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Polymer-Enhanced Subsurface Delivery and Distribution of Permanganate

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ACRONYMS AND ABBREVIATIONS

1D	one-dimensional
3D	three-dimensional
AST	aboveground storage tank
Ba	barium
bgs	below ground surface
CDISCO	conceptual design for ISCO (modeling tool)
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
<i>cis</i> -1,2-DCE	<i>cis</i> -1,2 dichloroethene
CMT	continuous multichannel tubing
COC	contaminant of concern
cP	centipoise
CPT	cone penetrometer test
Cr	chromium
CSM	Colorado School of Mines
DNAPL	dense nonaqueous phase liquid
DoD	Department of Defense
DPT	direct push technology
Eh	redox potential
ESTCP	Environmental Security Technology Certification Program
GC-MS	gas chromatography – mass spectroscopy
GMS	Groundwater Modeling System
gpm	gallon per minute
ISCO	in situ chemical oxidation
k	hydraulic conductivity
LPM	low permeability media
MCIEAST-MCB CAMLEJ	Marine Corps Installations East – Marine Corps Base Camp Lejeune
MCL	maximum contaminant level
MIP	membrane interface probe
MLS	multi-level sampling
Mn	manganese
MnO ₂	manganese dioxide
MnO ₄ ⁻	permanganate ion

ACRONYMS AND ABBREVIATIONS (continued)

NaMnO ₄	sodium permanganate
NAPL	nonaqueous phase liquid
NCAC	North Carolina Administrative Code
O&M	operations and maintenance
ORP	oxidation/reduction potential
OU	operable unit
PA-ISCO	polymer-amended ISCO
PCE	tetrachloroethylene (perchloroethylene)
PCS	process control system
PI	principal investigator
PSI	pounds per square inch
psig	pounds per square inch gauge
PV	pore volume
PVC	polyvinyl chloride
RI	remedial investigation
ROI	radius of influence
SERDP	Strategic Environmental Research and Development Program
SHMP	sodium hexametaphosphate
TCE	trichloroethylene
TOC	total organic carbon
<i>trans</i> -1,2-DCE	<i>trans</i> -1,2-dichloroethene
UIC	underground injection control
USEPA	U.S. Environmental Protection Agency
UST	underground storage tank
UV/Vis	ultraviolet-visible spectrophotometer
VOC	volatile organic compound

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EXECUTIVE SUMMARY

OBJECTIVES

The Department of Defense (DoD) ESTCP-funded the demonstration and validation of polymer-amended in situ chemical oxidation (ISCO) (PA-ISCO). PA-ISCO is the use of water-soluble polymers to enhance ISCO using permanganate. The demonstration was conducted at the Marine Corps Installations East – Marine Corps Base Camp Lejeune’s (MCIEAST-MCB CAMLEJ) Site 88, at which chlorinated solvents (trichloroethylene [TCE] and tetrachloroethylene [PCE]) are found in the subsurface. The two main goals of the project were: (1) to reduce the effects of site heterogeneities on oxidant delivery; and (2) manage the deposition of manganese dioxide (MnO_2) (permanganate oxidation byproduct) to improve the delivery of oxidant. With respect to these objectives, experiments were carried out using two polymers. Xanthan gum was used to improve sweep efficiency of the oxidant through lower permeability areas. Sodium hexametaphosphate (SHMP) was used to reduce the instance of MnO_2 precipitation and build-up. Through previous laboratory development funded by the DoD’s Strategic Environmental Research and Development Program (SERDP), the effectiveness of both polymers was tested. Both were deemed viable candidates for field study.

TECHNOLOGY DESCRIPTION

The test site consisted of two injection wells. One injection well received only permanganate (control plot); the other injection well received a mixture of oxidant and polymers (test plot). Multilevel wells were used to monitor groundwater prior to treatment, during treatment, and post-treatment. Real-time groundwater quality measurements included specific conductivity, oxidation-reduction potential (ORP), permanganate, and viscosity. Groundwater samples were collected from the multilevel monitoring wells for laboratory measurements of pH, ORP, solids concentration, cations, anions, cation exchange capacity (CEC), and anion exchange capacity toward understanding how polymer addition affects groundwater quality. A total of 12 to 15 soil cores per injection well were extracted at various distances from the injection site immediately following treatment. One year post-treatment, groundwater and soil cores were collected to investigate long-term effects of treatment on soil and groundwater chemistry and the fate of the polymer.

