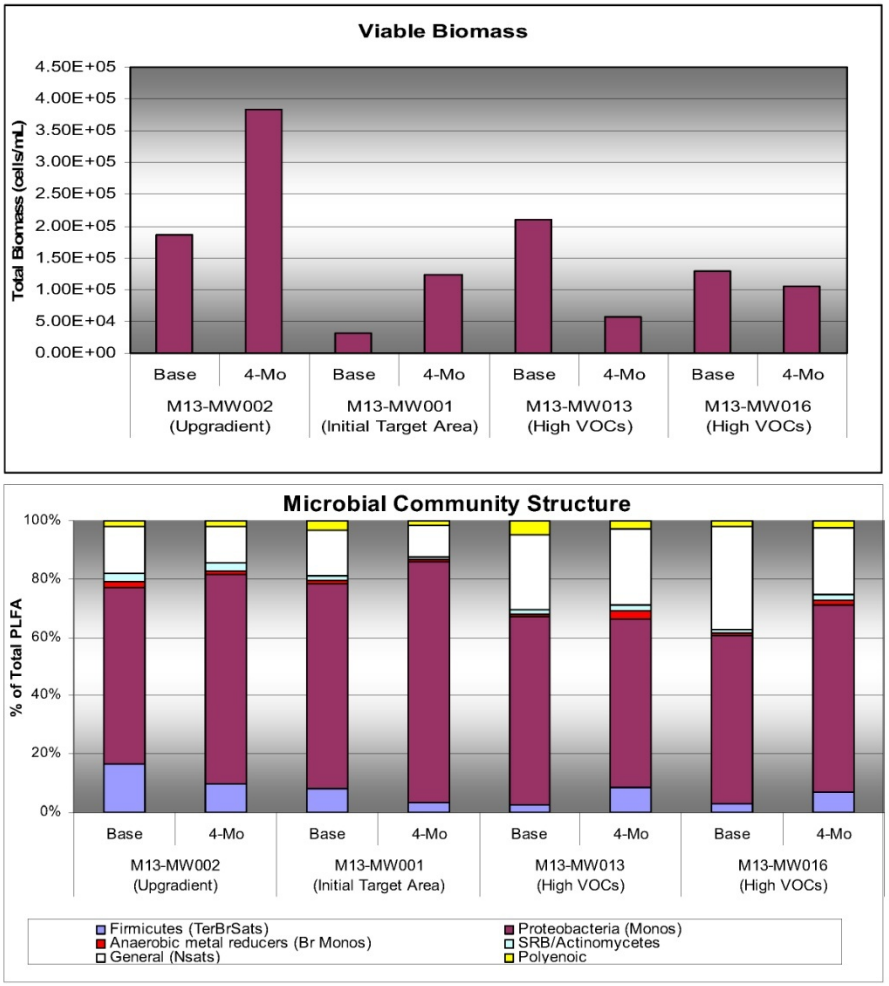

Figure 4-10. PLFA Results

4.8 Discussion

ISCO is a proven technology to aggressively treat contamination such as the COCs found at SWMU M-13. However, as at many sites, the primary challenge at this site was the ability to adequately distribute the oxidant into the target treatment area. The incomplete injections, the tight claylike soils, and the presence of the underground utilities resulted in a very uneven distribution of the oxidants at this site, which is evidenced by the variability in the pH, ORP, conductivity, and sulfate levels measured 1 month after completing the injections.

Initially, the oxidant was injected through 19 DPT points; however, clogging of the DPT points occurred as they were pushed through the overlying clay layer. It was postulated that the clay had been saturated with water because of heavy rain and smeared across the probes, thereby preventing adequate injection of the reagents. The system was optimized by converting the DPT locations into 1-inch-diameter wells, which were then used to inject the reagent. Although it was possible to inject about 13% of the design volume through these wells, surfacing of the reagent was observed to occur in a previously unknown outfall located along the Potomac River several hundred feet from the injection locations, as well as in two other locations: a storm drain adjacent to Building 2113 and a communication line manhole in the southwest portion of the site. As a result, injection of the remaining oxidant was halted.

Monitoring results at this site indicate that application of persulfate tends to increase metal levels, but that they may return to near baseline values as the persulfate is consumed and the sulfate levels and redox conditions return to baseline levels. Concentrations of metals in wells downgradient of the site did not appear to be elevated; however, it is not possible to accurately evaluate the potential for transporting these metals because of (1) the limited injections performed, (2) the fact that many subsurface conduits appeared to transport the reagents to unanticipated regions of the site, and (3) lack of longer-term monitoring data.

Additional conclusions and lessons learned during application and subsequent monitoring include the following:

- Using DPT technology was not feasible due to the tight clay soils. In addition, conductive layers available to transport the reagent into the wells were limited. Hence, it was not possible to achieve adequate distribution of the reagent in the subsurface. In several instances, the path of least resistance to flow appeared to be along utility corridors and to the surface. In particular, the presence of a former sewer line in the target treatment area provided a direct pathway for the oxidant to the river. An injection strategy incorporating recirculation could be a viable approach for this site; pilot testing would be necessary to determine the efficacy of such an approach at this site.
- Implementation challenges include buildings, structures, retaining walls, and a steep slope. Subsurface utilities, including electric, fuel, communications, water, natural gas, etc., constrained the remedial design. Areas in which injection points could be installed were limited due to the extensive network of subsurface utilities and surface features.
- In areas where good contact of persulfate with the contaminant mass occurred, reduction of TCE and TCB was observed. Reduction of TCE (50% to 96%) was greater than that of 1,2,4-TCB (12% to 61%).
- Total metals were elevated in wells that showed exposure to the ISCO reagents. The greatest increase in the concentration of total metals correlated well with wells in which high sulfate, conductivity, and ORP were measured. In general, concentrations were found to be highest during the 1-month sampling event and had decreased substantially 4 months after completing the ISCO injections. It is not possible to accurately determine if the concentration of metals downgradient of these wells was elevated; it was also not possible to determine the attenuation distance required downgradient of the treatment area for groundwater to return to baseline conditions due to the uneven distribution of reagents and the presence of subsurface conduits that may facilitate transfer of the reagents.
- Application of ISCO may temporarily inhibit microbial processes. PLFA results indicate reduced microbial activity in wells in which groundwater was influenced by the ISCO reagents. DO, ORP, and sulfate levels were observed to increase. However, these effects may be short-lived. Additional monitoring should be performed to better assess the microbial community and the monitored natural attenuation (MNA) potential.
- Concentrations of chloride were not reported and therefore cannot be used to gauge ISCO performance.

- Low levels of chloromethane and methylene chloride (THM precursors) were measured in several monitoring wells. However, the concentrations of chloroform, bromodichloromethane, and dibromochloromethane were not reported. Concentrations of bromoform were found not to be elevated after applying the reagents.
- The plume of TCE and 1,2,4-TCB extended beyond monitoring well MW016, which for the purpose of the pilot study, had been designated as a downgradient monitoring well. An accurate site conceptual model is necessary to design and implement a cost-effective remedy for any site.
- There is evidence that persulfate persisted in the aquifer 4 months after completing the ISCO injections. Elevated concentrations as high as 7,000 mg/L were measured in the injection points using colorimetric field test kits.

Section 5.0: PERSULFATE APPLICATION AT ALAMEDA

5.1 Introduction

This section describes the persulfate application that is in progress at Installation Restoration (IR) Site 14 at former NAS Alameda Point, Alameda, California. Documents reviewed included the *Final Remedial Design/Remedial Action Work Plan Installation Restoration Site 14, Alameda Point, Alameda, California* (Battelle, 2008) and the *Workplan for Data Gap Sampling Investigation, Installation Restoration Site 14* (ITSI, 2007). In addition, all project files and data pertaining to implementation were available for review and incorporation into this report.

NAS Alameda was operated as an active naval facility from 1940 to 1997. Historically, operations included aircraft, engine, firearms, avionics maintenance, fueling activities, metal plating, stripping, and painting. The Navy operated two power plants, a transportation shop, and a pesticide shop. The base had a deepwater port capable of berthing aircraft carriers and a fuel-distribution pipeline network that transported aviation and diesel fuel to various areas on the base. IR Site 14 is approximately 14.4 acres in size and is located in the northwestern section of Alameda Point (Figure 5-1). The northern boundary of the site is adjacent to the Oakland Inner Harbor and the southern boundary is located north of former Runway 7/25. The site was used to store airfield-related materials and equipment, with the northwestern portion of the site used for firefighter training activities. It was originally designated as an IR site based on concerns related to the fire-training activities. Petroleum-related constituents in soil were the primary concern. Subsequent investigations revealed the presence of chlorinated solvents in groundwater, and these solvents are the focus of the current groundwater investigation and proposed site remediation.

IR Site 14 is primarily open space and is partially paved, with a generally flat topography. The site currently includes five buildings; two closed aboveground storage tanks (ASTs) that contained non-potable water; petroleum corrective action area CAA-2, which is the administrative unit designating the location of contamination from former underground storage tank (UST) FS-1; and several storm and sanitary sewer lines (Figure 5-2). IR Site 14 also contains multiple SWMUs: former generator accumulation points (GAPs) 9 and 11; washdown (WD) area 528; petroleum-related SWMU Areas of Concern (AOCs) 357, AST-179, and AST-528; and a Firefighter Training Area.

The principal COC is VC, although groundwater sampling has confirmed that the parent compounds TCE and DCE are present at low concentrations in a few of the monitoring wells. The remedy selected for the site consists of ISCO to rapidly break down source contaminants, followed by MNA and long-term institutional controls to limit human exposure to VC. The primary future route of exposure is thought to be exposure to VOCs in indoor air, which may volatilize from groundwater. The target treatment area for ISCO application is the entire VC plume; it is defined by the area of groundwater having a VC concentration greater than 15 µg/L, which is the remedial goal (RG) for the site.

An ISCO pilot test was conducted in October 2007 (Battelle, 2008) to assess the effectiveness of the process to reduce contaminant mass in the subsurface at IR Site 14; to evaluate the impact of variations in injection parameters (including injection pressure, injection flow rate, and reagent volumes); and to evaluate the effective radius of influence (ROI) of the injected reagent. The pilot test consisted of injecting potassium permanganate at a point located in the southern portion of the plume and injecting sodium persulfate at a point in the northern portion of the plume. The results of the pilot test were used to finalize the design and implement full-scale ISCO.

Figure 5-1. Location of IR Site 14 at Alameda Point, California

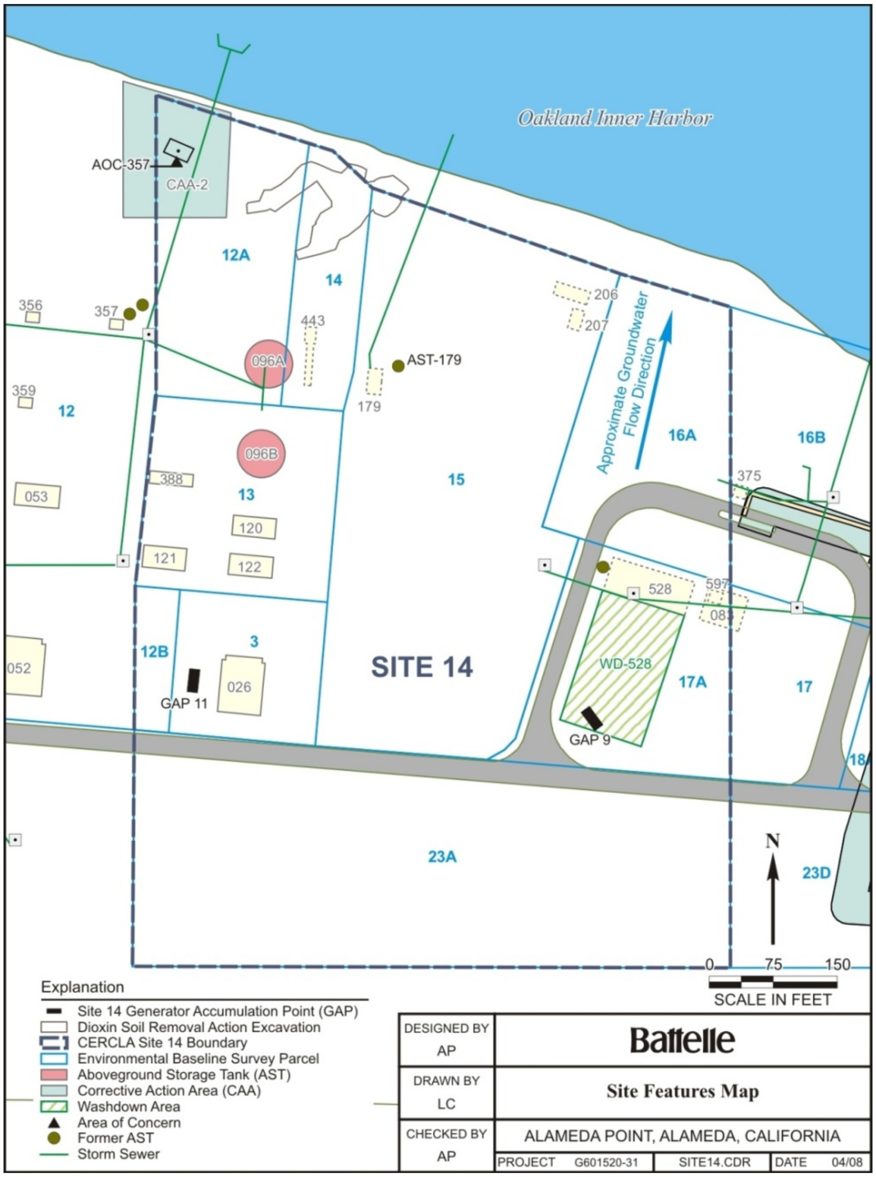

Figure 5-2. IR Site 14 Features

The VC concentrations at each monitoring point within the contaminant plume will be compared to the established RG of 15 µg/L to assess whether the VC RG has been achieved. As agreed upon with the regulatory agencies, four consecutive quarters of monitoring data at each well must meet this established RG in order for the remedy to be considered complete.

5.2 Geology and Hydrogeology

The general geology of Alameda Point can be described as a mixed layer of locally derived fill materials emplaced in modern times over native Bay sediments dating from Holocene to Pleistocene in age. The fill materials were emplaced during several episodes of land building that occurred from about 1887 to as late as 1963. The fill material extends from the ground surface to 12 to 18 feet bgs. The Bay Sediment Unit (BSU), which was encountered below the fill layer at IR Site 14, is composed of estuarine deposits of low- to high-plasticity clay with discontinuous silty and clayey sand layers, and has been observed to be up to 55 feet thick at Alameda Point. Within IR Site 14, the BSU thickens to the south due to its presence there as channel-fill deposits cut into the underlying units; thus, the BSU is present beneath the artificial fill to a depth of 40 feet in the northern portion of IR Site 14, but to 70 feet in the southern portion of the site.

The shallow first water-bearing zone (FWBZ) at IR Site 14 is in the fill material overlying the BSU, and depth to groundwater varies from approximately 1 to 6 feet bgs. The shallow groundwater depths are encountered during the wet seasons (winter and spring), with greater depths observed in the dry season. Investigations at IR Site 14 have reported an average horizontal hydraulic gradient of 0.006 foot/foot in the FWBZ, with groundwater flow direction generally toward the north-northeast, directly toward the Oakland Inner Harbor. Slug testing conducted during the RI in the FWBZ at IR Site 14 produced a hydraulic conductivity value range of 1.3×10^{-3} to 1.7×10^{-3} centimeters/second (cm/sec) (Tetra Tech EMI, 2003). Slug testing conducted during the ISCO pilot test on a larger number of wells (seven) yielded slightly higher hydraulic conductivities, ranging from 3.7×10^{-4} to 5.2×10^{-3} cm/sec. In contrast, the BSU underlying the FWBZ has yielded much lower hydraulic conductivities, ranging from 8.85×10^{-7} to 3.55×10^{-5} cm/sec.

5.3 Contaminant Distribution

VC is the primary groundwater COC. The RG for VC is 15 µg/L. There is no evidence of the presence of DNAPLs, which typically make site remediation much more complicated. Based on baseline sampling, which was performed prior to the full-scale ISCO injections, the estimated area exceeding the RG was 100,000 square feet. The depth of contamination ranges from approximately 5 to 15 feet bgs. The maximum concentration was 390 µg/L.

5.4 Technology Implementation

A recirculation approach using iron-activated sodium persulfate was employed at IR Site 14 to treat VC that exceeded the RG of 15 µg/L. Figure 5-3 shows the ISCO injections were performed in three phases as highlighted in the schedule of key activities.

To supplement the information acquired during the pilot test, a series of bench-scale tests was conducted, using four soil samples collected from within the target treatment area. The bench-scale tests included soil oxidant demand (SOD) screening for both persulfate and permanganate on a composite sample from the soil collected at the four locations; SOD analysis for three different concentrations of persulfate and permanganate over 8 days; and moisture content on each of the samples. The results show that the persulfate had a lower SOD than potassium permanganate for each soil type and at each time point. An average of the 8-day SOD values for the four soil samples shows that unactivated persulfate had a SOD of 2.1, 5.2, and 7.2 g/kg at the tested concentrations of 7.5 g/L, 15 g/L, and 30 g/L, respectively. A similar average of the SOD values for potassium permanganate showed SOD values of 3.7, 8.5, and 13.1 g/kg for loadings of 10 g/L, 20 g/L, and 30 g/L, respectively.

Additional bench-scale tests were performed to evaluate different activation techniques. Ferrous sulfate, calcium peroxide, hydrogen peroxide, and ferrous sulfate were tested. Based on results, which indicate that iron-activation had very high destruction (>99% VC) within a short period of time[10] and a relatively low cost, iron activation was selected for the full-scale application.

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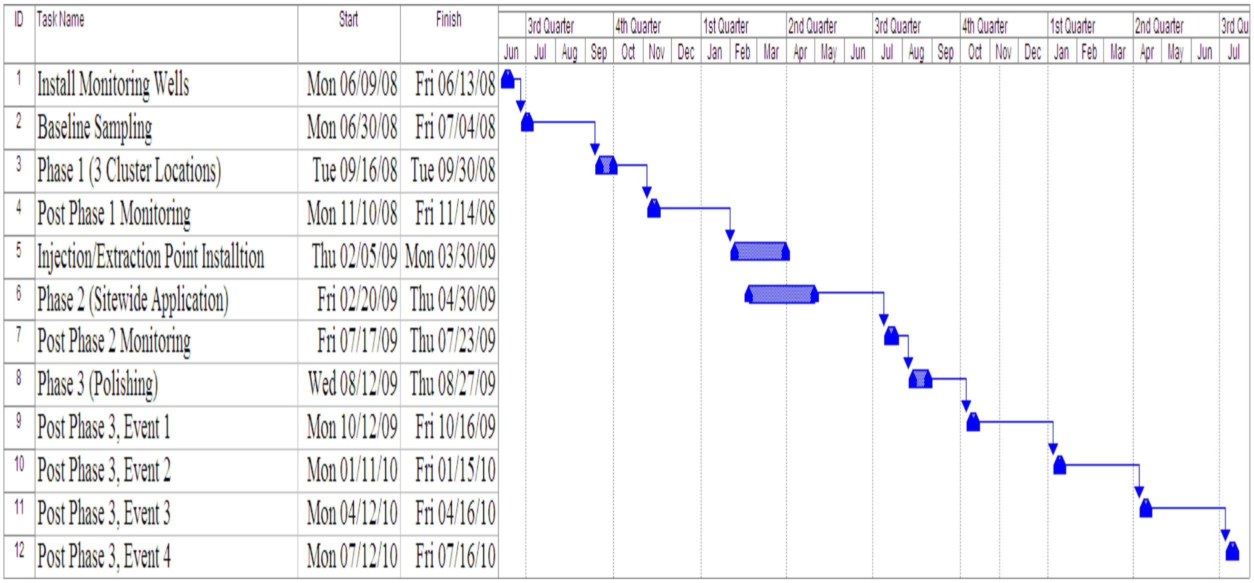
[10] Because of potential regulatory concerns pertaining to the reinjection of groundwater contaminated with VC, the system was designed to ensure that the VC would be mostly oxidized prior to reinjection into the aquifer.