Comparisons between test and control plots were used to assess treatment performance. Key indicators of performance for the polymer included:

- Movement of permanganate into lower permeability layers/strata
- Preferential flow around areas of high contaminant mass due to MnO_2 deposition
- Potential for rebound
- Treatment effectiveness
- Injection pressure
- Groundwater quality

RESULTS

The addition of polymer improved oxidant movement into lower permeability strata, reduced preferential flow, and greatly improved the overall sweep efficiency of the PA-ISCO fluid compared to the permanganate control plot where polymer was not used. As a result, a greater percentage of the aquifer was contacted by the oxidant. Specifically, one pore volume (PV) of solution was introduced to each plot; the use of polymer resulted in a test plot sweep efficiency of 67%, double that of the control plot (sweep efficiency=33%). Because a greater portion of the aquifer was swept, overall treatment was more effective and there was lower rebound. It is important to note that even with polymer, the oxidant solution did not contact 100% of the contaminated media in one PV. Rebound could still be expected if an insufficient volume of oxidant is applied. The volume appropriate for treatment should be determined on a site-by-site basis. However, based on this demonstration, the use of polymer can reduce the necessary volume of solution by more than an order of magnitude. Importantly, the polymer-amended solution did not negatively affect injection pressure during this demonstration.

Groundwater quality data collected included parameters associated with the soil that can affect groundwater concentrations of contaminant and key cations and anions. Most geochemical outcomes using polymer were similar to those without polymer; however, changes due to ISCO were slower to appear downgradient of the polymer-treated plot. Two possible reasons for this observation include retention within, and groundwater flow around, the more viscous polymer solution. Polymer was still present at the site one year post-treatment. Geochemical analyses indicated the polymer was “retreating” from its leading edge and releasing the geochemical signature of the amended oxidant solution rather than being flushed through the treated zone by upgradient solution as was measured in the control plot. This has important implications with respect to appropriate monitoring of treatment performance. Byproducts of permanganate oxidation (e.g., MnO_2 solids) and short-term mobilization of metals (e.g., chromium) observed at some ISCO sites may be sequestered within the viscous PA-ISCO solution during treatment and held within the treated zone post-treatment until viscosity dissipates. Long-term post-treatment viscosity could also be leveraged in future PA-ISCO applications to sequester permanganate within the treatment zone providing longer-term treatment to address contaminant rebound from low permeability media (e.g., fine silts or clays) that are not swept during the initial PA-ISCO treatment.

Lessons learned beyond those tied to specific performance objectives included:

- Results of the control plot exemplified the surprising extent to which preferential flow occurs in the subsurface, even within lithology that appears the same or similar.
- Site characterization and monitoring efforts must be designed based on site-specific factors. In order to prepare an appropriate treatment system design and to capture treatment outcomes effectively, operational and performance monitoring strategies must match the operational goals and the physico-chemical characteristics of the amendments applied.
- Soil core data were more valuable than groundwater data with respect to making accurate pre- and post-treatment subsurface evaluations of treatment performance for PA-ISCO.

- Simple geochemical field measurements, such as conductivity and ORP, provided valuable, real-time information with respect to operational performance. High data density using real-time monitoring approaches added significant value with respect to making real-time, cost-saving decisions in the field.
- Automated amendment delivery schemes, while costly, will add value to field operations by allowing for round-the-clock, unmanned injection. This will be particularly valuable at sites where unescorted activity is not possible.

The primary objective of this first pilot demonstration was to evaluate sweep efficiency improvement for a polymer-amended permanganate solution and learn from the results of this test to better understand the efficacy of the technology for future full-scale application. As a result, the PA-ISCO formulation was not designed to completely remediate the treatment volume, which complicates a comparative analysis of the life cycle costs of PA-ISCO treatment versus traditional permanganate ISCO. To facilitate the cost analysis, it was assumed that a 2 PV PA-ISCO treatment, utilizing the same polymer and oxidant concentrations, would provide maximal sweep efficiency improvement to contact 100% of the PV within a template site (described in Section 7, table 11). Under this scenario, the additional cost of PA-ISCO (i.e., costs in addition to the normal cost of traditional permanganate ISCO implemented in the same manner) would be \$118,440 or \$185 per cubic meter (m^3). Roughly 56% (or \$69K) of the total cost was related to the purchase, shipping, and subcontractor labor associated with the process control system used in this pilot demonstration. The requirement of 24-hour injection for PA-ISCO necessitates a similar equipment purchase and therefore would be a fixed cost, regardless of the scale of implementation. However, the unit cost of this equipment would decrease with increasing scale of implementation. As PA-ISCO develops, the project team expects this equipment, along with the polymer mixing equipment at \$20K (17% of total cost), to become available for rent, with the total costs normalized over multiple sites over multiple years. If, for example, the equipment is purchased by a vendor who wants to realize a return on investment within 2 years, and we assume the equipment can be applied to a minimum of 6 sites per year, \$89K (75%) of the total costs would be reduced to approximately \$7.5K per project. Thus, total costs of PA-ISCO above and beyond traditional ISCO are estimated as \$36,940, or \$58/ m^3 . In a recent review of traditional ISCO application at over 200 individual sites, the average unit cost of ISCO was found to be \$123/ m^3 (Krembs et al., 2010). Therefore, the unit cost of PA-ISCO (estimated as \$181/ m^3) is competitive with traditional ISCO, particularly considering the potential benefit.

The active remediation timeframe for injection of two PVs of amendments is estimated at 10-12 days based on the duration of this 1 PV demonstration. Accordingly, a permanganate-only plot would require approximately 6 PVs and 1-month or more field time; and theory dictates that while sweep would be improved without polymer in 6 PVs, there would still be significant preferential flow. Assuming 100% contact, though, the cost savings of PA-ISCO at a minimum are the costs associated with approximately 20 days of field time. A conservative estimate of field costs at \$800/day for labor and travel (hotel, per diem, etc.) translates to a savings of \$16K, or \$25/ m^3 in the example case evaluated here, which is approximately 40% of the estimated costs associated with use of PA-ISCO above and beyond traditional ISCO (assuming rented equipment with total costs normalized over 2 years and multiple sites, as discussed above). For a worst case

scenario, PA-ISCO costs \$33/m³ above traditional ISCO for the same benefit as traditional ISCO.

If we assume PA-ISCO achieves treatment goals and results in site closure within 5 years of implementation, but ISCO without polymer does not reach treatment goals because of incomplete sweep (resulting in 30 years of long-term monitoring), the costs saved using PA-ISCO include 25 years of monitoring costs. Assuming a cost of approximately \$50K per year for long-term monitoring, a simple estimate of the associated cost savings indicates savings of up to \$1.25 million per site.

Key differences in the cost of PA-ISCO relative to traditional ISCO included the cost of the polymers, the on-site polymer mixing equipment, and the associated shipping of these items to the field demonstration site. Further, an automated process control system was employed to allow 24-hour injection, which was important for maintaining the viscosity of the injection solution at design levels during injection. Key drivers of total project cost included the nature and extent of contamination, degree of heterogeneity, and rate of injection achievable (average hydraulic conductivity).

There were no apparent regulatory barriers to PA-ISCO for the polymers and oxidants employed. Technical and/or implementation issues associated with PA-ISCO included:

- Uncertainty regarding the influence of polymer on hydraulic conductivity over the long-term within the treated area.
- Uncertainty regarding the degree of heterogeneity the polymer can overcome.
- Concern over the potential for daylighting evoked by the use of a higher viscosity solution.
- Improved sweep efficiency could be achieved by increasing injection volume for any delivered amendment, particularly for more reactive (short-lived) amendments. Polymer can significantly reduce required injection volumes; however, low volume delivery is not appropriate for most remediation approaches that involve the delivery of aqueous phase amendments, including ISCO. This translates to longer duration delivery and increased field time per injection event.
- The dry powdered form of xanthan gum and SHMP used in this demonstration required expensive (~20% of total equipment cost) hydrodynamic mixing equipment. Procuring polymer in liquid form that could be trucked to the site in tanker trailers may be more cost-effective, particularly for larger-scale operations.