ID	Task Name	Start	Finish
1	Install Monitoring Wells	Mon 06/09/08	Fri 06/13/08
2	Baseline Sampling	Mon 06/30/08	Fri 07/04/08
3	Phase 1 (3 Cluster Locations)	Tue 09/16/08	Tue 09/30/08
4	Post Phase 1 Monitoring	Mon 11/10/08	Fri 11/14/08
5	Injection/Extraction Point Installtion	Thu 02/05/09	Mon 03/30/09
6	Phase 2 (Sitewide Application)	Fri 02/20/09	Thu 04/30/09
7	Post Phase 2 Monitoring	Fri 07/17/09	Thu 07/23/09
8	Phase 3 (Polishing)	Wed 08/12/09	Thu 08/27/09
9	Post Phase 3, Event 1	Mon 10/12/09	Fri 10/16/09
10	Post Phase 3, Event 2	Mon 01/11/10	Fri 01/15/10
11	Post Phase 3, Event 3	Mon 04/12/10	Fri 04/16/10
12	Post Phase 3, Event 4	Mon 07/12/10	Fri 07/16/10

Figure 5-3. Full-Scale ISCO Injections and Monitoring Schedule

Capture modeling, including injection and extraction particle tracking, was performed to determine an optimum arrangement of injection and extraction wells based on site-specific geology and hydrogeology. Based on modeling results, the approximately 100,000 square-foot target area was divided into 17 smaller “modules”. Each treatment module consisted of 22 extraction wells and seven injection wells installed in a series of concentric rings. In general, each module had a radius of 45 feet, with alternating rings of injection and extraction wells spaced 15 feet apart. Injection wells were spaced about 17.5 feet apart along the circumference of each ring, and the extraction wells were spaced about 31 feet apart. Figure 5-4 illustrates a typical module.[11]

A total of 416 temporary direct-push wells were installed, which consisted of 119 injection and 297 extraction wells. One hundred and twenty-nine of the wells were constructed of 2-inch-diameter PVC, and the remainder was constructed of 1½-inch-diameter PVC. Wells were installed using a Series 7700 DPT rig. The screened interval of each well varied, depending on its location at the site. To best target the placement of the ISCO reagents, the extraction and injection wells were screened in accordance with the vertical intervals containing concentrations of VC above the 15 µg/L RG. Based on results presented in the Data Gap Evaluation Report (Battelle, 2008), the site was conceptually divided into three areas as shown in Figure 5-5. The injection and extraction wells located in Area 1 were screened from 9 to 17 feet bgs, from 8 to 14 feet bgs in Area 2, and from 4 to 12 feet bgs in Area 3.

Two recirculation systems were used to perform the injections. Each recirculation system (Figure 5-6) consisted of a number of pneumatically operated diaphragm pumps (one per extraction well) mounted onto a secondary containment skid. Because of the shallow water table, downhole pumps were not necessary. Flexible tubing, the ends of which were placed at about the midpoint of the screen interval in each well, was used to feed the groundwater from the wells, through a series of manifolds, and into a 1,100-gallon PVC tank. The water extracted from the individual wells was combined in the PVC tank, and any vapor was separated. A small 1/3-horsepower regenerative blower, having a maximum flow

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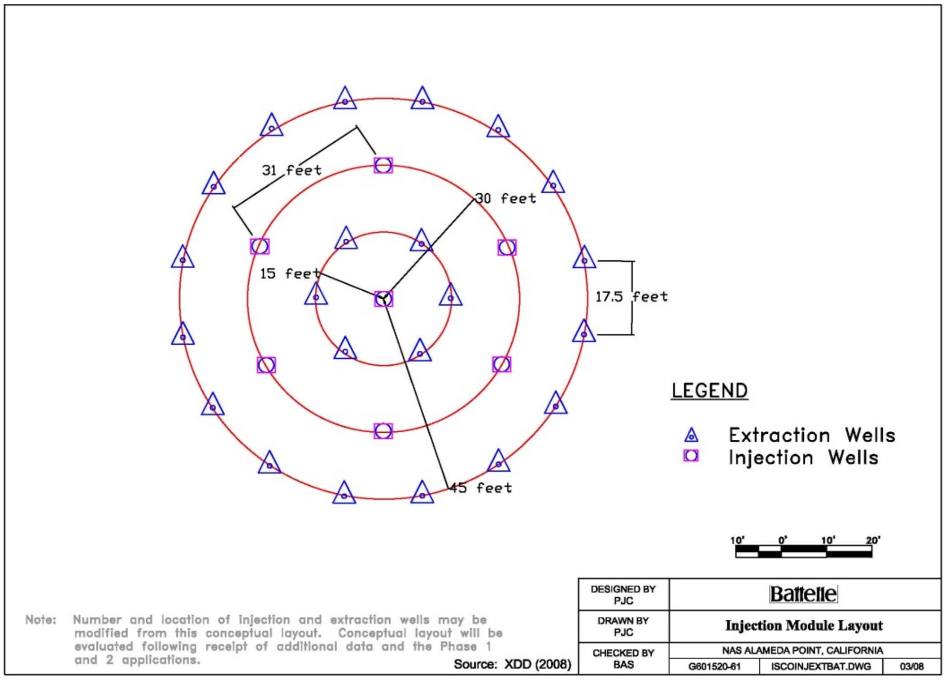
[11] The layout of several modules was modified to accommodate the presence of underground utilities and aboveground structures and/or to optimize the number of wells required to treat the target area.



Note: Number and location of injection and extraction wells may be modified from this conceptual layout. Conceptual layout will be evaluated following receipt of additional data and the Phase 1 and 2 applications.

Source: XDD (2008)

Figure 5-4. Conceptual Illustration of a Recirculation Module

capacity of 42 standard cubic feet per minute (SCFM), was operated continuously to withdraw the headspace from the tank and discharge it through two 55-gallon drums of activated carbon installed in series to treat any VC present in the vapor stream. Figure 5-7 shows a photo of the system. Note that the chemical feed tanks are not depicted.

The sodium persulfate solution was made up in a second 1,100-gallon PVC tank. A 1-ton “supersack” of sodium persulfate was added to approximately 880 gallons of water to make a solution of approximately 300 g/L. Ferrous sulfate and citric acid were mixed with water in a separate, smaller PVC tank. The reagents were mixed using a pneumatically operated stirrer until no solids were visible at the bottom of the tank. The solution from this tank was metered into the discharge stream from the groundwater mixing tank and blended with the groundwater using an in-line mixer. The amended water was split into several streams through a PVC manifold, and then pumped into each injection well through flexible hoses and a centralized diaphragm pump.

The first phase of injections (the Preliminary Phase) was performed from September 16 through September 30, 2008. The Preliminary Phase targeted areas that historically had contained the greatest concentrations of VC, which included Modules 1, 2, and 3. These three areas are considered to be potential sources of the dilute chlorinated solvent plume. Recirculation was performed for approximately four 10-hour days at each location, during which extracted groundwater was amended with sodium persulfate and ferrous sulfate. Three 2,200-pound supersacks of sodium persulfate were applied to each of the three treatment areas. The volume of groundwater that was extracted and recirculated in each area varied significantly as a result of the heterogeneous fill material in which the wells were installed. Hence, although the mass injected into each area was the same, the resulting average concentration of the oxidant varied in the injected groundwater.

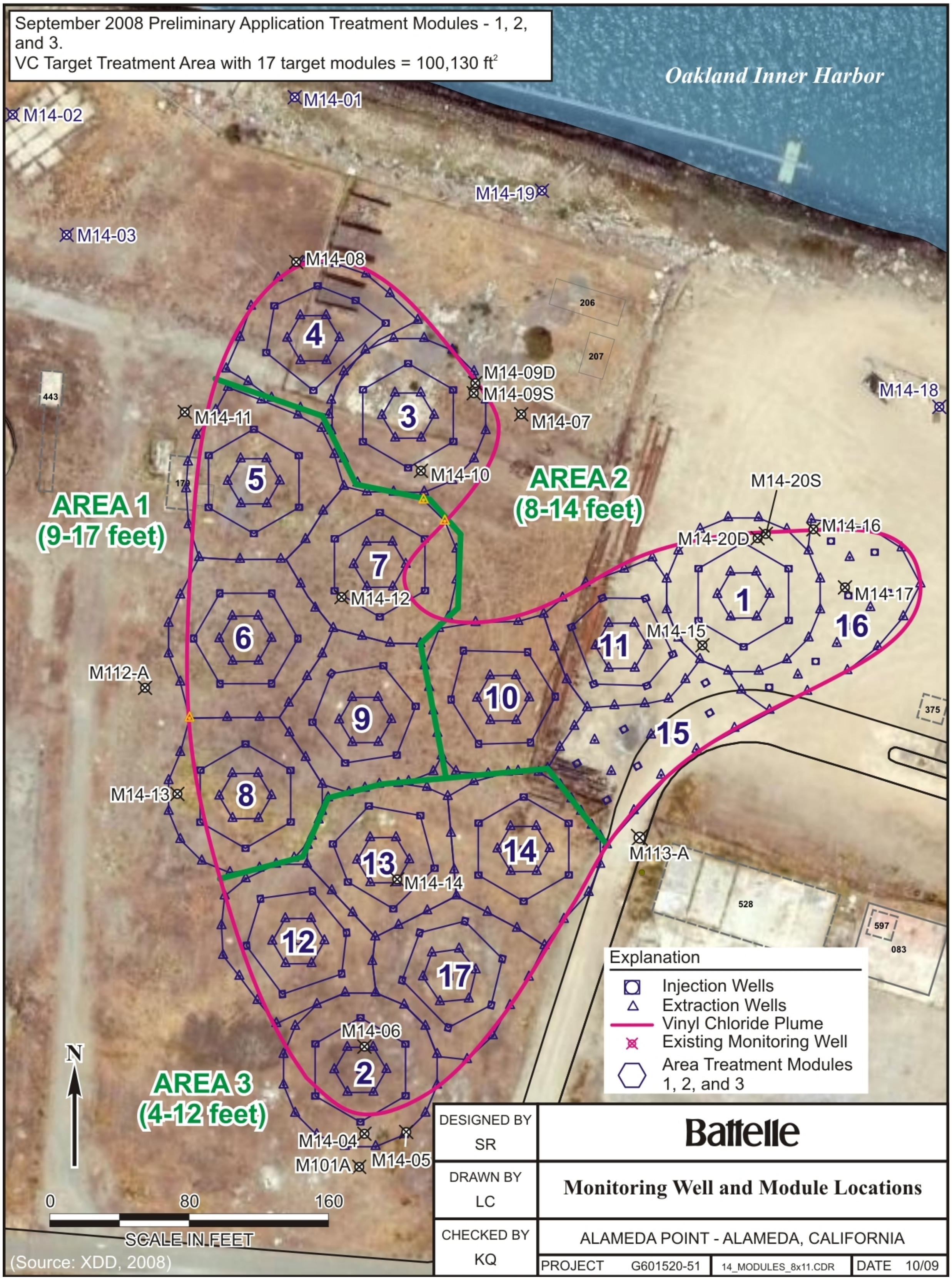


Figure 5-5. Recirculation Modules

The second (site-wide application) included performing ISCO injections in all areas of the site containing groundwater with VC concentrations greater than 15 µg/L. All 17 modules were used during this application. Figure 5-5 shows the module locations.

The site-wide application began the week of February 23, 2009, and was completed on April 29, 2009. Approximately 914,000 gallons of groundwater were extracted, which represents about 0.68 of a pore volume, based on the estimated size of the treatment area. The extracted groundwater was amended with a total of 112,256 pounds of sodium persulfate and reinjected into the subsurface. Similar to the Preliminary Phase, groundwater was amended and recirculated for 4 days in each treatment area.

The last ISCO application (the Polishing Phase) was performed from August 12 through August 27, 2009. Four areas were selected, all of which contained groundwater exhibiting concentrations of VC greater than the RG of 15 µg/L. These areas were 1, 2, 13, and 16 (Figure 5-5). Recirculation was performed for about 5 days in Modules 2 and 13. However, a modified injection/extraction strategy was used at Modules 1 and 16. Rather than using the dedicated injection and extraction wells as in the first two rounds of injections, the modules were combined, the injection and extraction wells were interchanged, and the injection time was increased. Fluids were injected and extracted from 30 wells.

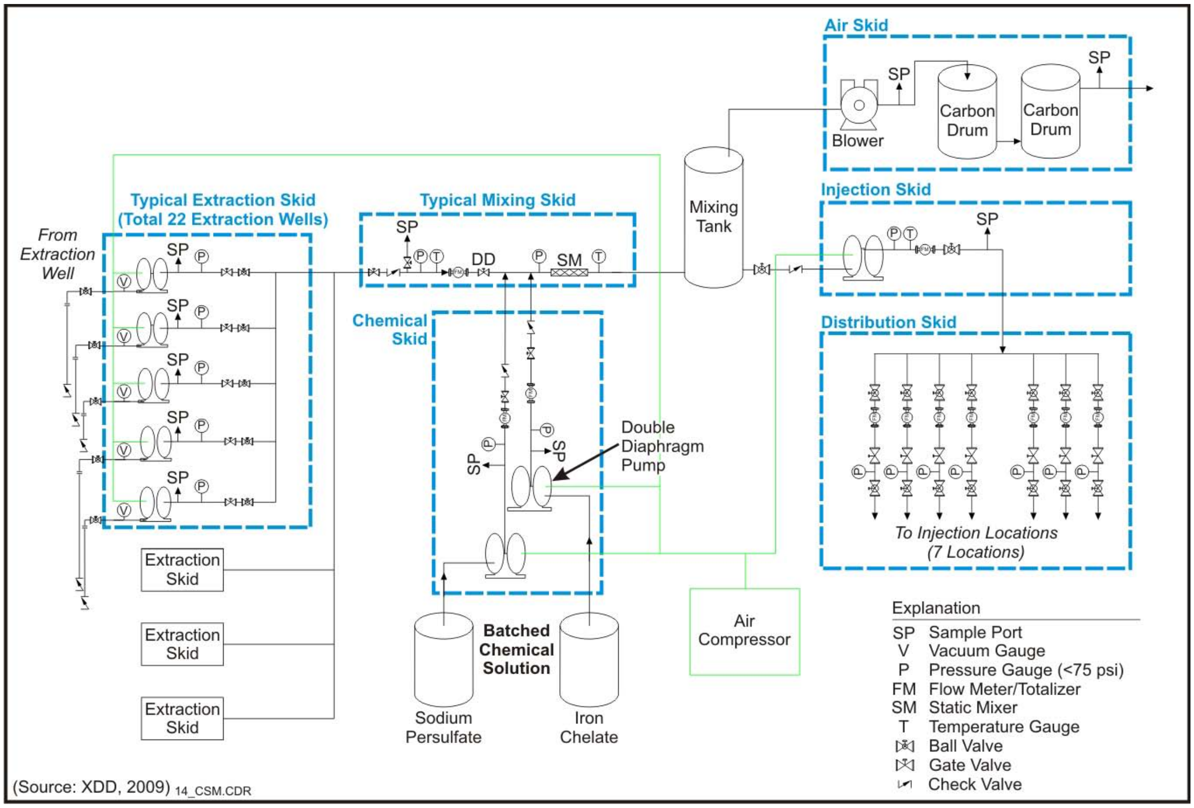
Injection pressures ranged from near zero to about 10 psi. Some wells were used as both injection and extraction wells at various times during the application to compensate for low flow from certain wells and to minimize daylighting of reagent that was observed to occur occasionally. This optimization of the injection approach was performed because the monitoring data indicated that only portions of each target area exceeded the RG for VC, and it was decided that injecting additional oxidant over a longer period would better treat this area. Operating in this fashion provided the advantages of (1) focusing treatment in the area that appeared to be most contaminated; (2) overcoming preferential pathways created during the first phases of injection, allowing the reagent to contact previously untreated groundwater/soil; and (3) improving contact and distribution of the reagent by increasing the duration of treatment to 10 days. A total of 26,400 pounds of persulfate was injected and recirculated with groundwater during this event, which was equivalent to 84% of a full pore volume.

5.5 Performance Evaluation Approach

A network of 25 groundwater monitoring wells was used to evaluate ISCO performance. Figure 5-5 shows well locations. Fifteen of these wells, including two well clusters, were installed specifically for evaluating ISCO performance. The wells were installed between June 9 and June 11, 2008. Table 5-1 lists the screen intervals of these wells.

Table 5-1. Monitoring-Well Screen Intervals

Well Identification	Screened Interval (ft bgs)	
	Top	Bottom
M101-A	2.5	12.5
M112-A	NA	NA
M113-A	NA	NA
M14-01	NA	NA
M14-02	NA	NA
M14-03	NA	NA
M14-04	5	12
M14-05	5	13
M14-06	5	12
M14-07	8	14
M14-08	9	14
M14-09S	8	10
M14-09D	12	14
M14-10	10	17
M14-11	10	17
M14-12	10	17
M14-13	10	17
M14-14	5	12
M14-15	9	14
M14-16	8	10
M14-17	9	14
M14-18	9	14
M14-19	9	14
M14-20S	8	10
M14-20D	12	13



(Source: XDD, 2009) 14_CSM.CDR

Figure 5-6. Recirculation Module Process and Instrumentation Diagram

Figure 5-7. Injection and Extraction Equipment

Four sampling events have been performed and are summarized in Table 5-2. A minimum of three additional events will be performed as required by the regulatory agencies in order to demonstrate compliance with the RG.[12] In general, each post-ISCO sampling event was performed 5 to 6 weeks after completing each phase of injections. However, because of the persistence of persulfate in several of the monitoring wells after completing the site-wide application, the site was allowed to equilibrate for a longer time so that residual persulfate would react/dissipate and concentrations of VOCs in groundwater would reequilibrate prior to post-Phase 2 monitoring.

The first sampling event, which consisted of measuring baseline conditions, was performed from August 14 through August 20, 2008, prior to beginning the full-scale ISCO injections. All 25 monitoring wells were analyzed for VOCs by United States Environmental Protection Agency (U.S. EPA) Method 8260B, and for metals by U.S. EPA Method 6010B/6020.

Table 5-2. Summary of ISCO Monitoring Events

Sampling Event	Date	Weeks after Completing Injections	Number of Wells Sampled
Baseline	Aug 08	NA	25
Post-Phase 1	Nov 08	5	13
Post-Phase 2	Jul 09	11	25
Post-Phase 3, Event 1(a)	Oct 09	6	25

NA – not applicable

(a) Three additional quarterly monitoring events are planned.

Water quality parameters were measured in the field to establish baseline conditions for: pH, ORP, DO, temperature, and conductivity. Groundwater levels also were measured to evaluate groundwater flow direction and gradient.

Sampling was performed after each phase of ISCO injections. Similar to the baseline event, the wells were sampled for VOCs and metals. In addition, the concentration of persulfate was measured in the field using a Chemetrics® colorimetric test kit. Water quality parameters and depth to groundwater also were measured. The primary difference is that during the first post-ISCO sampling event, only the 13 wells located in the immediate vicinity of the three recirculation modules were sampled. These included wells M14-04, -05, -06, -07, -09S, -09D, -10, -15, -16, -17, -20S, -20D and M101A. All 25 site wells were sampled during the monitoring events conducted after the site-wide event and after the polishing event. In addition, four extraction wells were sampled after the site-wide application to provide additional data to help optimize the treatment locations for the polishing application.

During the ISCO application, the total volume of fluid injected into each well was measured during each day of operation. The mass of sodium persulfate and activator solution injected also was carefully tracked on a daily basis. It was not possible to measure the flowrates from individual extraction wells because the meters were fouled due to air and particulates in the extracted fluid and because there was occasional freezing of the pneumatic extraction pumps, which interfered with obtaining accurate measurements.

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[12] The agencies require that the VC concentration in each well be less than 15 µg/L during four consecutive rounds of sampling.

Groundwater samples also were collected periodically from the combined extracted groundwater stream and from the amended (injection) stream during application of the ISCO reagents. These were analyzed for chlorinated VOCs, including TCE, DCE, and VC, and the results were used to gauge the aboveground destruction efficiency of the chlorinated VOCs. Vapor samples were collected from the granular activated carbon effluent toward the end of the Phase 1 and Phase 3 applications and once per month during the site-wide application to ensure that COCs were not being discharged to the atmosphere.

5.6 Technology Performance

Results of the three full-scale ISCO applications are summarized in this section. Quarterly monitoring, which consists of collecting samples from all site groundwater-monitoring wells for analysis of VOCs, metals, and natural attenuation parameters, is in progress. Results of this monitoring beyond the Post-Phase 3, Event 1 (see Figure 5-3) are not yet available for inclusion in this document.

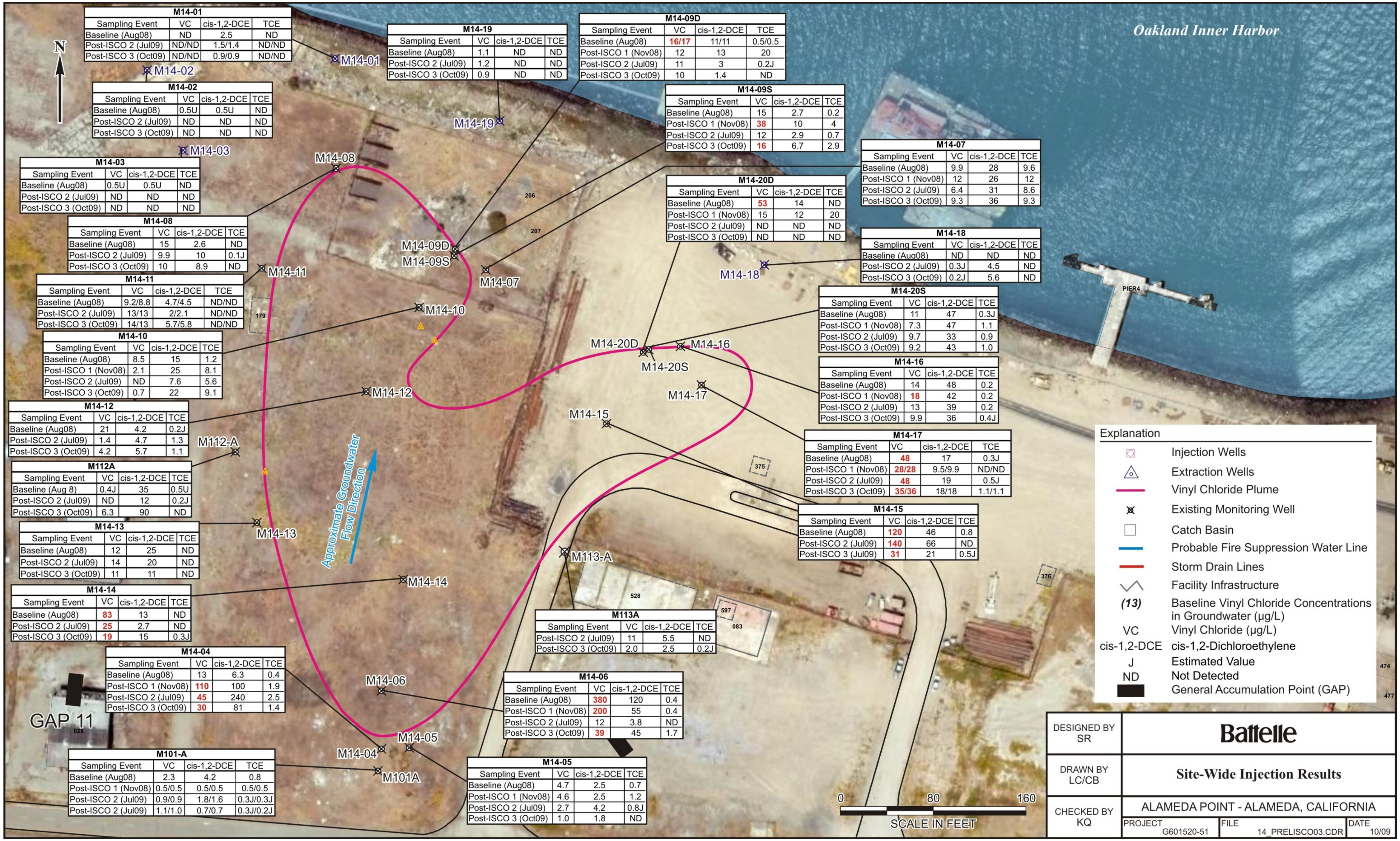
Figures 5-8 through 5-15 present key results. Figure 5-8 compares the concentration of chlorinated ethenes measured during baseline with concentrations measured during each of the post-ISCO sampling events. Figures 5-9 through 5-12 show changes in groundwater quality parameters in wells located near Modules 1 and 2, including conductivity, ORP, DO, and pH, which were treated during each application. Figures 5-13 through 5-16 summarize changes in the concentration of several metals including arsenic, chromium, iron, and manganese. The formation of THMs also was evaluated, and the results are summarized in Figure 5-17. Specific results and conclusions pertaining to these data and each of the three ISCO applications performed at IR Site 14 are discussed in the remainder of this section. Additional data are included, as necessary, to support these discussions. *All data should be considered preliminary because the project is still ongoing as of the preparation of this report.* The application data will be further evaluated as part of an Interim Remedial Action Completion Report (I-RACR).

5.6.1 Preliminary Application. Table 5-3 summarizes injection and extraction volumes achieved during the preliminary phase. Each of the three treatment areas received an equivalent mass of sodium persulfate, which consisted of approximately 6,600 pounds (i.e., three supersacks). The volume of water extracted from the subsurface varied by module due to subsurface heterogeneities. Hence, the average persulfate concentration, which was calculated as the total mass of sodium persulfate divided by the total volume of amended groundwater reinjected, varied among treatment areas. The average concentration of ferrous sulfate and citric acid also varied. The groundwater in Areas 1, 2, and 3 was amended with an average of 0.48, 1.0, and 0.79 g/L ferrous sulfate, respectively, and with an average of 0.54, 1.2, and 0.90 g/L citric acid, respectively.

Table 5-3. Injection Summary for Preliminary Application

Target Area	Volume Extracted[a]		Volume Injected[b,c] (gallon)	Sodium Persulfate			Activator Solution[b,e] (gallon)
	Volume (gallon)	% Pore Volume[f] (gallon)		Volume Solution[d] (gallon)	Mass (pounds)	Conc. (g/L)	
1	60,400	60	63,700	2,600	6,600	12	727
2	34,600	46	38,500	3,060	6,600	21	839
3	41,800	41	45,000	2,440	6,600	18	782
Totals	136,800		147,200	8,100	19,800		2,348

(a) Based on subtracting reagent volumes from volume injected.
(b) Includes volumes of sodium persulfate solution and activator solution.
(c) Based on flow totalizer readings.
(d) ~300 mg/L concentration, which is equivalent to one supersack (2,200 pounds) mixed into 880 gallons of water.
(e) Approximately 80 pounds of citric acid and 70 pounds of ferrous sulfate dissolved into 200 gallons of water.
(f) Assumes a soil porosity of 0.3 and 87.5% accessible pore space.



M14-01

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	ND	2.5	ND
Post-ISCO 2 (Jul09)	ND/ND	1.5/1.4	ND/ND
Post-ISCO 3 (Oct09)	ND/ND	0.9/0.9	ND/ND

M14-02

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	0.5U	0.5U	ND
Post-ISCO 2 (Jul09)	ND	ND	ND
Post-ISCO 3 (Oct09)	ND	ND	ND

M14-03

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	0.5U	0.5U	ND
Post-ISCO 2 (Jul09)	ND	ND	ND
Post-ISCO 3 (Oct09)	ND	ND	ND

M14-08

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	15	2.6	ND
Post-ISCO 2 (Jul09)	9.9	10	0.1J
Post-ISCO 3 (Oct09)	10	8.9	ND

M14-11

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	9.2/8.8	4.7/4.5	ND/ND
Post-ISCO 2 (Jul09)	13/13	2/2.1	ND/ND
Post-ISCO 3 (Oct09)	14/13	5.7/5.8	ND/ND

M14-10

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	8.5	15	1.2
Post-ISCO 1 (Nov08)	2.1	25	8.1
Post-ISCO 2 (Jul09)	ND	7.6	5.6
Post-ISCO 3 (Oct09)	0.7	22	9.1

M14-12

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	21	4.2	0.2J
Post-ISCO 2 (Jul09)	1.4	4.7	1.3
Post-ISCO 3 (Oct09)	4.2	5.7	1.1

M112A

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug 8)	0.4J	35	0.5U
Post-ISCO 2 (Jul09)	ND	12	0.2J
Post-ISCO 3 (Oct09)	6.3	90	ND

M14-13

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	12	25	ND
Post-ISCO 2 (Jul09)	14	20	ND
Post-ISCO 3 (Oct09)	11	11	ND

M14-14

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	83	13	ND
Post-ISCO 2 (Jul09)	25	2.7	ND
Post-ISCO 3 (Oct09)	19	15	0.3J

M14-04

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	13	6.3	0.4
Post-ISCO 1 (Nov08)	110	100	1.9
Post-ISCO 2 (Jul09)	45	240	2.5
Post-ISCO 3 (Oct09)	30	81	1.4

M101-A

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	2.3	4.2	0.8
Post-ISCO 1 (Nov08)	0.5/0.5	0.5/0.5	0.5/0.5
Post-ISCO 2 (Jul09)	0.9/0.9	1.8/1.6	0.3J/0.3J
Post-ISCO 2 (Jul09)	1.1/1.0	0.7/0.7	0.3J/0.2J

M14-19

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	1.1	ND	ND
Post-ISCO 2 (Jul09)	1.2	ND	ND
Post-ISCO 3 (Oct09)	0.9	ND	ND

M14-09D

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	16/17	11/11	0.5/0.5
Post-ISCO 1 (Nov08)	12	13	20
Post-ISCO 2 (Jul09)	11	3	0.2J
Post-ISCO 3 (Oct09)	10	1.4	ND

M14-09S

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	15	2.7	0.2
Post-ISCO 1 (Nov08)	38	10	4
Post-ISCO 2 (Jul09)	12	2.9	0.7
Post-ISCO 3 (Oct09)	16	6.7	2.9

M14-20D

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	53	14	ND
Post-ISCO 1 (Nov08)	15	12	20
Post-ISCO 2 (Jul09)	ND	ND	ND
Post-ISCO 3 (Oct09)	ND	ND	ND

M14-07

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	9.9	28	9.6
Post-ISCO 1 (Nov08)	12	26	12
Post-ISCO 2 (Jul09)	6.4	31	8.6
Post-ISCO 3 (Oct09)	9.3	36	9.3

M14-18

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	ND	ND	ND
Post-ISCO 2 (Jul09)	0.3J	4.5	ND
Post-ISCO 3 (Oct09)	0.2J	5.6	ND

M14-20S

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	11	47	0.3J
Post-ISCO 1 (Nov08)	7.3	47	1.1
Post-ISCO 2 (Jul09)	9.7	33	0.9
Post-ISCO 3 (Oct09)	9.2	43	1.0

M14-16

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	14	48	0.2
Post-ISCO 1 (Nov08)	18	42	0.2
Post-ISCO 2 (Jul09)	13	39	0.2
Post-ISCO 3 (Oct09)	9.9	36	0.4J

M14-17

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	48	17	0.3J
Post-ISCO 1 (Nov08)	28/28	9.5/9.9	ND/ND
Post-ISCO 2 (Jul09)	48	19	0.5J
Post-ISCO 3 (Oct09)	35/36	18/18	1.1/1.1

M14-15

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	120	46	0.8
Post-ISCO 2 (Jul09)	140	66	ND
Post-ISCO 3 (Jul09)	31	21	0.5J

M113A

Sampling Event	VC	cis-1,2-DCE	TCE
Post-ISCO 2 (Jul09)	11	5.5	ND
Post-ISCO 3 (Oct09)	2.0	2.5	0.2J

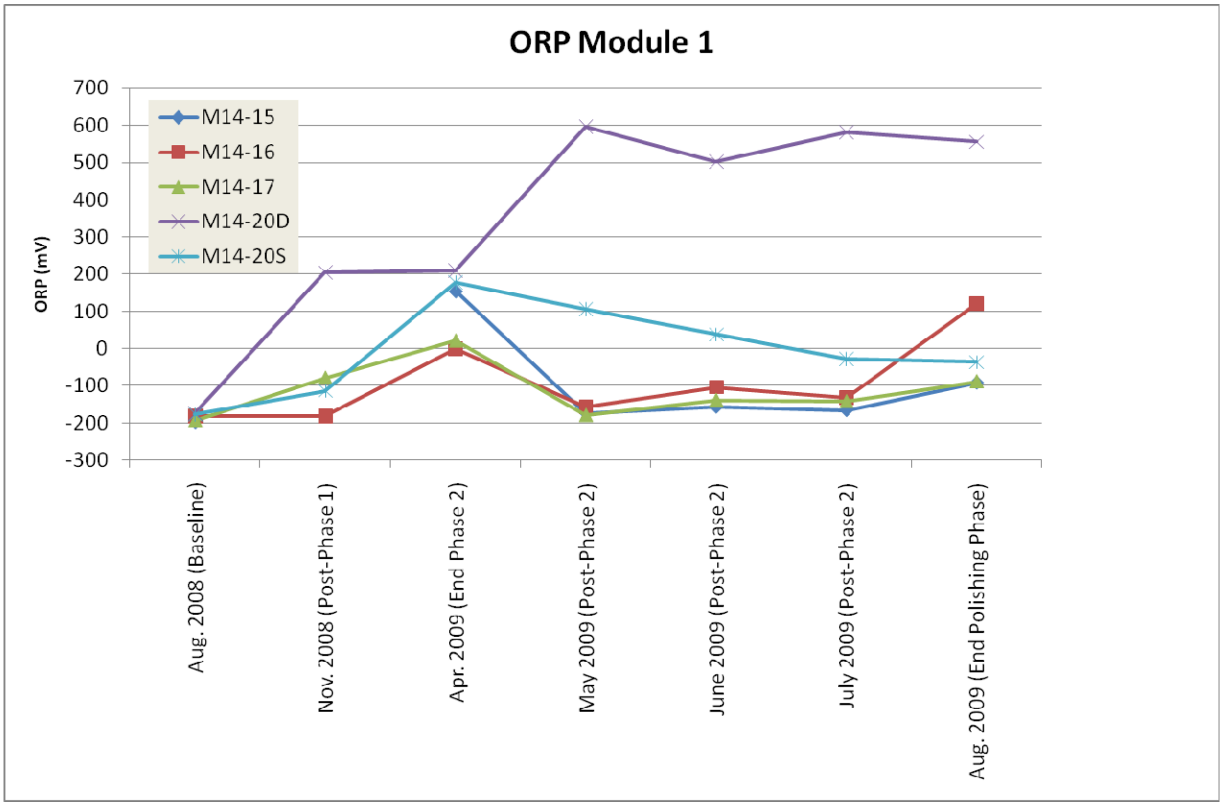
M14-06

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	380	120	0.4
Post-ISCO 1 (Nov08)	200	55	0.4
Post-ISCO 2 (Jul09)	12	3.8	ND
Post-ISCO 3 (Oct09)	39	45	1.7

M14-05

Sampling Event	VC	cis-1,2-DCE	TCE
Baseline (Aug08)	4.7	2.5	0.7
Post-ISCO 1 (Nov08)	4.6	2.5	1.2
Post-ISCO 2 (Jul09)	2.7	4.2	0.8J
Post-ISCO 3 (Oct09)	1.0	1.8	ND

Figure 5-8. Post-ISCO Monitoring Results for VC, TCE, and DCE



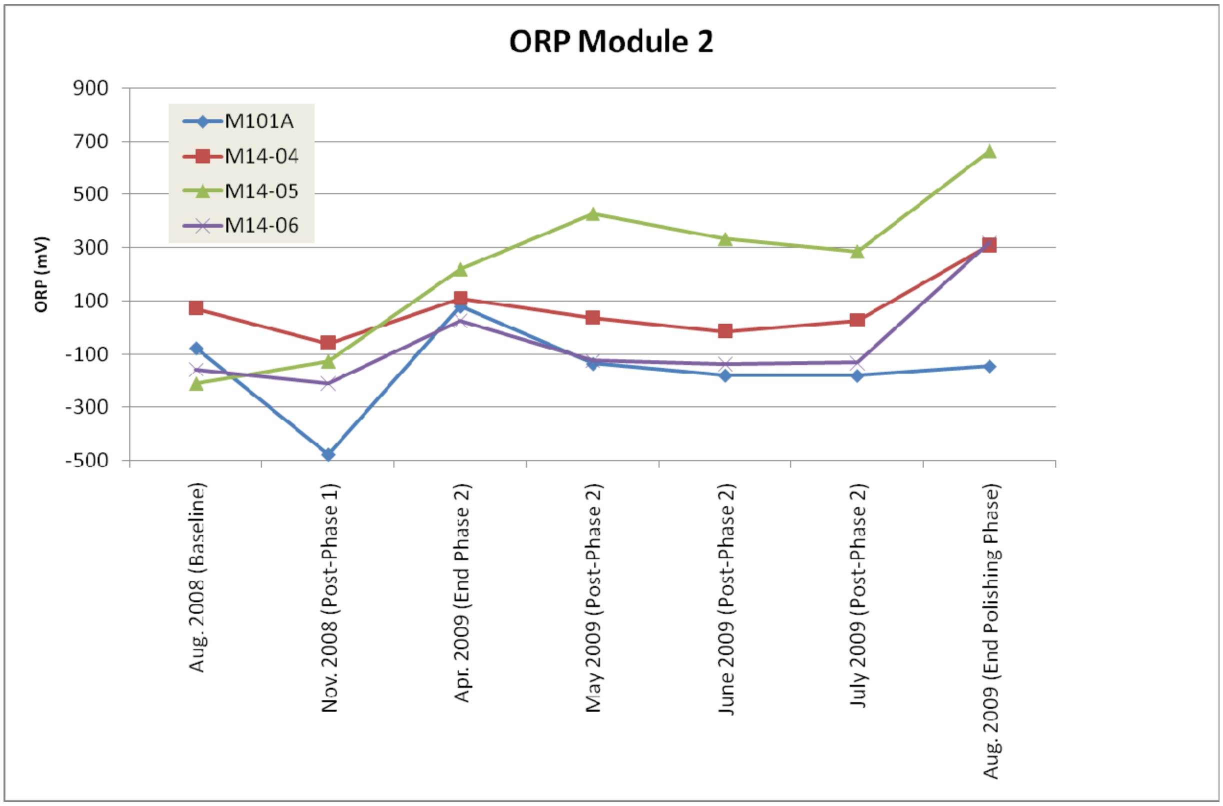
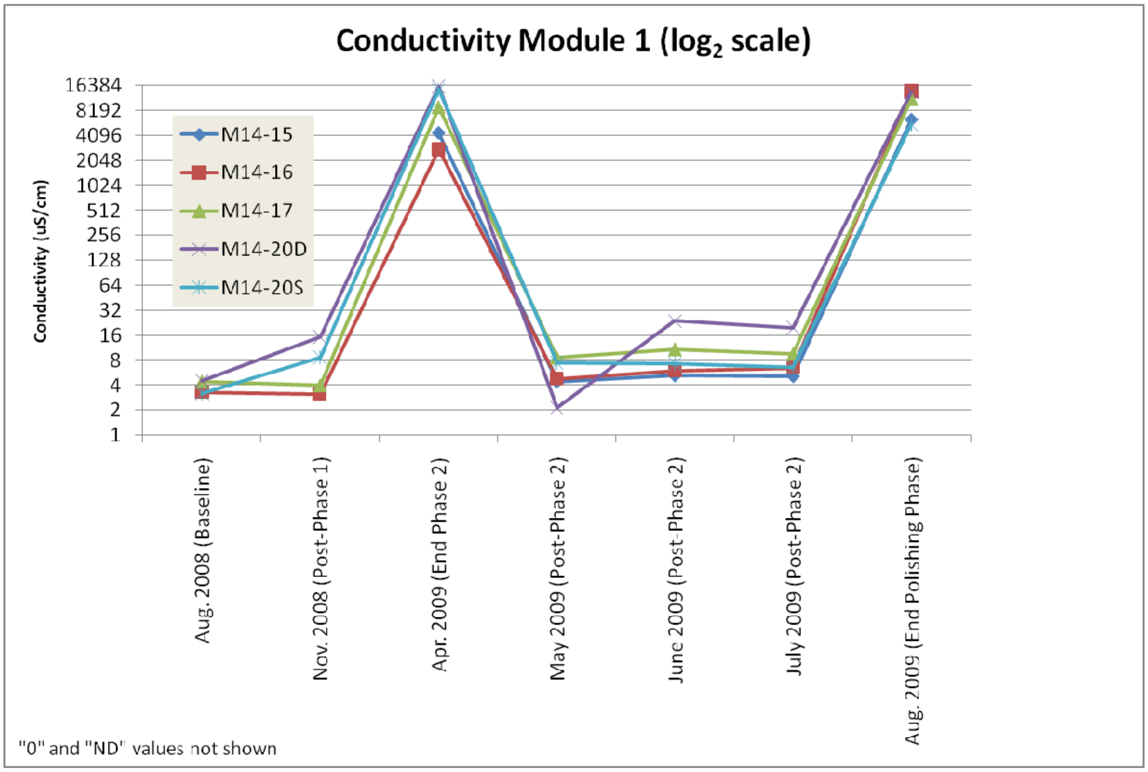