BENEFITS

The benefits of PA-ISCO over traditional ISCO include:

- Greater movement of contaminant into areas of lower hydraulic conductivity – less preferential flow and contaminant bypass
- Improved sweep efficiency

- Lower injection volume requirement
- Lower field time requirement
- Greater applicability of ISCO to moderately heterogeneous sites
- Lower probability of contaminant rebound

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1.0 INTRODUCTION

1.1 BACKGROUND

In situ chemical oxidation (ISCO) using permanganate is an established remediation technology being applied at hazardous waste sites throughout the United States and abroad. Field applications of ISCO continue to grow and have demonstrated that ISCO can achieve destruction of contaminants and achieve clean-up goals. However, some field-scale applications have had uncertain or poor in situ treatment performance. Poor performance is often attributed to poor uniformity of oxidant delivery caused by zones of low permeability media (LPM) and site heterogeneity and excessive oxidant consumption by natural subsurface materials. A second permanganate ISCO challenge is the management of manganese dioxide (MnO_2) particles, which are a byproduct of the reaction of permanganate with organic contaminants and naturally-reduced subsurface materials. These particles have the potential to deposit in the well and subsurface, and impact flow in and around the well screen, filter pack, and the surrounding subsurface formation. This is a particular challenge for sites with excessive oxidant consumption due to the presence of natural materials or large masses of nonaqueous phase liquids (NAPLs). This demonstration/validation focused on (1) diminishing the detrimental effects of site heterogeneities with respect to the uniformity of oxidant delivery, and (2) managing MnO_2 aggregation and deposition.

1.2 OBJECTIVE OF THE DEMONSTRATION

This project goal was to demonstrate and validate the use of a water-soluble polymer with permanganate for ISCO of organic contaminants with the dual primary objectives of: (1) improving the sweep efficiency of permanganate through heterogeneous media containing lower permeability media, and (2) controlling MnO_2 particles to improve oxidant delivery and flow, thereby enhancing contaminant destruction. A secondary project objective was to compare post-delivery/treatment groundwater quality for “permanganate only” and “permanganate + polymer” test areas.

1.3 REGULATORY DRIVERS

This project addresses contaminants amenable to ISCO using permanganate; most commonly chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Over 3,000 Department of Defense (DoD) sites are contaminated by chlorinated solvents, including dense nonaqueous phase liquid (DNAPL) present at high mass density, which challenge many remediation technologies, as well as very low concentrations emanating from contaminant trapped in lower permeability layers that the majority of treatment technologies have difficulty accessing. The U.S. Environmental Protection Agency’s (USEPA) maximum contaminant level (MCL) for TCE and PCE is 5 micrograms per liter ($\mu\text{g/L}$). This concentration is lower than typically present at sites containing even very dilute concentrations of these contaminants. These MCLs, and others related to contaminants amenable to permanganate ISCO, are the regulatory driver for advancing approaches for their treatment. Specific to the site for this particular demonstration, Marine Corps Installations East – Marine Corps Base Camp Lejeune (MCIEAST-MCB CAMLEJ), remediation activities are conducted in accordance with the North Carolina

Groundwater Quality Standards specified in 15A North Carolina Administrative Code (NCAC)
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2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION AND DEVELOPMENT

ISCO using permanganate is an established remediation technology being applied at hazardous waste sites throughout the United States and abroad. A wide variety of organic contaminants have been successfully oxidized by permanganate, with high treatment effectiveness (e.g., >90% mass destruction) for common contaminants such as chlorinated ethenes (e.g., TCE, PCE) with very fast reaction rates (e.g., 90% destruction in minutes). Field applications of ISCO continue to grow and have demonstrated that ISCO can achieve destruction of contaminants and achieve clean-up goals. However, some field-scale applications have had uncertain or poor in situ treatment performance. Two challenges with any in situ remediation technology are: treatment amendment delivery limitations due to site heterogeneities, and minimizing unfavorable impacts of technology implementation. With respect to permanganate ISCO, these challenges specifically relate to the ability to deliver into LPM (versus preferential flow and bypassing of the LPM), and deposition of oxidation reaction byproduct MnO_2 particles, preventing effective distribution and contact with contaminants.

This demonstration focused on diminishing the effects of site heterogeneities with respect to the uniformity of oxidant delivery, and managing MnO_2 aggregation and deposition. We demonstrated the use of water-soluble polymers (xanthan gum and sodium hexametaphosphate [SHMP]) to improve the delivery and distribution of permanganate oxidant solutions within heterogeneous contaminated aquifers. Xanthan gum biopolymers have a long history of use in the petroleum industry, and their contribution toward improving the sweep efficiency of injected fluids by minimizing the effects of the aquifer heterogeneities is well-documented (Lake, 1989; Sorbie, 1989 and references therein). SERDP Project ER-1486 verified that xanthan gum can significantly enhance the sweep efficiency of permanganate through heterogeneous media. Additionally, SERDP Project ER-1484 found that SHMP stabilizes MnO_2 particles in solution via electrostatic repulsion, preventing particle aggregation and inhibiting permeability reductions due to in situ deposition. Both of these projects have shown xanthan gum and SHMP to be compatible with permanganate solutions and amenable to co-injection.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The advantages and limitations associated with introducing each polymer to a standard permanganate ISCO operation are presented in Table 1.