Figure 5-9. ORP Measurements During Full-Scale Application



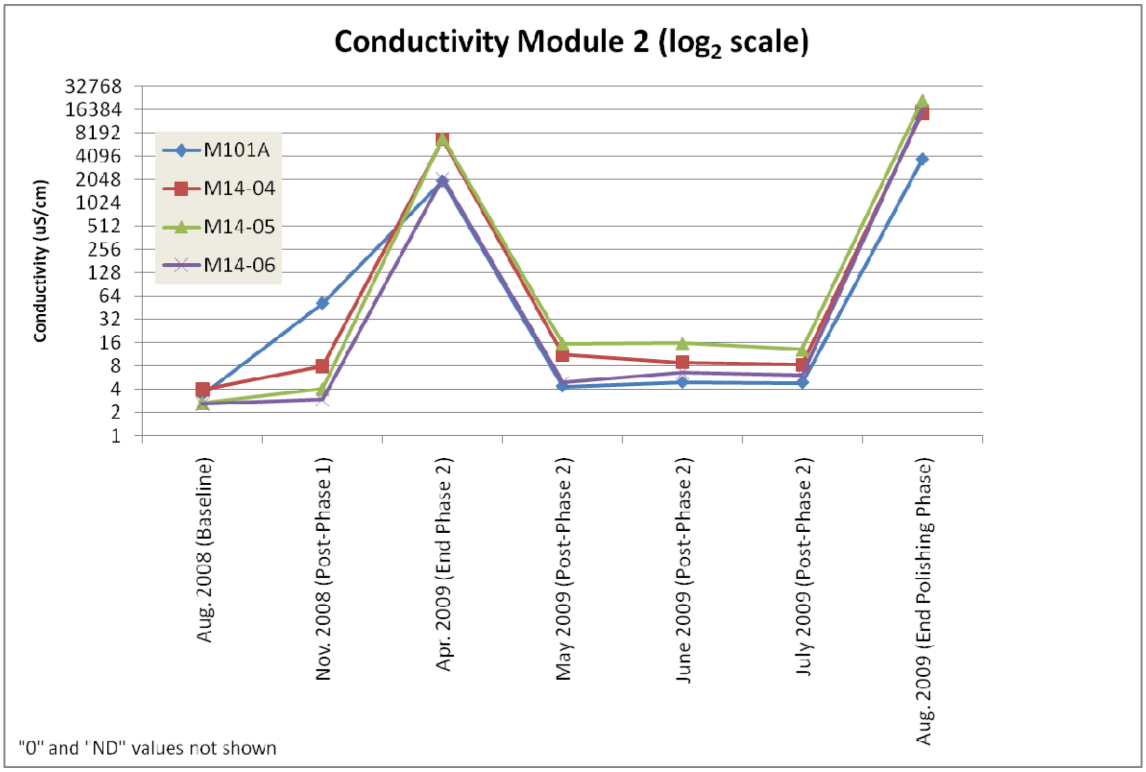
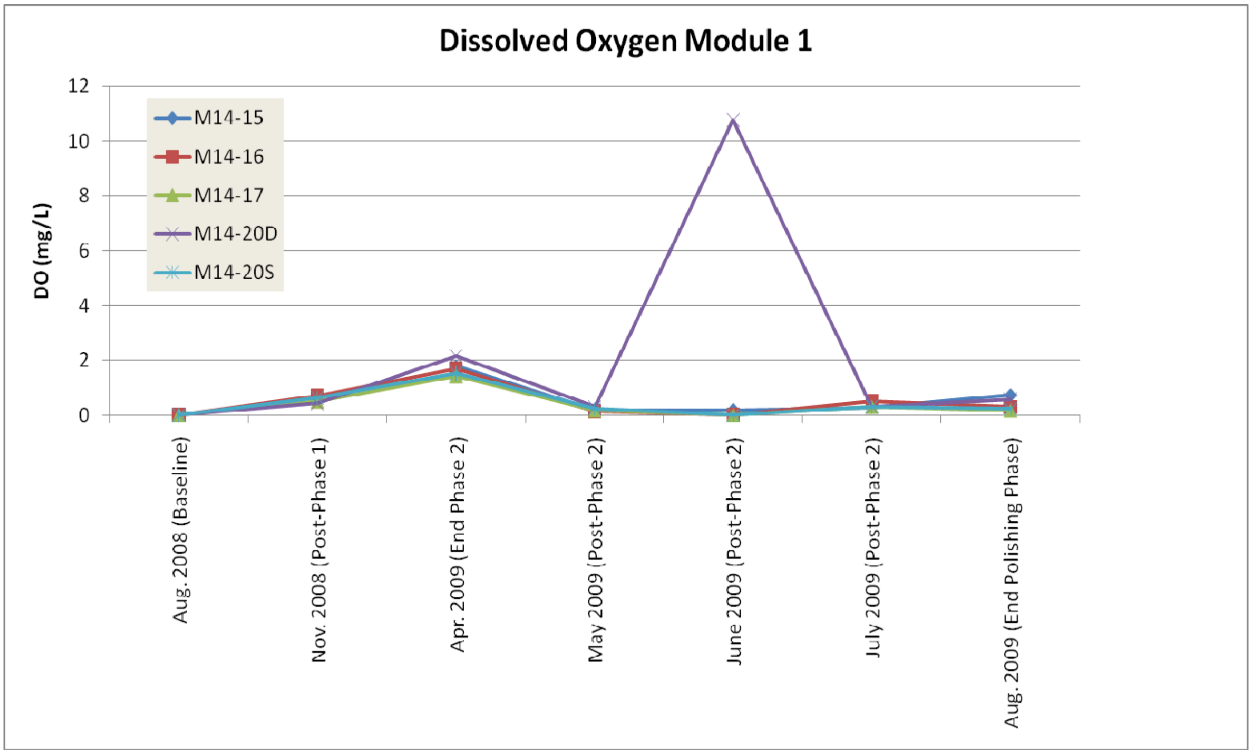


Figure 5-10. Conductivity Measurements During Full-Scale Application



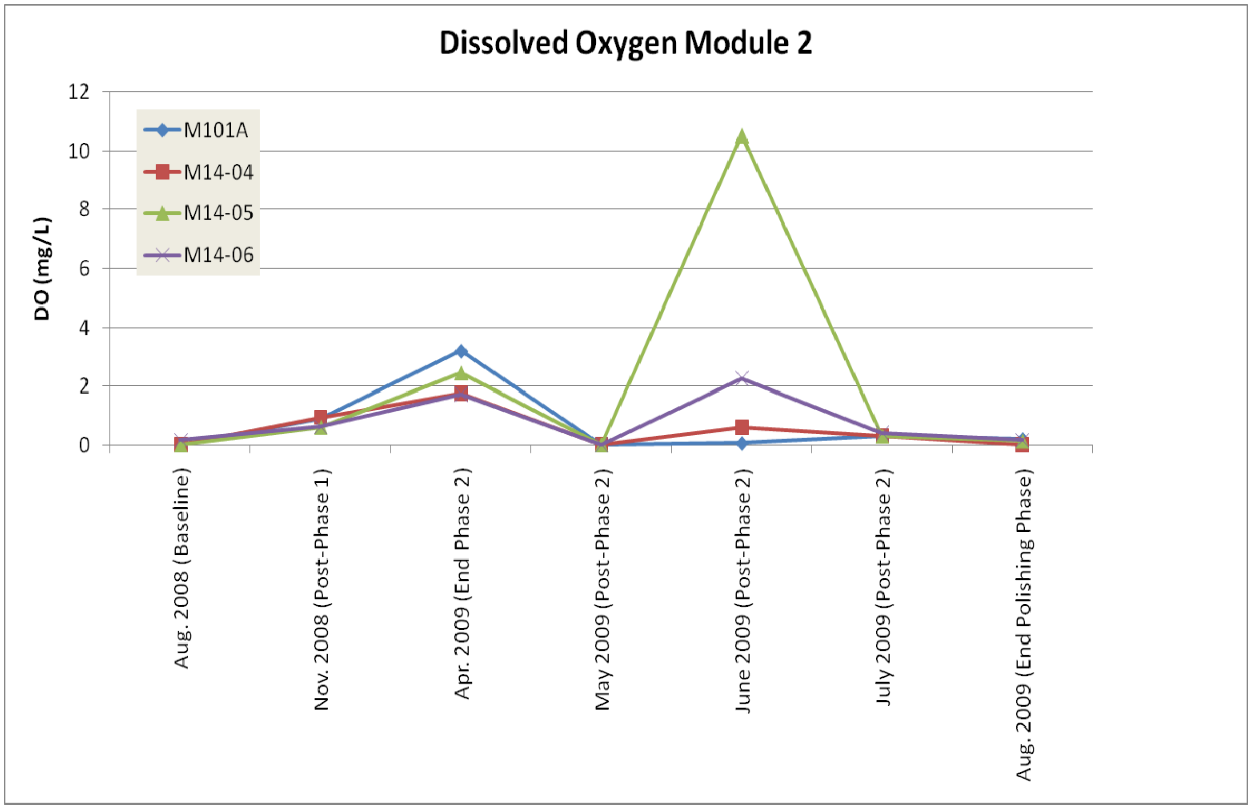
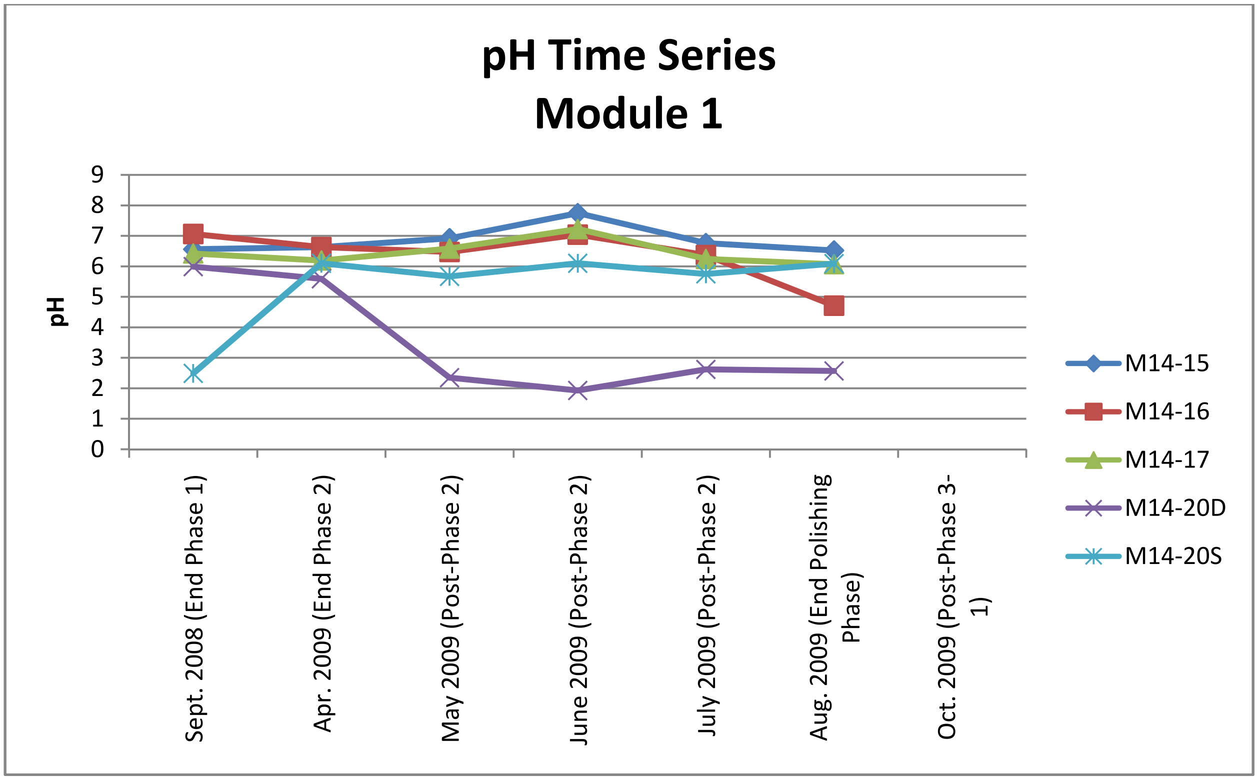