Table 1. Advantages and limitations of enhanced permanganate ISCO using water soluble polymers.

Xanthan Gum	
Advantages	Improves injected fluid's sweep efficiency within heterogeneous porous media. Increased injection fluid viscosity promotes mobility reduction in the principal flow direction (longitudinal for vertically installed wells) and encourages transverse fluid movement (or cross-flow) of fluids between strata of differing permeability.
	Improved sweep efficiency results in improved distribution of co-injected remediation agent and improved contact between the amendment and the target contaminant.
	In the presence of permanganate, xanthan gum will slowly oxidize into simple sugars. During the Treatability Study the project team found that, depending on the specific concentrations of oxidant and polymer, the co-injected solution will lose roughly half its initial viscosity in one week after emplacement. Initially, the enhanced viscosity could hydraulically isolate the treatment zone, improving contact times. As the polymer is oxidized the hydraulic properties of the treatment area should be largely restored.
	Xanthan gum costs are approximately 60% of the permanganate costs. Costs relative to permanganate depend on xanthan gum type and concentration employed, which depend on media characteristics. Because of the relatively lower permeability of this demonstration area, relative cost here is higher than may be typical.
Limitations	Increased injected fluid viscosity results in reduced fluid mobility during transport within porous media. "Mobility" refers to the fluid-specific component of hydraulic conductivity. Therefore, a reduction in mobility results in a reduction in hydraulic conductivity. This hydraulic conductivity reduction can limit the rate of fluid injection within shallow aquifer systems.
	Larger polymer molecules can become trapped within narrow pores during transport with porous media, reducing the permeability to polymer and in severe cases to water. This entrapment mechanism becomes apparent as the intrinsic permeability of the porous media decreases and the mean pore diameter approaches the effective hydrodynamic diameter of the polymer molecule (which is generally considered to be about 1 micron (Dominguez and Willhite, 1977)). Permeability reduction compounds the reduced injectivity of the polymer-amended fluid resulting from the increased viscosity. Therefore, the effects of mobility reduction and permeability reduction must be accounted for during implementation design.
	Polymer mixing and filtration equipment costs must be added to the design and treatment costs. Costs for this demonstration, which depend on scale, are ~\$20K for the added equipment.
SHMP	
Advantages	Maintains MnO ₂ particles suspended in solution, inhibiting their deposition in the subsurface. This can result in improved contact with contaminant and increased remediation efficiency.
	Does not react with permanganate therefore there is no additional demand for oxidant.
	Aside from an additional line to introduce SHMP to permanganate solution prior to subsurface delivery, there are no additional modifications to a typical permanganate system design for implementation.
	SHMP costs are approximately 40% of the permanganate costs. Costs relative to permanganate depend on the SHMP concentration employed, which depends on media characteristics. Because of the relatively low permeability of this demonstration area and high concentration of SHMP to be employed, cost here is higher than may be typical.
Limitations	The impacts of adding excess "salt" to the subsurface system are expected to be minimal and harmless, yet they have not been investigated.
	The addition of SHMP will increase total dissolved solids concentrations in the treatment zone and possibly downgradient.

3.0 PERFORMANCE OBJECTIVES

The demonstration's performance objectives, data requirements, success criteria, and results are shown in Table 2. The results are discussed in more detail in Section 6.0.

Table 2. Performance objectives.