Figure 5-11. Dissolved Oxygen Measurements During Full-Scale Application



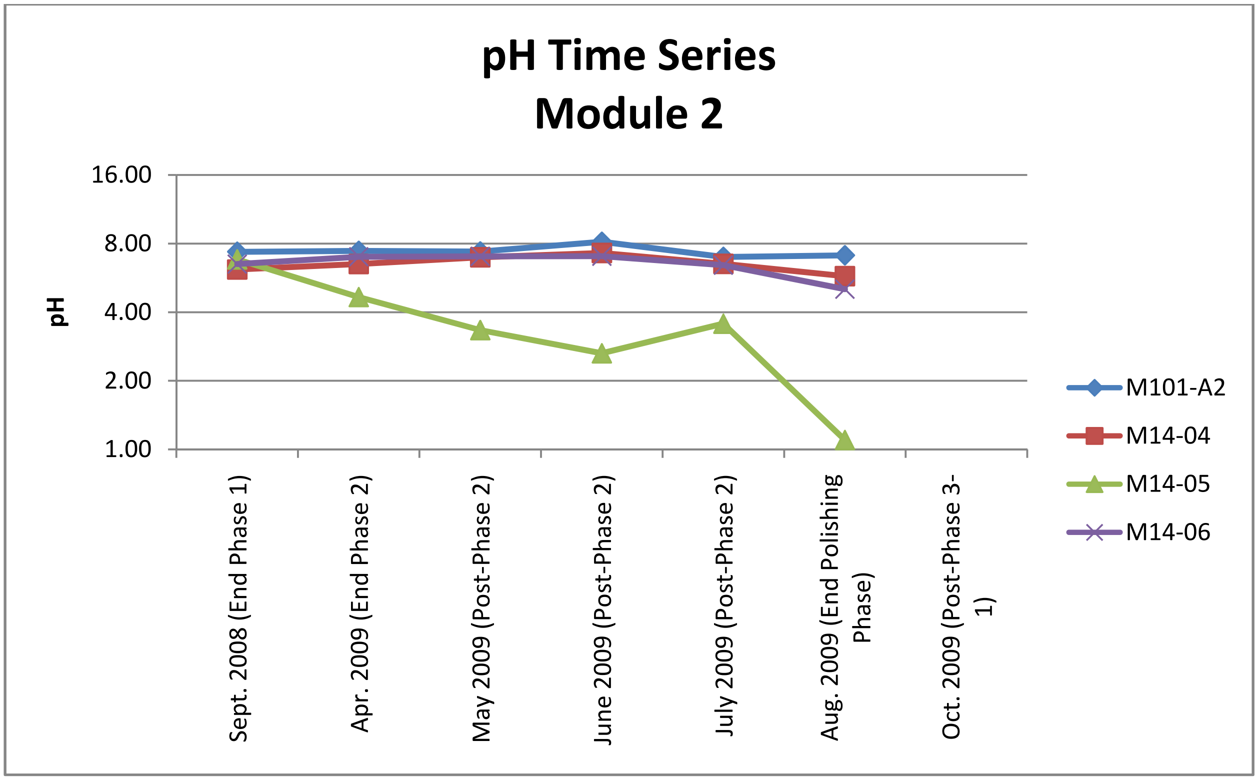


Figure 5-12. pH Measurements During Full-Scale Application

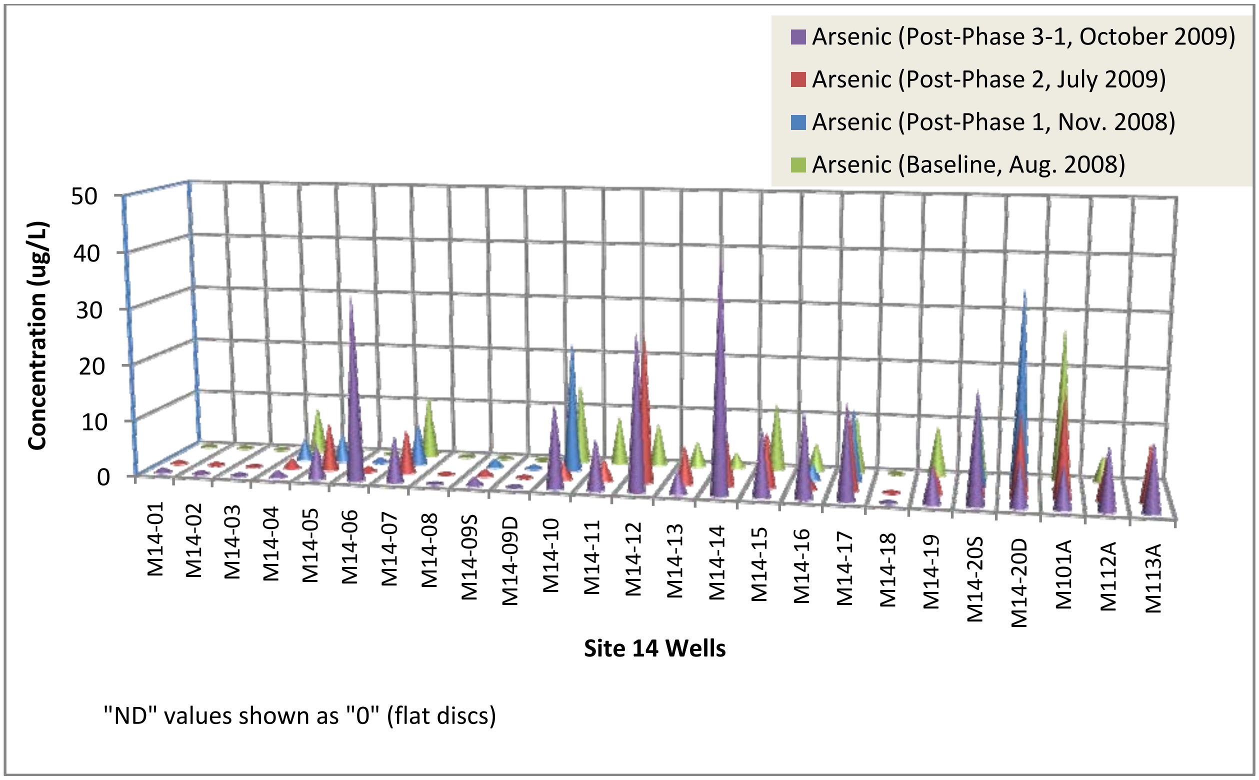


Figure 5-13. Arsenic Concentrations in Groundwater

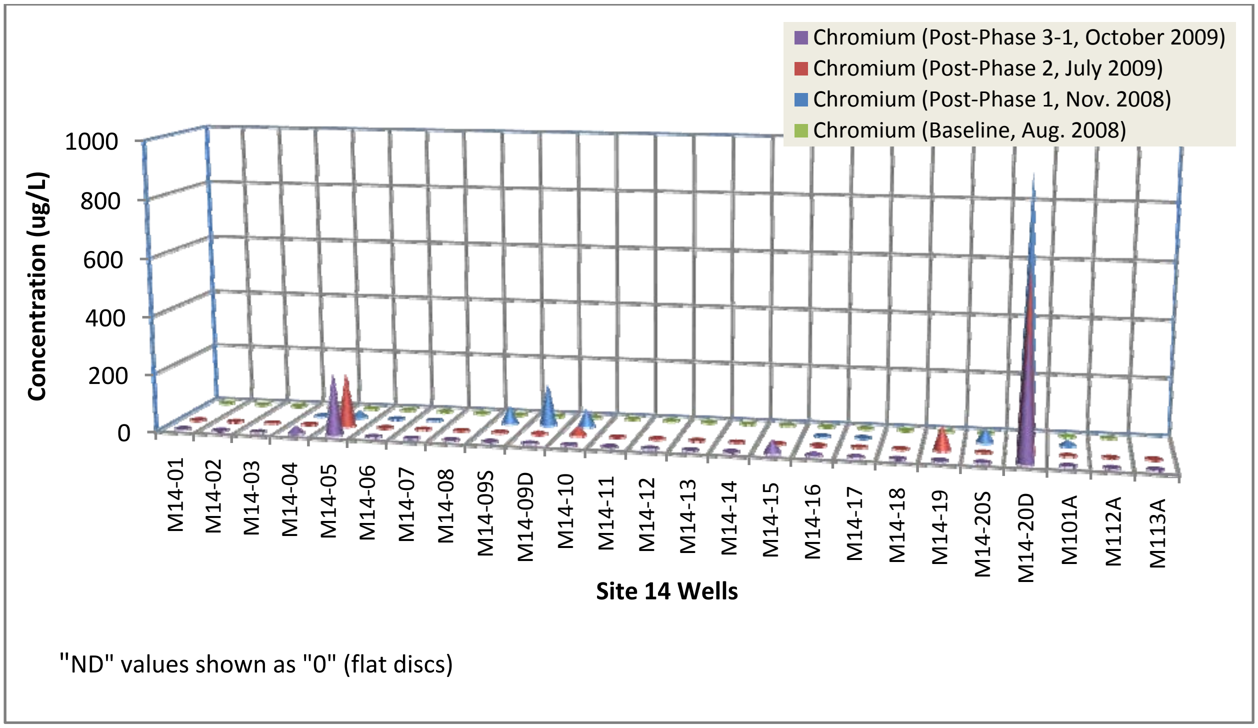


Figure 5-14. Chromium Concentrations in Groundwater

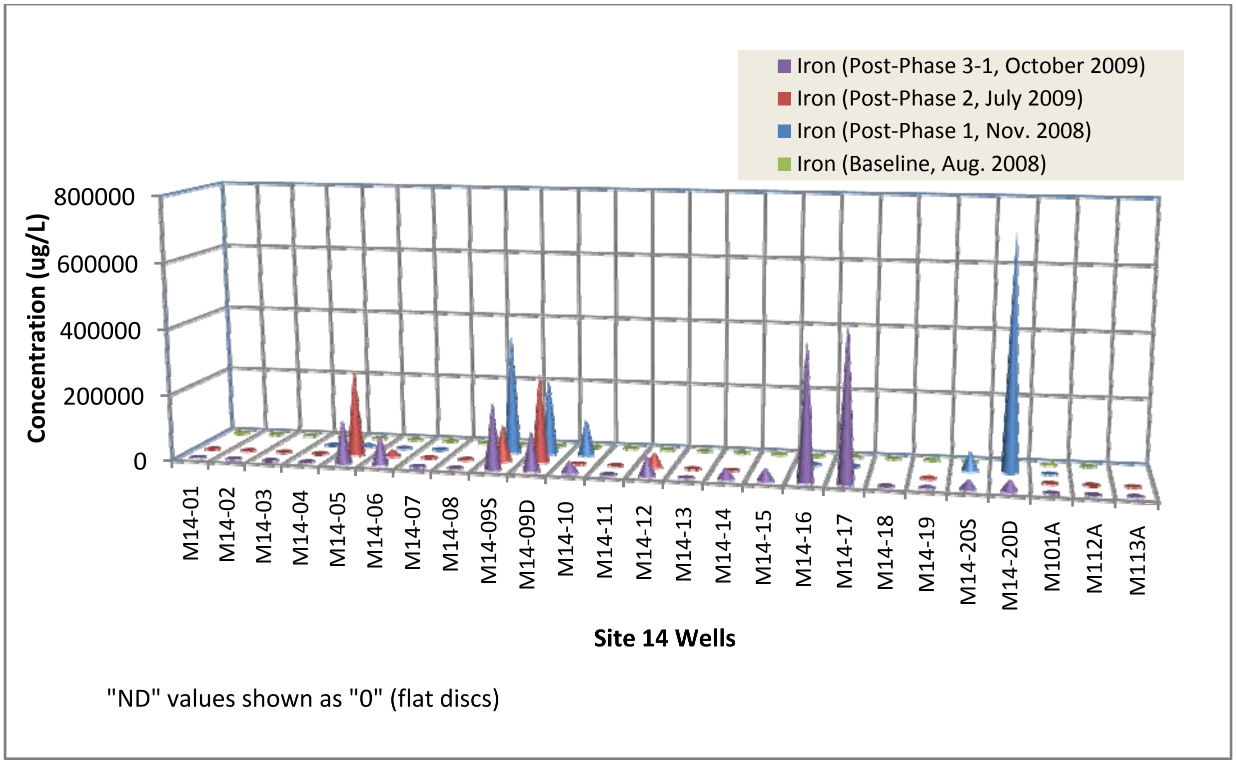


Figure 5-15. Iron Concentrations in Groundwater

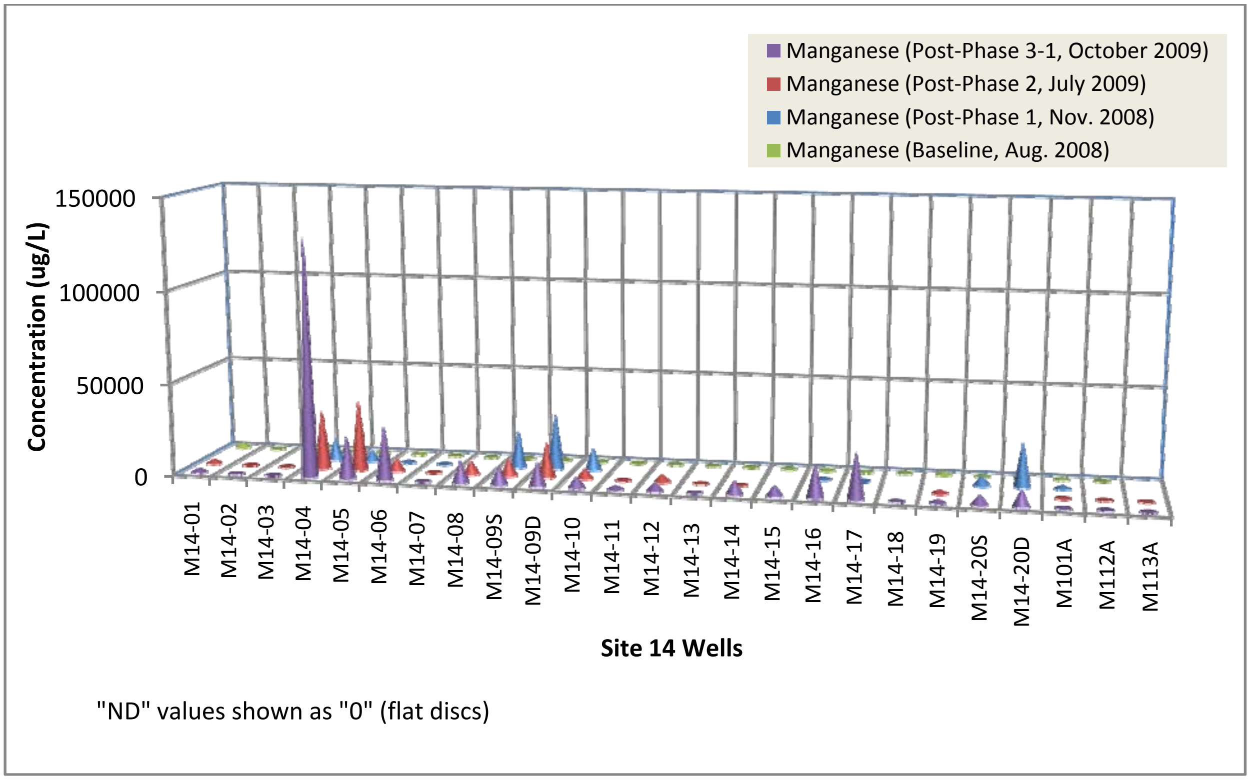


Figure 5-16. Manganese Concentrations in Groundwater

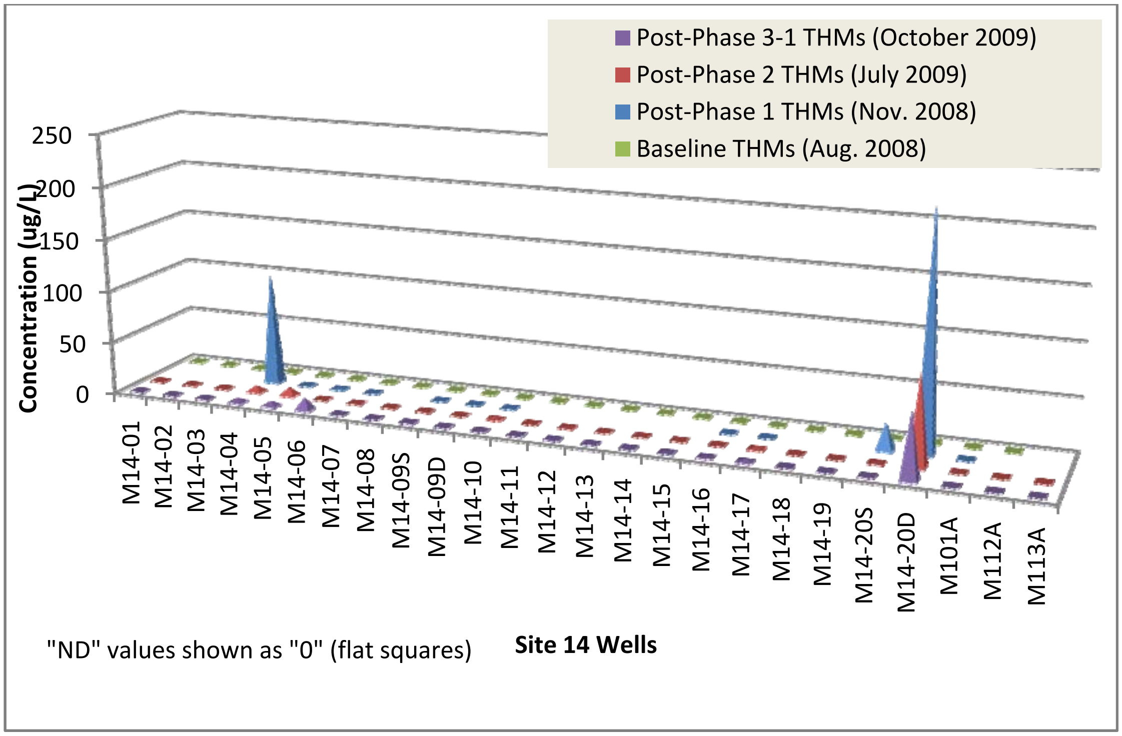


Figure 5-17. Total Trihalomethanes

The primary challenge encountered during implementation was to achieve adequate distribution of the reagents in the subsurface. Heterogeneities in the subsurface limited and, in some cases prevented, the removal of groundwater from several extraction wells. Surfacing of groundwater and reagent also was noted occasionally during application (Figure 5-18). Hence, it was necessary to reduce the flowrate into several injection wells at various times. Although the target mass of oxidant was injected into each of the areas, the pore volume of groundwater that was extracted and recirculated varied considerably (ranging from 41% in Area 3 to 60% in Area 1), and it is likely that an uneven distribution of the oxidant occurred in the aquifer.

Table 5-4. Reduction of Chlorinated Ethenes in Extracted Groundwater

	Contaminant of Concern	Extracted Water (µg/L)	Injected Water (µg/L)
Area 1	VC	24	<0.5
	DCE	72	<0.5
	TCE	<0.5	<0.5
Area 2	VC	6.3	<0.5
	TCE	15	<0.5
	DCE	3.1	<0.5

During treatment in Areas 2 and 3, groundwater samples were collected from the mixing tank and from the injection stream that had been amended with the ISCO reagents. The samples were analyzed for VOCs. Results were used to calculate the aboveground removal efficiency (Table 5-4). The sample collected during operation of the Area 2 module was collected on the fourth day of recirculation, and the sample collected during operation of the Area 3 module was collected on the second day of operation. The results indicate that during the approximate 30-minute contact of the groundwater with the reagents, the chlorinated ethenes were reduced to non-detectable levels.
The monitoring wells located in the immediate vicinity of the three treatment areas were sampled for VOCs during the post-ISCO sampling event and were compared to baseline data. The results are

Figure 5-18. Daylighting During ISCO Injections

illustrated in Figure 5-8.[13] A comparison of the baseline values with the post-ISCO results indicate that a substantial reduction of VC did not occur in the majority of monitoring wells. Some decrease was noted in wells M14-17 and M14-20S, and -20D in Area 1; M14-06 and M101A in Area 2; and M14-09D and M14-10 in Module 3. In most cases, changes in concentrations were very minimal and could be, in part, a result of dilution, as more contaminated groundwater was mixed with less contaminated water during recirculation.

The concentrations of VC and its parent compounds TCE and DCE were observed to increase in several of the monitoring wells. With respect to the VC, which does not significantly adsorb onto the soil organic matter, the increase may have been a result of redistribution of the contaminant during recirculation. However, the increase of TCE and DCE may be a result of partitioning from the soil to the aqueous phase as the organic carbon fraction of soil was oxidized, which is a frequent observation at ISCO sites.

Data indicate that the reagents were at least partially distributed within the treatment area during the application. ORP increased in the majority of points from approximately -100 to 300 mV. With the exception of M14-20D and M14-05, pH showed a general decrease of about 1 to 2 units in the majority of points, which was commonly observed as persulfate is introduced into the aquifer. The pH in M14-20D and M14-05 decreased to about 2 and a little less than 4, respectively. Conductivity does not appear to have increased significantly in the majority of points (with the exception of MW-20S), which would be expected if the sulfate ion was present in the groundwater. The large change noted in MW-20D, which increased from about 3,000 to 19,000 µs/cm, combined with the large observed pH drop, indicates that relatively high concentrations of persulfate may have short-circuited from the injection points to this monitoring point.

The concentration of persulfate was measured using Chemetrics® test kits in several of the groundwater-monitoring wells in Modules 2 and 3, as well as in a few of the extraction wells. Low levels of persulfate were detected in the majority of the monitoring and extraction wells sampled. Concentrations tended to increase toward the end of recirculation (i.e., Days 4 and 5) within each module.

Groundwater samples were analyzed for geochemical parameters and dissolved metals during the baseline monitoring event and each of the post-ISCO events to determine if oxidizing conditions induced by the application of the ISCO reagents resulted in the dissolution and migration of metals. Figures 5-13 through 5-16 illustrate changes for arsenic, chromium, iron, and manganese. The baseline conditions prior to injecting the reagents are denoted by the green cones, and the blue cones denote results after the first application. The red and purple cones denote concentrations measured after the second and third applications, and are discussed in detail in Sections 5.6.2 and 5.6.3, respectively. Only wells in the immediate vicinity of the three treatment areas were analyzed. In general, results were mixed. Arsenic, iron, and chromium were generally observed to increase, but also remained the same or decreased in other wells. For instance, well M14-20D exhibited sharp increases of arsenic, chromium, and vanadium, but concentrations of these same elements in wells M14-20S, M14-16, and M14-17 did not show much, if any, change.

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[13] Only monitoring wells located in the immediate vicinity of the three treatment areas were sampled during this event.

Concentrations of dissolved iron are typically a function of the overall redox and pH status of the groundwater environment. High concentrations of dissolved iron may be indicative that reducing conditions are prevalent, and dissolution of iron oxides is expected. At lower pH, such as measured in MW-20D, ferric iron is more likely to dissolve due to acid-promoted dissolution. Low concentrations of dissolved iron indicate that oxidizing conditions and circumneutral pH are prevalent, and that precipitation of hydrous ferric oxides is expected.

The concentration of dissolved iron measured during the Post-Phase 1 monitoring event was above baseline in six of the 13 wells sampled, including wells M14-05, M14-095, M14-09D, M14-10, M14-20S, and M14-20D. Iron was injected at concentrations ranging from 157 to 334 mg Fe/L, and dissolved iron was measured at above 700 mg/L in M14-20D and over 300 mg/L in Well M14-09S. Therefore, it is likely that the dissolved iron in these wells is, in part, derived from an in situ source, such as the reductive dissolution of native iron oxides and/or other iron-bearing minerals. The citric acid that was co-injected with the ferrous sulfate may have contributed to the high levels of dissolved iron arising from both the dissolution of iron oxides via chelation-promoted mineral dissolution or the complexation of ferrous sulfate that remains complexed and soluble after oxidation to ferric complexes. High concentration of dissolved iron also may be a consequence of a greater intrinsic solubility at low pH and mineral dissolution as a consequence of overall acidification. Acid-promoted dissolution of iron-bearing minerals is a possibility, since groundwater from wells M14-05 and M14-20D was observed to have pH values below 4. Dissolved manganese was detected in the same six monitoring wells as the high dissolved iron. The co-occurrence of elevated levels of manganese and iron is a consequence of either overall reducing conditions in this part of the groundwater aquifer, driving the reductive dissolution of insoluble Mn(IV) and Fe(III) minerals to their more soluble Mn(II) and Fe(III) analogs, or elevated acidity (low pH) driving dissolution of the relatively insoluble oxidized species.

The contaminant metals arsenic and chromium are often inversely correlated, with oxidizing conditions favoring the immobilization of As(V) onto oxides and the mobilization of Cr(VI). Reducing conditions lead to the dissolution of oxides (and subsequent release of As(V)/As(III)) and reductive precipitation of Cr(III) solid phases (immobile). Interestingly, chromium was detected at very high levels in M14-20D, the same well in which high levels of dissolved iron and manganese were measured. The reason for high concentration of chromium in this environment can be attributed to the low pH, where high concentrations of iron, manganese, and chromium may occur concomitantly. Arsenic was detected in nearly every monitoring well during the baseline sampling event and in monitoring performed after each phase of treatment. Beyond the relationship between arsenic and redox conditions, arsenic is known to be mobilized concurrently with iron due to dissolution of iron oxides by acid, organic ligands, or reduction. In this scenario, the elevated levels of arsenic following Phase 1 injection (35 μg/L) in well MW14-20D is likely a consequence of the low pH and not the reducing conditions (ORP of +206 mV); however, in MW14-12, higher concentrations of arsenic following Phase 2 injection (27 μg/L) may be due to local reducing conditions near this well. The expectation at an ISCO site being treated with iron-activated persulfate is that the groundwater aquifer should experience significant precipitation of ferric oxide minerals, which are good sorbents for arsenic. In this case, the concentrations of arsenic are usually relatively stable or increasing, indicating that there is no significant sequestration of arsenic onto ferric minerals in the timeframe between injection and sampling.

Similar to disinfection byproduct (DBP) chemistry, the combination of radicals, halogens (chlorine or bromine), and NOM during application of persulfate can result in the formation of THMs, including chloroform, bromoform, bromodichloromethane, and dibromochloromethane. Figure 5-17 compares the total THMs measured during baseline with those measured after the first and second applications of ISCO. Elevated concentrations were measured in three of the 12 wells sampled during the Post-Phase 1 sampling event.

5.6.2 Site-Wide Application. Table 5-5 summarizes injection and extraction flowrates achieved during the site-wide application. The mass of oxidant injected into each area was approximately 6,600 pounds. Similar to the preliminary application, the average concentration injected varied between modules based on the groundwater extraction flowrate. The concentration ranged from a low of 9 g/L in Area 6 to a high of 22 g/L in Module 14, with a site-wide average of 14 g/L.

The average concentration of ferrous sulfate and citric acid also was reduced based on results of additional bench testing. Testing indicated that a lower dosage would provide sufficient activation of the persulfate, but would result in the formation of fewer THMs and their precursors, as well as reduce the likelihood of mobilizing and transporting metals downgradient of the treatment area. The average concentration of each, calculated by dividing the mass added by the total volume injected, ranged from 0.15 to 0.30 g/L, with a site-wide average of 0.20 g/L.

In general, the volume of groundwater extracted and recirculated was greater than the volume recirculated during the preliminary application. As shown in Table 5-5, the percent pore volume recirculated ranged from a low of 36% in Area 14 to a high of 117% in Area 16. The average pore volume recirculated across the entire site was 68%, which was somewhat greater than was achieved during the preliminary application. Each module was operated from 40 to 48 hours, with the exception of Modules 1, 2, and 7, which were operated for 59, 51, and 53 hours, respectively, to better target the elevated concentrations known to be present in those areas of the site.

Table 5-5. Summary of System Performance During Site-Wide Application

Module	Hours of Operation	Treatment Volume		Sodium Persulfate		Module Area (square feet)	Target Interval (feet)	Pore Volume	
		Extracted (gallon)	Injected (gallon)	(pounds)	(g/L)			(gallon)	(percent)
1	59	51,412	54,700	6,600	14	6,200	6	73,042	75
2	51	56,828	60,327	6,600	13	6,200	8	97,390	62
3	41	46,611	49,963	6,600	16	6,250	6	73,631	68
4	40	37,398	41,142	6,600	19	5,550	6	65,385	63
5	39	64,724	68,285	6,600	12	6,600	8	103,673	66
6	47	82,110	85,474	6,600	9	6,750	8	106,029	81
7	53	72,350	77,574	6,600	10	6,500	8	102,102	76
8	40	63,231	67,030	6,600	12	6,300	8	98,960	68
9	39	53,684	57,171	6,600	14	6,150	8	96,604	59
10	39	52,057	55,198	6,334	14	6,400	6	75,398	73
11	40	52,691	56,033	6,922	15	5,000	6	58,905	95
12	40	39,387	43,153	6,600	18	5,650	8	88,750	49
13	47	42,590	46,044	6,600	17	5,550	8	87,179	53
14	41	30,749	35,204	6,600	22	6,300	8	98,960	36
15	44	49,341	51,938	6,600	15	5,600	6	65,974	79
16	46	66,005	68,638	6,600	12	5,000	6	58,905	117
17	47	52,688	55,894	6,600	14	5,000	8	78,540	71
Totals	753	913,855	973,768	112,256	14	101,000		1,429,428	68

Similar problems associated with distributing the reagent in the subsurface occurred during the site-wide application as in the Phase 1 application; these were the inability to extract fluids at design flowrates from some wells, and the surfacing of groundwater and reagents. Surfacing of the reagents was a particular problem during the application because of a high water table associated with unusually heavy rainfall during March 2009. The inability to extract water from wells was improved by installing a well seal on the extraction wells on a case-by-case basis. The diaphragm pump would then generate a small vacuum inside the well, which helped increase groundwater flowrate into the wells. The recirculation time also was increased from the design time of 40 hours to improve contact time during operation of several of the modules.

Figure 5-8 presents the concentration of VC in groundwater samples collected during the monitoring performed approximately 11 weeks after the site-wide application. The majority of site wells was found to contain VC at levels less than the 15 µg/L RG. Samples that exceeded the RG were collected from two of the suspected source areas, including the areas encompassing Module 2 and Modules 1 and 16. Well M14-14, located in Module 3, also exhibited an elevated concentration of VC. It also should be noted that the concentration of TCE and DCE was observed to increase in well M14-04, which could be a result of partitioning from the solid phase to the aqueous phase as the fraction of organic carbon was oxidized by the persulfate.

The concentration of persulfate was measured in the extracted groundwater and in the site monitoring wells at various times during the site-wide application. Low levels of persulfate were detected in the extracted groundwater in each of the 14 modules for which measurements were taken, indicating some degree of mixing and distribution of reagents within each treatment area. The extracted groundwater contained concentrations ranging from a few mg/L up to about 200 mg/L in all but Module 7, in which a concentration of 1,750 mg/L was measured.

Table 5-6 shows the concentration of persulfate measured in several of the monitoring wells shortly after completing recirculation in each area. Concentrations vary by several orders of magnitude, indicating that the reagents were not uniformly distributed in the aquifer. Also shown in Table 5-6 are the persulfate levels measured about 11 weeks after completing the site-wide injections. Concentrations had decreased to nearly zero in the majority of monitoring wells, with the exception of MW-20D, in which nearly 3,000 mg/L remained.

Table 5-6. Persulfate Concentration During Site-Wide Application

Well ID	Persulfate Concentration (mg/L)	
	April 09	July 09
M112A	0.07	2.1
M14-04	56	2.1
M14-05	2,800	4.2
M14-06	2	0
M14-08	0	0
M14-101A2	2.1	0
M14-11	0	0
M14-12	700	0
M14-14	7	0
M14-15	14	0
M14-16	0	0
M14-17	4	0
M14-20D	2,800	2,940
M14-20S	5,600	0

Groundwater parameters were measured daily in monitoring wells during the application of reagents. Figure 5-19 shows the pH and DO measured in site wells during application in Areas 1, 2, and 3, and Figure 5-20 presents ORP and conductivities measured at the same locations. The measurements indicate that the oxidant was distributed through the formation and came into contact with groundwater in the monitoring wells. Increases in ORP and conductivity were observed, and there appears to be a slight decrease in pH, all of which are commonly observed under oxidizing conditions as the persulfate comes into contact with the groundwater. Monitoring performed subsequent to the site-wide application indicates that with a couple of exceptions, such as MW14-20D and MW14-05, which had unusually low pH and high ORP, the groundwater conditions at 11 weeks after ISCO were approaching baseline values (see Figures 5-9 through 5-12).

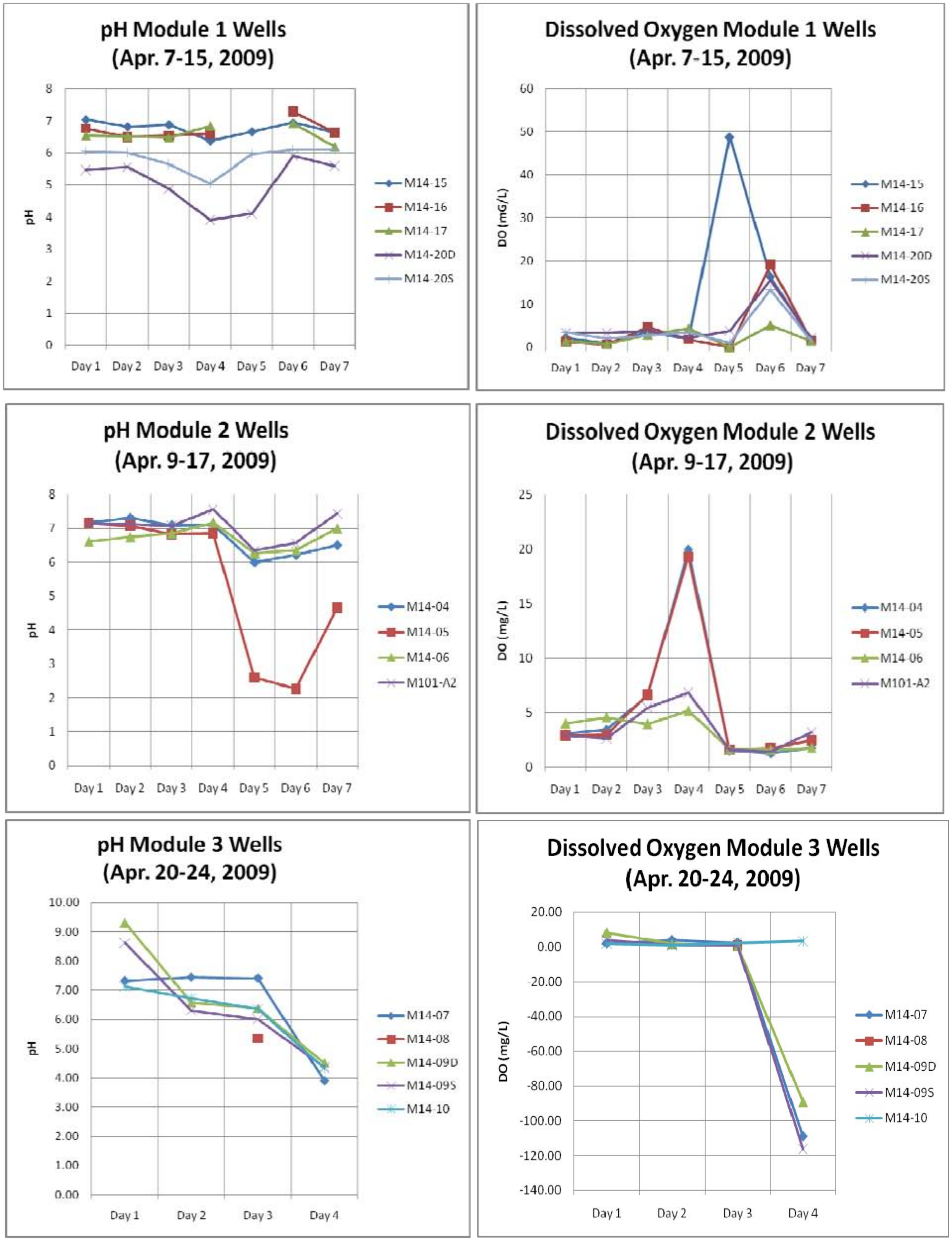

Figure 5-19. Trends in pH and Dissolved Oxygen During Site-Wide ISCO Application

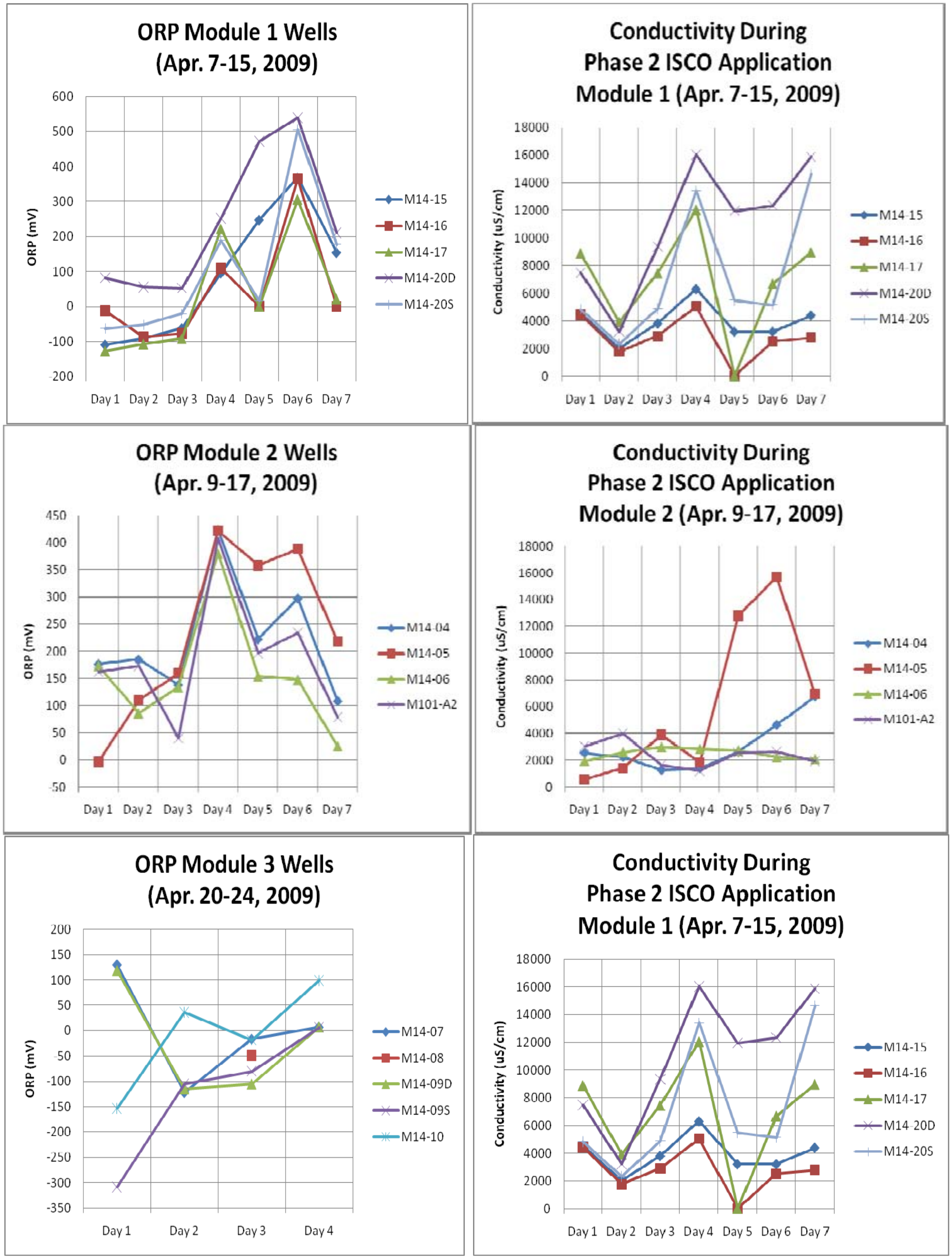

Figure 5-20. Trends in ORP and Conductivity During Site-Wide ISCO Application

Similar to monitoring results after the preliminary application, concentrations of metals were observed to be elevated in several of the monitoring wells compared to baseline values (Figures 5-13 through 5-16). However, although elevated, concentrations measured after the site-wide application appeared to be less than those measured after the preliminary application (as measured in the wells sampled after both applications). Two factors likely contributed to this reduction: (1) the concentration of citric acid had been reduced, which may have limited solubilization of naturally occurring metals in the subsurface and (2) the site equilibrated for about 11 weeks prior to collecting the post site-wide application samples, whereas the post preliminary application samples were collected only 5 weeks after application. The longer time after the site-wide application may have resulted in additional attenuation of the metals.

A particular concern was the potential for metals to migrate toward the Bay during the site-wide application. The water table, which had risen considerably during March due to heavy rains, may have intersected old storm drains running from the treatment area to the Bay. The bedding material around the drains may have served as a conduit to transport dissolved metals (and reagents) toward the Bay. However, with the exception of well M14-19, which exhibited a slight increase in chromium, the concentration of metals downgradient of the treatment area did not appear to increase. The concentration of metals will be monitored during future groundwater events to ensure that elevated concentrations in the treatment area are attenuating and not migrating downgradient of the site.

The concentrations of THMs measured after the site-wide application, designated by the red cones in Figure 5-17, were much less than those observed during the preliminary application, which may be a result of the decreased concentration of citric acid and ferrous sulfate that was added during the site-wide application. It might also possibly be due to the additional time that the groundwater was allowed to attenuate after concluding the injections prior to collecting the post site-wide application samples.

5.6.3 Polishing Application. Table 5-7 summarizes injection and extraction flowrates achieved during the polishing application. The hours of operation were lengthened to treat the combined Modules 1 and 16, and the mass of sodium persulfate was increased from the 6,600 pounds injected during previous applications to a total of 11,000 pounds. These modifications were made in an effort to provide more contact time and a greater mass of residual oxidant in the subsurface. This was because monitoring data collected after the site-wide application indicated that a small amount of DCE and TCE might still reside on soil and might be gradually partitioning into groundwater, both naturally and as a result of applying the ISCO reagents. The mass of oxidant injected into Module 2 was increased by 33% to 8,800 pounds for similar reasons. Injection into Module 13 was performed using a mass of oxidant and an operating time similar to those used during the site-wide application.

Table 5-7. Summary of System Performance During Polishing Application

Module	Hours of Operation	Treatment Volume		Sodium Persulfate		Module Area (square feet)	Target Interval (feet)	Pore Volume	
		Extracted (gallon)	Injected (gallon)	(pounds)	(g/L)			(gallon)	**(%)**
1 & 16	100	105,032	110,403	11,000	12	6,200	6	73,042	151
2	53	50,378	53,221	8,800	20	6,200	8	97,390	55
13	46	49,654	52,965	6,600	15	5,550	8	87,179	61
Totals	199	205,064	216,589	26,400	15	17,950		257,611	**84**

Figure 5-8 shows the concentrations of VC, DCE, and TCE measured in samples collected about 5 weeks after completing the polishing round of injections. In general, VC was observed to decrease or remain about the same in monitoring wells located within the influence of the four treatment modules (i.e., wells M101-A, M14-04, -05, -15, -16, -17, -20S, and -20D). However, a slight increase was noted in well M14-06. Similarly, the concentrations of DCE and TCE either decreased slightly or remained about the same in the majority of wells. Concentrations of DCE and TCE increased to various degrees in wells M14-06, M14-14, and M14-20S. The largest increase in the concentration of DCE was noted in well M14-16, which was measured at 3.8 µg/L after the site-wide application and 45 µg/L during this monitoring event.

Chlorinated ethane concentrations in other areas of the site, which were not likely impacted by the last round of ISCO injections, remained about the same. The 15 µg/L RG was not exceeded in these areas.

Mass reduction of COCs in the treatment area can be calculated using the estimated total mass of COCs present before and after treatment. The total mass of COCs was calculated by summing the estimated mass in soil and in groundwater. Although concentrations of the COCs in soil were not measured, the concentrations measured in groundwater can be used to estimate the mass present in the soil, based on calculated distribution coefficients for each COC. The total mass of VC and DCE within the treatment area, calculated using baseline values measured in the 20 wells located in or in close proximity to the treatment area, was estimated to be 0.69 and 0.49 pounds, respectively. After treatment, using the post-polishing monitoring results from the same set of wells, the total mass was estimated to be 0.21 and 0.49 pounds, respectively. Although an approximate 70% reduction of VC was realized, there was virtually no change in the mass of DCE present.

Groundwater quality parameters followed trends similar to what was observed during the previous applications at the site: ORP and conductivity increased in wells impacted by the persulfate, pH declined slightly, and there was little or no increase in DO.

Figures 5-13 through 5-16 show analytical results for select metals for samples collected during the post-polishing sampling event. The concentration of arsenic was elevated in the monitoring wells near areas where the injections were performed. Well M14-12, which should not have been impacted by the third ISCO, exhibited a concentration of arsenic similar to that measured during sampling performed 11 weeks after completing the Site-Wide ISCO Application; this may indicate that elevated levels can persist for some time after completing oxidation. However, there was no evidence of downgradient migration of the arsenic into the monitoring wells located between the treatment areas and the Bay (i.e., wells MW14-01, -18, and -19).

Elevated levels of other metals, including chromium, vanadium, manganese, and iron, were noted periodically in wells located in the vicinity of the treatment areas. Both increases and decreases compared to the post site-wide application monitoring results were noted.

The formation of THMs appeared to be less of a problem during the polishing application. Only two wells, M14-06 and M14-20D, exhibited elevated levels of THMs (see Figure 5-17). The concentration detected in well M14-20D may have been, in part, a result of THMs persisting in the aquifer from the previous application, as opposed to having been formed during the third application. It should also be noted that elevated concentrations of THMs detected in the wells sampled after the first application had returned to near baseline values in all of the remaining wells.

5.7 Cost

Table 5-8 summarizes the cost to apply full-scale ISCO at IR Site 14. Similar to the cost tables presented in other sections, the costs presented do not include workplan preparation, design, or planning costs. Also not included are costs to perform the bench-scale tests, capture modeling, and the pilot test. The total capital cost is estimated to be about $400,000, which includes a cost of about $140,000 to procure two recirculation modules. The operating cost is estimated to be about $900,000. A large portion of this cost (nearly half) is labor and per diem costs to maintain three staff onsite to perform operation and maintenance of the recirculation systems. The cost of the reagents (about $286,000) also is a significant fraction, about one-third of the operating cost. Although the total cost to implement full-scale ISCO is relatively high at this site, the cost per cubic yard of soil treated is estimated to be only $38 due to the large target treatment area.

Table 5-8. Cost of Persulfate Application at IR Site 14, Alameda

No.	Item	Unit	No. of Units	Unit Cost	Cost
CAPITAL INVESTMENT (Fixed Cost)					
1	Site preparation (utility locating, debris removal, well installation, fencing)	Lump	1	$138,000	$160,000
2	Mobilization/demobilization (transportation to site, mobile office, storage, fabrication, assembly, setup, dismantle, well abandonment)	Lump	1	$60,000	$60,000
3	Equipment purchase	Lump	1	$139,000	$139,000
4	Labor (for transportation and on-site setup, unless included in mobilization)[a]	Lump	1	$40,000	$40,000
5	Other				
TOTAL CAPITAL COST:					$399,000
OPERATING COST (Variable Cost)					
6	Equipment leasing (e.g., storage tanks, pumps, compressor, generator)	Lump	1	$68,000	$68,000
7	Chemicals – sodium persulfate	Pound	158,400	$1.65	$261,000
8	Chemicals – ferrous sulfate	Pound	10,400	$0.60	$6,240
9	Chemicals – citric acid	Pound	12,000	$1.60	$19,200
10	Other consumables (estimated)	Lump	1	$10,000	$10,000
11	Power (diesel fuel)	gallons	4,000	$2.90	$11,600
12	Other utilities (Base-provided)	Lump	NA	$0	$0
13	Waste disposal (taken to Base IWP)	Lump	1	$5,300	$5,300
14	Labor[b] (for operating the system)	Lump	1	$430,000	$430,000
15	Other (rental vehicles, airfare)	Lump	1	$90,000	$94,000
TOTAL OPERATING COST:					$905,000
TOTAL TREATMENT COST FOR PROJECT (Capital + Operating)					$1,304,000
Volume of aquifer targeted for treatment				Cubic yard	34,700
Unit cost of treatment				$/Cubic yard	$38
Maximum depth of treatment				Feet bgs	17
Site Geology: Fill material extends from the ground surface to about 18 feet bgs. The BSU, which lies immediately beneath the fill material, contains interbedded clayey and silty units that are expected to act as a semi-confining unit beneath the FWBZ, inhibiting vertical migration of chemicals reported from the upper fill soils and groundwater to deeper native material.					

NA – not applicable

(a) Three events.

(b) Includes per diem.

5.8 Discussion

The IR Site 14 remedy is in progress at the time of this report preparation. Additional monitoring data collected during the following 9 months will be used to evaluate the long-term effects of ISCO. The discussion provided in this section is based on a preliminary evaluation of the results to date. The application data will be further evaluated, and will be presented as part of an I-RACR.

The remedy at IR Site 14 targeted a dilute plume of VC in groundwater, having a maximum concentration of 300 µg/L based on baseline measurements. Parent compounds, including DCE and TCE, also were detected at very low levels (120 µg/L for DCE and about 10 µg/L for TCE). A total of 158,400 pounds of sodium persulfate was injected into the aquifer. Groundwater in areas 1, 2, 3, and 16, which were considered to be locations of the source of contamination (based on slightly elevated concentrations of TCE and DCE), were amended with 18,700, 22,000, 13,200, and 12,100 pounds of persulfate, respectively. Groundwater in the remaining treatment areas was amended with about 6,600 pounds of persulfate.

The application of ISCO, using the recirculation approach, appears to have reduced the concentrations of VC in groundwater. About an order of magnitude reduction of VC was achieved in well M14-06, and many of the other wells exhibited reduction. The average concentration of VC calculated using results of samples collected from wells located within or immediately adjacent to the treatment area decreased from about 44 to about 13 µg/L – a 70% reduction. Similarly, the mass of VC within the treatment areas was calculated to decrease from 0.69 to 0.21 pounds, also about a 70% reduction. Based on the first monitoring event performed after the final polishing application, only five of the 25 site monitoring wells contained VC at a concentration greater than the 15 µg/L RG after the third application. Additional (quarterly) groundwater monitoring will be performed to evaluate changes in VOC concentrations due to rebound and/or continued reductions through natural attenuation processes.

In addition to the observed reduction of COCs, additional lines of evidence demonstrate that the reagents were distributed in the aquifer. For instance, changes in the geochemical indicators are congruent with the achievement of good oxidant distribution. ORP and conductivity typically were observed to increase in monitoring wells during the applications, while pH was observed to decrease. These changes are indicative of oxidant being transported from the injection wells to the monitoring wells. Also, persulfate measured using field test kits was detected in monitoring wells and in groundwater extracted during application of the reagents.

Although some degree of reagent distribution and a significant VC reduction were achieved, it is likely that the reagents were not evenly distributed, which may have limited the injections' performance. Lines of evidence include:

- During application, the extraction wells produced groundwater at different rates. Some wells even went dry. In some instances, well seals were used to allow the extraction pump to generate a small vacuum inside the wells to improve groundwater flow.
- Surfacing occurred in a number of locations. In these instances, the injection flowrate of amended groundwater was reduced to reduce surfacing.
- The concentration of persulfate measured in monitoring wells and in the extracted groundwater differed by more than two orders of magnitude.

One particular concern is that low levels of DCE and TCE persist at the site. In particular, the average concentration of DCE measured in the 20 monitoring wells located within or immediately adjacent to the treatment area was determined to be 22 µg/L during both the baseline and post-polishing monitoring events. Concentrations of these compounds increased in some wells and decreased in others, which likely is a direct result of oxidation of organic matter and associate desorption of DCE and TCE into groundwater; both of these adsorb onto organic matter to a greater degree than VC. Although there is not an established RG for either of these compounds, biologically mediated reductive dechlorination could result in the formation of additional VC. Hence, depending on other natural attenuation factors, there is potential for the VC concentration to rebound, resulting in further exceedance of the RG. Additional groundwater monitoring is necessary to evaluate long-term performance, rebound (if any), and potential for continued natural attenuation of the COCs.

The application of the ISCO reagents also appears to have elevated the concentration of metals in groundwater, which is known to occur at sites where ISCO has been applied. However, the site wells were not uniformly impacted; some wells displayed order-of-magnitude increases, while others exhibited little or no increase. This likely is another indicator of the relatively uneven distribution of the oxidant in the aquifer, as well as an indication of the very heterogeneous nature of the fill material in which the wells were installed. The concentration of metals remains elevated in some wells after the third application. Additional monitoring will be performed to track the fate of these metals. Water quality parameters also will be measured to better understand whether the concentration of trace metals return to background conditions as geochemical parameters return to their pretreatment levels.

THMs and their precursors, in particular methylene chloride and chloromethane, were measured in several wells after applying the ISCO reagents. The greatest concentrations were measured after the first round of ISCO injections. Although not completely understood, it is believed that the sulfate radical may be reacting with halogens, forming halogen-based radicals that react with reduced organic matter. The end result is a halogenated organic (e.g., chloromethane), which likely further reacts with a halogenated radical until it forms the final compound (e.g., chloroform). Supplemental bench-scale testing indicated that the formation of the THMs could be reduced by decreasing the concentration of citric acid and ferrous sulfate. Hence, the site-wide and polishing applications were performed using an average of about 0.2 g/L of each, as opposed to the 0.50 to 1.0 g/L ferrous sulfate and 0.5 to 0.9 g/L citric acid used during the preliminary application.

Additional conclusions and lessons learned during application monitoring include the following:

- During about 1 month of the site-wide injection, heavy rains occurred during March 2009, which caused the groundwater elevation to rise to near-surface. The high water levels interfered with the ISCO injections by increasing the amount of daylighting that occurred and by diluting the concentration of the injected reagents, both of which may have decreased performance.
- The pilot test provided invaluable data that were used to design the full-scale system. Based on the results of the pilot test, which indicated that a very small ROI could be achieved using direct injection, a recirculation approach was chosen. Recirculation generated a strong gradient that helped distribute the reagents into the groundwater. Also, a greater level of hydraulic control was achievable, which was a key consideration given the close proximity of the site to Oakland Inner Harbor.
- Although there was no indication of elevated metals concentrations migrating downgradient of the treatment site, sodium persulfate was detected in well 14MW-01 during post-monitoring after the site-wide application. It is likely that the persulfate was transported through old storm drains and their bedding material, which extended from the treatment area to Oakland Inner Harbor. Concentrations of VOCs, metals, and persulfate will continue to be monitored to assess long-term impacts.

- The aboveground system was very effective in treating the COCs to non-detect prior to injection. The percent reduction that occurred aboveground was determined to be greater than 99% most of the time, based on samples collected from the extracted groundwater stream and the amended water.
- Each extraction well was equipped with a dedicated aboveground pump that pumped the groundwater through a manifold into a central mixing tank. Since the groundwater flowrate from each well was low (less than 1/2 gpm/well) and the depth to groundwater was only a few feet, it is possible that the system design could be optimized to extract from two or more wells, using a single pump; this would reduce the system's capital cost.
- Chloride levels were not measured during the post-ISCO monitoring events. At some sites, changes in chloride concentrations can be used to evaluate the progress of ISCO, since oxidation of chlorinated ethenes results in increased chloride levels. However, at this site, high levels of chloride (300 to 800 mg/L) in groundwater would mask any changes resulting from the oxidation of the low levels of chlorinated ethenes present.
- Persulfate persists in the aquifer for considerable time after completing the injections. Trace amounts remained in groundwater 11 weeks after completing the site-wide application.

Section 6.0: FUTURE PLANS FOR WASHINGTON YARD PERSULFATE APPLICATION

This section describes the persulfate application planned at the Washington Navy Yard (WNY). The work plan reviewed was *Work Plan for ISCO Pilot Test Injection at Building 71 UST Case Site, Washington Navy Yard, Washington, D.C.* (CH2M HILL, 2009), as well as other documentation provided by the site RPM.

The past petroleum-storage and -handling activities at the Building 71 UST Site have caused contamination in the shallow groundwater. The COCs include free-phase petroleum product (i.e., light non-aqueous phase liquid [LNAPL] and dissolved-phase total petroleum hydrocarbons [TPH]) consisting of diesel range and gasoline range organics, benzene, and methyl tertbutyl ether. The extent of petroleum contamination in the shallow groundwater involves two LNAPL plumes: (1) the North Plume with an average free-product thickness of 0.01 foot, which is approximately 2,008 square feet in area and (2) the South Plume, with an average free product thickness of 0.1 foot, which occupies an area of approximately 896 square feet.

The topography of the Building 71 UST is relatively flat, but slopes slightly to the south toward the Anacostia River. The site lies on filled areas of the Anacostia River created during the expansion of the original WNY shoreline. The soil underlying the site consists of non-native and man-made fill and naturally deposited soil material. The fill, composed of clay, silt, sand, gravel, and man-made material consisting of construction materials, reinforced concrete, timbers, asphalt, brick, railroad tracks, and wood planking, underlies the paved surfaces. The fill ranges in thickness from 0 feet to 15 feet at Building 71. The general groundwater flow on the WNY is south toward the Anacostia River. The water table within the site, encountered in the fill material, ranges from approximately 2.5 to 7 feet below bgs.

Among the available in situ technologies, ISCO via DPT injection was considered to be the most effective contaminant mass removal option that would also minimize impacts to the brick pavement. Therefore, ISCO injection was selected as the corrective action for this phase of the project. Alkaline-activated sodium persulfate was selected as the oxidant of choice for two reasons:

- Its oxidation reactions are not exothermic, unlike the reactions produced by catalyzed hydrogen peroxide as the oxidant; therefore, its implementation is safer for remediation workers and the nearby surface and subsurface features.
- Sodium persulfate with alkaline activation has been demonstrated effective for treating longer-chain petroleum hydrocarbons.

The primary objective of the injection is to maximize contaminant mass removal at Building 71. This pilot study is not intended as a complete cleanup of the free-phase petroleum product plumes. Because the quantity of the free-phase petroleum product at the site is not known, additional ISCO injection events may be necessary if ISCO is selected as the final corrective action for the site.

The ISCO injection event at the Building 71 Former UST Site at the WNY occurred in June 2009. Monitoring will occur at 3, 6, and 12 months, with a final report prepared in 2010.

Section 7.0: SUMMARY OF CONCLUSIONS AND DISCUSSION

The ISCO projects described in this document provide valuable information on performing persulfate applications under varying site conditions. This report focused on applications using sodium persulfate, which is the newest and least understood form of oxidants typically used for ISCO. The lessons learned from these applications serve as a guide for future users who intend to implement ISCO using this reagent.

Table 7-1 presents a summary of key parameters for each site. Three of the four projects for which the ISCO injections have been completed were pilot tests. The only full-scale application reviewed is IR Site 14 at former NAS Alameda. Although the injections have been completed at that site, the application data have not yet been finalized. Additional quarterly monitoring is being performed to better gauge the impact of the ISCO injections, evaluate the potential for a transition to MNA, and monitor for rebound.

In general, a reduction of COC was observed at all four sites; however, reductions did not come close to achieving MCLs, or what may be typical cleanup goals, and this technology should be more effectively employed as part of a treatment train, as opposed to a stand-alone remedy. In addition, reductions were not uniform across the sites, which may be the direct result of not being able to evenly distribute the reagent throughout the target treatment areas. Typically, the greatest reductions were observed in areas near injection locations and/or areas known to have been exposed to a relatively large mass of oxidant. Specific conclusions pertaining to the reduction of COC at each site include:

- **OU 20 North Island –** Reduction of TCE and DCE was noted in all of the performance-monitoring wells. The sharpest reduction was noted in the monitoring wells located closest to the injection point. Rebound was noted within about 1 month of completing the injections, which may be attributed to the influx of contaminated groundwater from the upgradient portion of the aquifer into the treatment area, or may be a result of back diffusion from soil.

- **Site 1 ABL –** Three weeks after completing the ISCO injections, the average reduction of TCE was about 45%. TCE was observed to decrease in six of the eight monitoring wells and increase in the remaining two. Concentrations had rebounded by the 6 week event, possibly due to infiltration from the surrounding untreated aquifer and back-diffusion from soil. Based on samples collected 5 months after completing ISCO, the average TCE concentration had rebounded to about 67% of its baseline value.

- **SWMU 13 Quantico –** Although the application at this site was discontinued after only 13% of the design volume of reagent had been injected, reductions of TCE and TCE were observed. Reduction of TCE (50% to 96%) was greater than that of 1,2,4-TCB (12% to 61%) in wells that had good contact with the oxidant. Direct injection was determined to be ineffective; groundwater and reagents mounded and migrated along preferential pathways created by utility corridors at the site.

- **IR Site 14 Alameda –** The average concentration of VC calculated using results of samples collected from wells within or immediately adjacent to the treatment area decreased from about 44 to about 13 µg/L – a 70% reduction. Similarly, the mass of VC within the treatment areas was calculated to decrease from 0.69 to 0.21 pounds, also about a 70% reduction. Based on the first monitoring event performed after the final polishing application, only five of the 25 site monitoring wells contained VC at a concentration greater than 15 µg/L RG after the third ISCO application. The concentrations of TCE and DCE exhibited a significant reduction, possibly a result of very low initial concentrations and a continuing back diffusion of these compounds into the groundwater.

The remainder of this section discusses specific conclusions and lessons learned from these applications. In particular, the results are discussed with an emphasis on several key considerations for the design and successful implementation of ISCO, using persulfate, including oxidant demand and reagent dosing, reagent delivery and distribution, formation of byproducts and changes in groundwater chemistry, and potential for MNA after ISCO. A summary of known operational issues and lessons learned are also provided.

Table 7-1. Summary of Key Site-Specific Factors

	North Island	ABL	MCBQ	NAS Alameda	Washington Yard
Location	California	West Virginia	Virginia	California	District of Columbia
Treatment Area (square yard)	88	500	85	3,700	93
Target Treatment Interval (feet bgs)	44 to 54	16 to 30	10 to 15, 15 to 20, 23 to 28	Ranges from 4 to 12 to 9 to 17	3 to 6 and 4 to 7
Pore volume (gallons)	50,300	424,000	10,300[a]	1,840,000	11,300[i]
Lithology	Poorly graded fine to very fine sand/silty sand	Unconsolidated alluvial deposits of clay, silt, sand, and gravel	Silts and clays with discontinuous layers of sand	Fill material, silts, and sands	Fill comprised of clay, silt, sand, and gravel
Depth to groundwater (feet bgs)	19.3 to 20.3	16 to 21	6 to 13	1 to 6	2.5 to 7
Groundwater gradient (feet/feet)	0.001	0.03	NA	0.006	NA
Confined aquifer?	No	No	NA	No	NA
Average hydraulic conductivity (feet/day)	30	NA	NA	7.7	NA
Contaminants of concern	TCE, DCE	TCE, DCE	TCB, TCE, DCE, VC	VC[c]	Petroleum hydrocarbons
DNAPL present?	Yes	Yes	No	No	Yes (LNAPL)
Maximum concentration of COC	16,500 (TCE)	52,000 (TCE)	1,100 TCB	380 (VC)	Free phase
Pilot-scale or full-scale	Pilot	Pilot	Pilot[b]	Full	Full
Average oxidant concentration (g/L)	45.2	297	200	14[f]	100
Activation mechanism	None[d]	Steam and iron	Iron	Iron	Sodium hydroxide
Injection method	Recirculation	Direct injection	Direct injection	Recirculation	Direct injection
Volume injected (gallons)	64,000	3,150	1,652[j]	1,340,000	NP
Estimated mass oxidant/mass soil (g/kg)	10	0.40	5.7	1.6	NP
Cost ($/cubic yard)	$191	$58	$1,200	$38	NP

NA – not available; NP – application not performed and/or data not available at the time this report was prepared.

(a) Assumes 0.3 porosity
(b) Application was prematurely discontinued.
(c) Low levels of parent compounds DCE and TCE also present.
(d) Low temperature heat (20°C) reported as the activation mechanism. However, for purposes of this report, no activation is assumed, since the temperature of groundwater was not augmented via an external source (i.e., steam, resistive heating).
(e) Estimated value based on calculating mass of oxidant introduced divided by the target treatment mass of soil. Value assumes even distribution of oxidant.
(f) Average concentration during the site-wide application.
(g) Assumes a 5% by volume solution and a persulfate density of 2.4 g/mL.
(h) Does not include treatment in soil located downgradient of the injection wells.
(i) Assumes 0.2 effective porosity.
(j) Design volume was 12,400 gallons.

7.1 Oxidant Demand and Reagent Dosing

The concentration of oxidant applied at a site typically is based on results of bench tests that determine the efficacy of the oxidant to react with the COCs and to determine the oxidant demand at various concentrations, the type of application being used (e.g., direct injection versus recirculation), the practitioners' previous experience at other sites, and cost. Bench-scale tests were performed at the Alameda, Quantico, and North Island sites to evaluate oxidant demand. As shown in Table 7-2, which summarizes the results for the Alameda and Quantico sites,[14] the SODs (1) are site-specific, (2) appear to increase with increasing oxidant concentration, and (3) increase with increasing contact time.

Table 7-2. SOD Results

Site	Reaction Time (days)	Oxidant Conc. (g/L)	SOD (g/kg)
Site 14 NAS Alameda	4	7.5	0.9
		15	3.7
		30	6.7
	8	7.5	2.1
		15	5.2
		30	7.2
SWMU 13 Quantico	7	80	39
		240	87
	14	80	43
		240	97

The concentrations of oxidant injected at the two sites (North Island and Alameda), where a recirculation approach was applied, were about 45 and 14 g/L, respectively. The concentrations at the ABL and Quantico sites, where a direct injection approach was employed, were about 297 and 200 mg/L, respectively. The oxidant concentration injected at the two direct injection sites was much greater than that injected at the two recirculation sites. This is typical, since direct injection relies on the relatively small volume of water to minimize displacement of contaminants and on subsequent groundwater, density, and diffusion transport to distribute the reagents. On the other hand, recirculation systems extract large volumes of groundwater into which the oxidant is added and then reinjected. This process relies on both above-ground and below-ground mixing driven by hydraulic forces generated by the system itself. Because of the volumes of groundwater involved, the cost to amend to levels similar to direct injection could be prohibitive. However, sufficient oxidant should be added to ensure that residual oxidant remains in the subsurface to react with NOM and residual soil contamination.

Since chemical oxidation follows second-order reaction kinetics, the rate of reaction is dependent on the oxidant's concentration. Hence, during direct injection, a greater fraction of COCs and NOM may be oxidized before the oxidant is diluted by the groundwater in the surrounding aquifer, as compared to a site where recirculation is used.

Table 7-1 shows the estimated mass of oxidant injected per mass of soil treated. The estimate was based on the reported pore volumes treated, a soil porosity of 0.3 (unless otherwise noted), and a soil density of 1,700 kg/m^3. Results for the four sites where ISCO has already been applied range from 0.4 to 10 g/kg.

Equally important to achieving adequate distribution of the oxidant is achieving distribution of the activating agent at sufficient levels to activate the persulfate that creates the sulfate radical. Of the four completed sites, one site (North Island) did not use an activating agent, but relied on a groundwater temperature of 20 to 24°C to activate the persulfate, two sites used only iron (Alameda and Quantico), and one site used heat (via steam) and iron (ABL). Based on the ABL results, it is clear that heat was inadequately distributed (temperature increases were only noted in one well); therefore, it likely failed to activate the persulfate.

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[14] SOD data for other sites were not available for review at the time of this report preparation.

It is difficult to assess how effective the iron activation was at the three sites. Little information was provided in the reviewed literature regarding the rationale for selecting the concentration of iron at ABL and Quantico. At the ABL site, about 1.9 g/L of iron EDTA was injected with the persulfate. No information was provided for Quantico. Initially, 0.50- to 1.0-g/L ferrous sulfate and a 0.5- to 0.9-g/L citric acid were used at IR Site 14 Alameda; however, because of concern related to the formation of THMs that occurred at another Alameda site, additional bench-testing was performed, which indicated that the concentrations could be reduced to about 0.2 g/L and still achieve destruction of the COCs. Distribution of the iron activator was not monitored at any of the sites. For comparison purposes, guidance prepared by the Interstate Technology Regulatory Council (ITRC) (2005) recommends an optimal catalyst loading of 100 to 200 mg/L for ISCO, using persulfate.

One important observation at North Island and, to an extent at Alameda, is that some post-ISCO samples collected nearly 3 months after concluding the injections contained residual persulfate and COCs. The fact that residual persulfate was observed to co-exist with stable or increasing TCE levels in several wells at North Island, and similarly VC levels at Alameda, may indicate that a certain threshold level of persulfate may be required to initiate oxidation reactions responsible for contaminant destruction, or rather, a lack of sufficient activating agent (i.e., Fe^{2+}) was present.

Multiple injections of the reagents may be necessary to achieve adequate dosing of reagent and destruction of the COCs. However, only one series of injections was performed at North Island, ABL, and Quantico; therefore, it is not possible to gauge if additional injections would have further reduced the concentrations of COCs. However, the fact that samples at North Island contained both COCs and persulfate is an indication that either additional activating agent or a greater concentration of persulfate was needed to further oxidize the COCs in that area. Hence, the site may have benefited from additional injections of persulfate and/or ferrous sulfate. At Alameda, it is unclear if the multiple injections substantially benefited the site. Although the repeated injections in these areas generally appear to have somewhat reduced the concentration of VC, the concentration of DCE and TCE was observed to increase in several wells, likely due to desorption as NOM was further oxidized. In general, an evaluation must be made to determine if the net reduction is approaching an asymptotic level and if it would be more technically effective and cost-effective to transition to another technology, as opposed to continuing with additional injections of reagents. In the case of Alameda, additional injections or injections at greater concentrations likely would be cost-prohibitive compared to employing MNA, considering the very dilute concentrations remaining at the site.

7.2 Reagent Delivery and Distribution

Similar to other types of in situ remedies, achieving adequate distribution of the reagents may be the greatest challenge that must be overcome to ensure the remedy’s success. Three approaches were used to introduce the reagents into the aquifer at the sites reviewed in this report. These include direct-push injection, direct injection through injection wells, and recirculation. Direct-push injections, which were initially performed at Quantico, use a DPT rig to slowly advance a rod through which the oxidant is pushed under pressure into the formation at discrete intervals. Low injection flowrates typically are used to minimize displacement of groundwater. This technique relies on diffusive and density-driven transport of the reagent to fully distribute it in the aquifer. Problems encountered at Quantico using this technique were related to smearing clay across the injection rods, which necessitated the use of high pressure to inject the reagents. Little reagent was introduced into the formation, and daylighting occurred on several occasions. As a result, injection was discontinued, and dedicated injection wells were installed.

Direct injection of reagents using dedicated injection wells was performed at Quantico and ABL and is planned for the Washington Yard site. Similar to direct injection using a DPT rig, injection into dedicated wells relies on pressure to force the reagent into the formation, and/or diffusion and density-driven gradients to distribute the reagents further into the formation. Care must be taken to prevent over-pressurizing the well, which could damage the packing around the well and facilitate daylighting, as well as fracture the formation. One primary difference between DPT injection and injection wells is that unless a packer or nested wells are used to isolate the vertical intervals (neither of which was reported to have been performed at Quantico or ABL), injection of the reagent is performed along the entire screened interval as opposed to being applied in discrete intervals. Hence, it is likely that the reagent would be transported disproportionately through more conductive lenses in the formation (if present).

A recirculation approach was used at North Island and former NAS Alameda. At both sites, groundwater was extracted from the formation, amended with reagents, and reinjected into the aquifer. This approach offers the advantage of inducing a hydraulic gradient to facilitate mixing of the reagent and groundwater and to minimize pushing contaminated groundwater outside the treatment zone. Also, surfacing of the reagents/groundwater should be minimized, since nearly equivalent volumes of water are being extracted and injected; however, surfacing of reagent was noted to occur in several instances at Alameda. Recirculation systems may be designed to ensure that the COCs are destroyed aboveground as was done during the application at Alameda (99% reduction demonstrated). Excess oxidant also should be added to ensure in situ contact with soil to facilitate desorption and oxidation of COCs on soil. The downside of recirculation systems is the additional capital cost for the pumps, tanks, and associated controls; however, the additional cost may prove to be economical at large sites (e.g., IR Site 14 Alameda).

Based on the reviewed literature, it is not possible to conclude that one approach was better than another. Although it was evident that the DPT injections were not well-suited, given the site-specific conditions at Quantico, they may have been effective at one or more of the other sites. The dedicated injections and recirculation systems appear to have distributed the reagents to some degree at each of the sites. Changes in pH, ORP, conductivity, and field measurements of persulfate are good indicators of the distribution of the oxidant and should be included as part of all performance-monitoring programs. A review of these parameters indicated that the reagents were better distributed in some portions of the sites than others. Daylighting was reportedly a problem at both Quantico and Alameda. Both of these sites also reported that transport of the reagents occurred along preferential pathways created by underground pipes and sewers. These findings suggest that it may be beneficial to compare the different injection methods as part of pilot testing that should be conducted at any site prior to full-scale implementation. The pilot test should focus on optimizing the injection strategy to ensure a good distribution of chemicals, the results of which will maximize the sustainability of the full-scale system.

Although it is not possible to conclude which of the two approaches yielded greater destruction of COCs due to many site-specific variables, it is interesting to note that as described in Section 8.1, the direct injection approaches typically inject the oxidants at a greater concentration than recirculation. The chemical oxidation is described by second-order kinetics, which means that the rate is dependent on concentration (of the oxidant as well as the COCs, NOM, etc.); therefore, it stands to reason that the rate of reaction within the immediate vicinity of an injection well will occur at a greater rate, and possibly achieve a greater destruction efficiency at sites where direct injection is employed, as well as consume a greater mass of oxidant because of the higher SOD associated with higher oxidant doses. However, as was observed at Alameda, recirculation likely achieves a high aboveground destruction efficiency and a greater degree of mixing and distribution in the subsurface. Hence, a recirculation approach may be better suited at sites where the majority of contamination is present in the aqueous phase, as opposed to adsorbed onto soil (such as the VC plume at Alameda); in such cases, direct injection may be better suited for sites with relatively high concentrations of contaminants adsorbed to soil.

It is important to note that although initial distribution may not be uniform, persulfate offers the advantages of being more stable than other oxidants, such as hydrogen peroxide or ozone; this permits it to reside in the aquifer for an extended period of time. The sulfate anion does not have a tendency to adsorb onto the formation material (Huling & Pivetz, 2006). Also, as indicated by the bench-scale tests performed at Alameda, the NOD for persulfate is lower than that of permanganate. Hence, additional transport via diffusion or migration with groundwater flow can occur.

7.3 Formation of Byproducts, Changes in Geochemistry, and Mobilization of Metals

Application of ISCO using sodium persulfate results in the formation of innocuous products, including water, carbon dioxide, chloride,[15] and sulfate. However, several byproducts also can be formed that could potentially impact the aquifer's geochemistry and hydrology. Commonly formed oxidation byproducts include ketones such as acetone and 2-butanone. Less common, although observed to a degree at former NAS Alameda IR Site 14[16] and Quantico,[17] is the formation of disinfection byproducts including chloromethane, methylene chloride, and THMs. The formation of THMs and their precursors may be of particular concern considering that U.S. EPA's established drinking-water MCL is 80 µg/L for total THMs and is 5 µg/L for methylene chloride.

The formation of THMs during ISCO is not very well understood. However, a recent study that investigated the natural formation of THMs in soil concluded that THMs are formed when halide ions, organic matter, and iron are present (Huber et al., 2009), during oxidation using persulfate. Iron activation and chelating using citric acid may further enhance the production. At former NAS Alameda, a concentration of 110 µg/L of chloroform and 2,400 µg/L of methylene chloride were measured in a monitoring well about 5 weeks after completing ISCO. A reduction in the concentration of the citric acid and iron appears to have reduced the formation of the THMs and their precursors to some extent. It also should be noted that at least one study has shown that alkaline-activated persulfate has been very effective in oxidizing methylene chloride, which is a precursor to chloroform (Block et al., 2004).

Groundwater geochemistry is impacted by application of the ISCO reagents. The pH is expected to decrease to some extent due to the formation of sulfuric acid as a result of the oxidation reaction (see Equation 1). This pH drop was evidenced to a degree at sites for which data were available, including North Island, Alameda, and Quantico. In general, post-injection monitoring data indicate that the pH rebounds to pre-injection conditions. However, at sites containing low alkalinity to buffer the pH, the pH may display a considerable drop (as observed in wells 14MW-20D and 14MW-05 at former NAS Alameda). In these instances, it may be possible to buffer the groundwater by adding sodium carbonate, which slows the reaction kinetics, but reportedly does not inhibit destruction of the VOCs (ITRC, 2005).

ORP, conductivity, and DO are impacted by addition of the oxidant and are considered good indicators of the oxidant's distribution in the subsurface. At all of the reviewed sites, elevations of these groundwater quality parameters were noted in monitoring wells that showed evidenced of oxidant. The degree of change for each is based on many site-specific conditions; hence, it is important to establish baseline conditions for each prior to injecting reagents in order to compare values during and after applying the reagents. Data from the sites reviewed indicate that these parameters return to near baseline conditions within a few months of injecting the reagents.

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[15] Chloride is produced during the treatment of chlorinated ethenes.

[16] Elevated levels of THMs also were noted at a second site at Alameda where persulfate was applied after an application of hydrogen peroxide.

[17] Data were not available for the North Island site.

Trace-metal levels in the treatment zone wells were elevated in wells impacted by the oxidants, which is a typical occurrence at ISCO sites. The increases are associated with changes in groundwater chemistry, including parameters such as pH and ORP as well as desorption from NOM as it is oxidized. The fate of these metals is unclear. Based on the sites reviewed, there is evidence that some trace metals can remain elevated, even after geochemical parameters return to pre-treatment levels. Hence, sites should include monitoring of these metals over an extended period (at least several quarters) to better understand their fate and transport. At least three additional quarterly monitoring events are planned for the Alameda site.

It is possible that geochemical changes can create insoluble products that block the pore space in the formation. For instance, as Fe^{2+} is converted to Fe^{3+}, it will precipitate out of solution. At sites with high alkalinity, naturally occurring calcium carbonate can react with sulfate and drop out of solution. Slug tests to measure hydraulic conductivity can be measured before and after performing the ISCO injections to determine if the aquifer's hydrology will be impacted. Such tests were performed at the North Island site. Most results indicated no significant change in hydraulic conductivity. However, the hydraulic conductivity increased about five times in one well; the reason for this was unclear.

7.4 In-Situ Bioremediation and MNA after ISCO

While ISCO has not been shown to reduce VOCs to below cleanup goals, ISCO should be applied as part of a treatment train approach in order to achieve RGs for the site. In situ bioremediation (ISB) and MNA are two treatments typically considered after applying ISCO due to their efficacy in treating residual contamination cost-effectively. Research has indicated that ISCO applied prior to ISB or MNA may actually enhance these remedies by (1) reducing the concentration of contaminants that can cause microorganisms to go dormant, (2) introducing oxygen, which is necessary for aerobic biodegradation (but not for reductive dechlorination), and (3) oxidizing NOM, which releases the COC making them more bioavailable, as well as releasing other nutrients that are used by the microorganisms.

Although the concentrations of persulfate typically used at ISCO sites will kill microorganisms on contact, it is not likely that the application of ISCO, using persulfate, will completely inhibit microbial activity across the site. First, as shown by results at the sites described in this report, it is not possible to achieve uniform distribution of the oxidants across the entire treatment area. Hence, there will be areas containing bacteria that will repopulate the aquifer when geochemical properties return to levels conducive to microbial growth for the species in question. Second, naturally occurring bacteria will continue to proliferate in the aquifer outside the treatment area and eventually will multiply and re-populate the area.

The Quantico project evaluated the potential for natural attenuation after ISCO. Observed increases in DO, ORP, and sulfate levels are not conducive for anaerobic reductive dechlorination. However, these effects may be short-lived. The PLFA results did indicate reduced microbial activity in wells in which groundwater was influenced by the ISCO reagents. Although the biomass decreased by more than an order of magnitude after treatment, a low but considerable concentration remained (10^4 to 10^5 cells). Furthermore, the results also indicated a shift in the composition of the microbial community supporting anaerobic degradation of VOCs in wells containing high levels of VOCs. Additional monitoring was recommended for that site to better assess the microbial community and potential for natural attenuation.

IR Site 14 at Alameda also is being evaluated for the possibility of using MNA. Although this project is ongoing and additional results are not available, preliminary data indicate that the geochemistry may be returning to baseline values. However, there are AOCs, such as the very low pH

(<2) measured in two of the wells, that can inhibit microbial activity. Hence, additional quarterly monitoring is planned to better assess the potential for MNA.

7.5 Performance and Process Monitoring

Experience at these sites shows that a detailed performance and process-monitoring program must be included as part of every ISCO project. Performance monitoring is performed to evaluate effectiveness of the remedy (e.g., removal of COCs, reduction of risk), the potential for contaminant rebound, and, to a lesser extent, cost. Process monitoring is performed to evaluate and optimize distribution of the ISCO reagents, estimate time to completion, and ensure that the application is performed in a manner safe to human health and the environment.

Performance monitoring is involving comparing baseline data with post-application data to determine short- and long-term impacts that the remedy had on the site. One particular challenge is to estimate the mass of contaminants remaining in the aquifer to determine if additional applications of ISCO are needed or if it would be more appropriate to transition to an alternative remedy such as MNA. The sites reviewed in this report primarily measured changes in concentrations of COCs in groundwater to estimate mass removal. However, although a useful indicator, measuring reductions of COCs in groundwater does not account for reductions that may have occurred in soil resulting from the oxidation of NOM and desorption of COCs. Also, as observed at all of these sites, contaminant levels will increase and decrease as the concentrations in soil and groundwater re-equilibrate after the application, after geochemical parameters return to baseline conditions, and after residual persulfate is consumed. Ultimately, rebound of contaminants into the groundwater from COCs remaining sorbed to soil may occur. Hence, minimum performance should consider multiple quarters of post-ISCO monitoring results before finalizing future plans for the site. Although not performed in the studies reviewed, analysis of soil samples can also provide additional information regarding changes in COC and geochemistry that will be useful for assessing the remedy's success.

Monitoring programs must be designed to confirm that the COCs have been removed via the oxidation process and not through groundwater advection to a location outside the treatment area; through vertical migration either downward through density-driven migration or upward via groundwater mounding and surfacing; or through volatilization in the case of heat-activated persulfate. Monitoring wells (in some cases nested or clustered) and soil vapor points and thermocouples (in the case of heat application) should be installed to monitor these potential pathways of contaminant migration.

In addition to changes in COCs, monitoring should be performed for other chemical indicators, such as groundwater quality indicators, including DO, ORP, pH, conductivity, and temperature parameters. Changes in concentrations of reaction products such as chloride and sulfate ion concentrations and observation of increasing levels of the oxidant in monitoring and extraction wells (in the case of recirculation) are useful performance indicators and should be analyzed. For example, at ABL, a large increase in the ORP measurements (150 to 500 mV) occurred at the three-month monitoring event. This increase likely was a result of an upwelling of groundwater laden with potassium permanganate that occurred when the groundwater extraction system was turned off.

The sites reviewed indicate that ISCO reactions and geochemical changes can result in the formation of a number of reaction byproducts and can increase the concentrations of some dissolved metals in the aquifer; some of these can have regulatory standards associated with them. For instance, the results at Alameda indicate that there is a potential to form methylene chloride and THMs. Increased levels of metals including arsenic and chromium were measured in several wells at the reviewed sites. Also, secondary drinking water standards for contaminants, such as iron, manganese, and sulfate, can be exceeded during ISCO injections using persulfate. Hence, it is important to perform necessary monitoring to ensure that levels of these additional COCs are not produced at levels that will impact human health and the environment and will attenuate in a reasonable timeframe.

Mass flux modeling, as was performed at the ABL site, also may be a good way to evaluate the impact the remedy had on the aquifer. In the case of a pilot test, the results help to assess recontamination due to rebound from influx of contaminated groundwater in areas surrounding the pilot-test results. During full-scale application, especially in the case of DNAPL sites, mass flux modeling is a useful tool to determine if the treatment has resulted in sufficient contaminant decrease in the source area to alleviate the risk to a downgradient receptor.

Process monitoring includes measuring various parameters before, during, and immediately after the ISCO injections, such as flowrates, injection pressures, temperatures, and groundwater quality indicators such as ORP, pH, conductivity, and DO. These measurements can be used to evaluate the distribution of oxidant in the subsurface, ensure that the system is operating according to design and in a safe manner, and identify any potential problems and optimize as necessary. Depth to water in wells should be measured to gauge mounding and the potential for surfacing. Ideally, it is beneficial to take real-time field measurements, which, if necessary, can be supplemented with data from samples sent to a laboratory. For instance, Chemetrics® field kits were used at Quantico and Alameda to assess the distribution of reagent in the aquifer.

7.6 Operational Issues

As with any remediation technology, there were operational challenges at the ISCO application sites. In most cases, the vendors have proved resourceful at addressing these challenges through engineering modifications, and it may be possible to anticipate and address these issues during the design phase at future sites. Some of the operational issues encountered at the four sites where the application has been completed include:

- Transport of reagents through pre-existing infrastructure was believed to have occurred at two of the sites investigated. At former NAS Alameda, sodium persulfate was measured in well 14MW-01 located about 100 feet downgradient of the treatment area. Transport of the reagent likely occurred during heavy rain, which elevated the water table to near surface, enabling the reagent to flow along old storm drains and their bedding. At MCBQ, the ISCO application was prematurely terminated when reagent was discovered to have traveled along bedding that led to an outfall at the Potomac River. These occurrences highlight the need to (1) ensure a detailed understanding of subsurface lithology and infrastructure prior to applying ISCO and (2) take necessary precautions to prevent potential migration, such as installing barriers or injecting reagents when the water table is low.
- Reagents were noted to surface at former NAS Alameda and Quantico. Although small amounts of surfacing occurred during all three applications at Alameda, most were noted when the water table was high during the site-wide application. At both sites, surfacing was minimized by reducing flow or turning off injection wells near the area where surfacing was observed. At Quantico, absorbent material was placed around sewers to prevent reagents from entering.
- Some wells at Alameda did not produce sufficient water and went dry, which was due to the very heterogeneous nature of the fill material at the site. Well seals were installed so that the pump would generate a small vacuum in those wells to improve flow.

- At Alameda, it was not possible to measure the flowrates from individual extraction wells because the meters were fouled by air and particulates in the extracted fluid, and because of occasional freezing of the pneumatic extraction pumps, which interfered with obtaining accurate measurements.
- At ABL, which was the only site to use steam to activate the persulfate, it was determined that hard water hindered the steam generation. To alleviate this problem, softeners were added to the hydrant water to prevent the buildup of calcium, lime, and rust.
- Uneven heating of the aquifer with steam occurred at ABL, reportedly resulting from heterogeneous subsurface conditions.

7.7 Costs

Application costs are summarized in the last row of Table 7-1. Site-specific or situation-specific costs, such as work plan preparation, design, planning, permitting, and monitoring, have been excluded from this cost comparison. The focus is on the cost required to mobilize to the site, conduct the treatment, and demobilize. A total treatment cost for the project was estimated by adding the capital investment and operating costs. This cost was then divided by the estimated treatment volume of soil. Costs ranged from $38/cubic yard at Alameda to $1,200/cubic yard at Quantico. The wide range in cost is attributed to the fact that only one of the sites (Alameda) was a full-scale application. The other sites were pilot-scale applications, which treated a limited portion of the plume. Scale of operation has a tremendous influence on the unit cost numbers, since many of the inputs, including equipment costs, mobilization costs, and demobilization costs, are not highly dependent on the treatment area size. Caution also should be exercised in interpreting the unit cost number for the pilot test since each pilot test had different objectives: one test was prematurely terminated, and it is not possible to accurately determine the mass of contamination removed. It is interesting to note that at the sites for which data were available, the cost for the chemical reagents ranged from about 10% to 20% of the total project cost and from about 30% to 85% of the operating cost.

7.8 Summary of Lessons Learned

The review of the ISCO application performed at the four sites provided considerable information on the performance and challenges at different types of sites. The lessons learned from the review are summarized as follows:

- A reduction of COC was observed at all four sites at which persulfate was injected; however, reductions were not uniform across the sites; that is likely the direct result of not being able to evenly distribute the reagent throughout the target treatment areas. Typically, the greatest reductions were observed in areas near injection locations and/or known to have been exposed to a relatively large mass of oxidant. Results indicate that multiple rounds of ISCO injections are necessary to significantly reduce a site’s level of contaminants. However, it should not be assumed that injecting reagents multiple times at a site will guarantee compliance with RGs. ISCO should be considered as part of a treatment train approach. The practicability of applying additional rounds of ISCO must be compared against the cost (and time required) to implement an alternative treatment technology for achieving the site’s final RGs.
- Direct injection and recirculation of the ISCO reagents are both somewhat effective means of reducing the concentration of COCs. However, distribution was not uniform at any of the sites. Also, both methods of application have advantages and disadvantages. The conceptual site model and remedial objectives must be carefully considered in order

to choose the best method of application for a site. Recirculation may be better suited at sites where greater control over the destination of the reagents is required, such as at sites near potential receptors (e.g., surface water); at sites where surfacing may be more problematic, since recirculation should, in theory, minimize the potential for surfacing; at sites with low groundwater velocity; and possibly at sites with relatively impermeable soils. Since the application method depends on many site-specific factors, pilot testing should be performed to compare the different injection methods so as to optimize the injection strategy and achieve good distribution of chemicals, while minimizing the amount of chemicals used. Various configurations can be used for a recirculation system's injection layout. Capture modeling is useful to optimize the configuration of injection and extraction wells.

- Real-time measurements are useful for performing process monitoring during ISCO application. Groundwater quality indicators such as conductivity, pH, ORP, and temperature should be measured and used to assess the distribution of oxidant. In addition, field test kits to measure persulfate are a cost-effective method to evaluate the distribution of oxidant.
- If an activating agent is used (e.g., iron, heat, alkaline) monitoring should be performed to gauge the distribution of the activating agent to ensure that the persulfate is being activated according to design. Residual persulfate was measured in samples that also contained COCs at two of the sites reviewed. This may indicate that sufficient activation agent was present to initiate oxidation reactions responsible for contaminant destruction.
- Multiple applications, separated by several weeks/months to allow the site to begin reestablishing equilibrium between the dissolved and adsorbed phases may be necessary to achieve RGs. However, a typical cost-benefit tradeoff should be evaluated between the costs of longer time in the field and greater chemical use versus the benefits of additional CVOC removal and transition to another less costly technology such as MNA.
- Reaction byproducts are generated as sodium persulfate reacts with COCs, NOM, and reduced metals species. Byproducts can include sulfuric acid, chloride and sulfate ions, ketones such as acetone and 1,2-butanone, and disinfection byproducts such as methylene chloride and THMs. Some of these byproducts are useful, such as chloride and sulfate ions, which can be monitored and tracked to help assess ISCO performance. However, others can be detrimental to the aquifer and pose risks to human health and the environment. For instance, if sufficient alkalinity is not occurring naturally, produced sulfuric acid can lower the aquifer's pH as was observed in two monitoring wells at Alameda. Some disinfection byproducts are recalcitrant and have drinking-water MCLs associated with them, such as methylene chloride (5 µg/L) and total THMs (80 µg/L). Also, sulfate has a secondary drinking water standard of 250 mg/L.
- ISCO appears to elevate the concentration of some metals in groundwater. Concentration of these metals may remain elevated, even after the geochemical properties of the groundwater return to baseline conditions. Some of these metals, such as arsenic or chromium (VI), can have both human and environmental impacts; others, such as iron and manganese, have secondary drinking water standards associated with them. Hence, long-term monitoring is necessary to evaluate the potential for migration of these metals.
- Subsurface utilities and infrastructure must be accounted for during the design. Infrastructure can serve as a conduit to transport the oxidant and other reaction products from the treatment area to potential receptors.

- Bench-scale tests are useful tools to determine oxidant concentration, oxidant demand, and theoretical reductions of COC prior to designing and implementing ISCO at either the pilot- or full-scale levels. SOD values are site-specific, increase with increased contact time, and oxidant concentration.
- Persulfate persists in the subsurface for weeks, which indicates that the soil's NOD for persulfate is low. This also indicates that the performance-monitoring program should include multiple rounds of post-ISCO sampling to better evaluate changes that occur as residual persulfate is consumed.
- It may not always be necessary to add an activating agent depending on site-specific conditions. Substantial declines in TCE and DCE were noted at the North Island site where the application of persulfate was performed at groundwater temperatures of 20 to 24°C without the addition of a specific activation agent (heat, sodium hydroxide, or iron).
- Rebound observed at North Island and ABL may largely have been due to influx of contaminated groundwater from the upgradient portion of the aquifer, which demonstrates the difficulty in selecting and evaluating results obtained from a pilot test. It is best to locate the pilot-test plot in an area off to the side of a plume, which is less likely to be impacted by contaminated groundwater outside the treatment area. Modeling of mass flux downgradient of the treatment area is a useful tool to estimate the impact of the pilot test on downgradient receptors.
- Since the success of this technology appears to hinge on achieving adequate contact between the contaminants and the reagents, ISCO using persulfate will be more successful (i.e., greater overall contaminant reduction, lower cost) at sites consisting of more permeable materials such as sands as opposed to impermeable silts and clays. The vertical extent of contamination and depth of the contamination also will significantly impact cost and ease of application, since it will be more difficult to inject the reagents and achieve uniform distribution across larger vertical horizons. Sites that have a significant mass of contaminants adsorbed to soil in the unsaturated zone also may not be well-suited for this technology, since it may be difficult to achieve adequate contact between the reagents and the contaminated soil for extended periods.

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