Performance Criteria	Data Requirements	Success Criteria (with use of polymer)	Results
Quantitative Performance Objectives			
Increased penetration of oxidant into lower permeability layers/strata	<ul style="list-style-type: none"> - Examination of soil cores for evidence of permanganate or MnO₂ - If LPM of thickness appropriate for discrete groundwater sampling is present, then permanganate ion (MnO₄⁻)/MnO₂ concentrations measured in groundwater over space and time 	<ul style="list-style-type: none"> - 50% longer distance of permanganate penetration into lower permeability layers/strata - 25% higher permanganate concentration at expected time of arrival in each monitoring well - Demonstrated improvement in vertical sweep efficiency within lower permeability layers/strata - Demonstrated improvement in overall vertical sweep efficiency in test plot 	Objective met
Decreased flow bypassing (increased lateral sweep efficiency) of areas of high contaminant mass	<ul style="list-style-type: none"> - Examination of soil cores for evidence of permanganate or MnO₂ in media with high contaminant concentration - Soil core extractions for MnO₂ and measurements of MnO₄⁻ and MnO₂ in groundwater over time and distance - Soil core extractions for contaminant with distance 	<ul style="list-style-type: none"> - 50% lower mass of MnO₂ in given mass of media (indicative of inhibition of deposition that can increase bypass) - 25% greater mobile MnO₂ concentration at given time point in monitoring well - 50% lower mass of contaminant in high concentration cores 	Objective partially met; sweep was improved, however not specifically associated with high contaminant mass
Evaluate long-term potential for and short-term occurrence of contaminant rebound	<ul style="list-style-type: none"> - Contaminant concentrations in groundwater over time and distance - Contaminant concentrations in soil cores pre- and post-treatment 	<ul style="list-style-type: none"> - Data collected and are representative of test plots - Post-treatment groundwater monitoring results remain below baseline concentrations 	Objective partially met
Improved contaminant treatment effectiveness	<ul style="list-style-type: none"> - Contaminant concentrations in groundwater over time and distance from injection - Contaminant mass in soil over time and distance 	Statistically significant reduction in contaminant mass as compared to a control plot	Objective met
Qualitative Performance Objectives			
Decreased impact of MnO ₂ on injection pressure	Injection well pressure over time	No increase in injection pressure attributable to MnO ₂	Objective met
Improved understanding of impacts of polymers on groundwater quality	pH, ORP, key metals, solids concentrations, conductivity, bioactivity	Note differences	Objective met

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4.0 SITE DESCRIPTION

4.1 SITE LOCATION AND HISTORY

MCIEAST-MCB CAMLEJ Operable Unit (OU) 15, Site 88, was selected for the technology demonstration because it best fulfilled the preferred technical criteria, including chloroethene concentration, depth to groundwater, minimum interference, utility access, bulk hydraulic conductivity, and heterogeneous lithology.

The test area is located in Jacksonville, North Carolina. MCIEAST-MCB CAMLEJ covers approximately 236 square miles and is a training base for the United States Marine Corps. The test area is located within OU 15, Site 88, which consists of the former Base Dry Cleaning facility (former Building 25), located approximately 500 feet (ft) east of the intersection of Post Lane Road and McHugh Boulevard. The test area is located within and immediately west of the footprint of the former Building 25 (Figure 1).

Former Building 25 operated as a dry cleaning facility from the 1940s until 2004 when operations ceased and the building was demolished. Five 750-gallon underground storage tanks (USTs) were installed on the north side of the building to store dry cleaning fluids. Initially, Varsol™, a petroleum hydrocarbon-based stoddard solvent, was used in dry cleaning operations at Building 25. Due to flammability concerns, the use of Varsol was discontinued in the 1970s and was replaced with PCE. PCE was stored in a 150-gallon aboveground storage tank (AST) adjacent to the north wall of Building 25, in the same vicinity as the USTs. PCE was reportedly stored in the AST from the 1970s until the mid-1990s. The USTs and AST were removed in November 1995. Facility employees have reported that during this time spent PCE was disposed of in floor drains that discharged into the sanitary sewer system on the north side of the building (Figure 1). Groundwater analytical results identified wide-spread chlorinated solvent contamination (PCE, TCE, and *cis*-1,2-dichloroethene [*cis*-1,2-DCE]), which had impacted the Surficial Aquifer (less than 25 ft below ground surface [bgs]) and the upper portion of the Castle Hayne Aquifer (25-80 ft bgs). A distinct contaminant plume was identified, which suggested Building 25 was the source area. The results also suggested the presence of DNAPL in this area.

4.2 SITE GEOLOGY AND HYDROGEOLOGY

4.2.1 Geology

Southeastern North Carolina and MCIEAST-MCB CAMLEJ are within the Tidewater region of the Atlantic Coastal Plain physiographic province. The MCIEAST-MCB CAMLEJ area is underlain by a westward (inland) thinning wedge of marine and non-marine sediments ranging in age from early Cretaceous to Holocene. Along the coastline, several thousands of feet of interlayered, unconsolidated sediment are present, consisting of gravel, sand, silt, clay deposits, calcareous clays, shell beds, sandstone and limestone that was deposited over pre-Cretaceous crystalline basement rock.

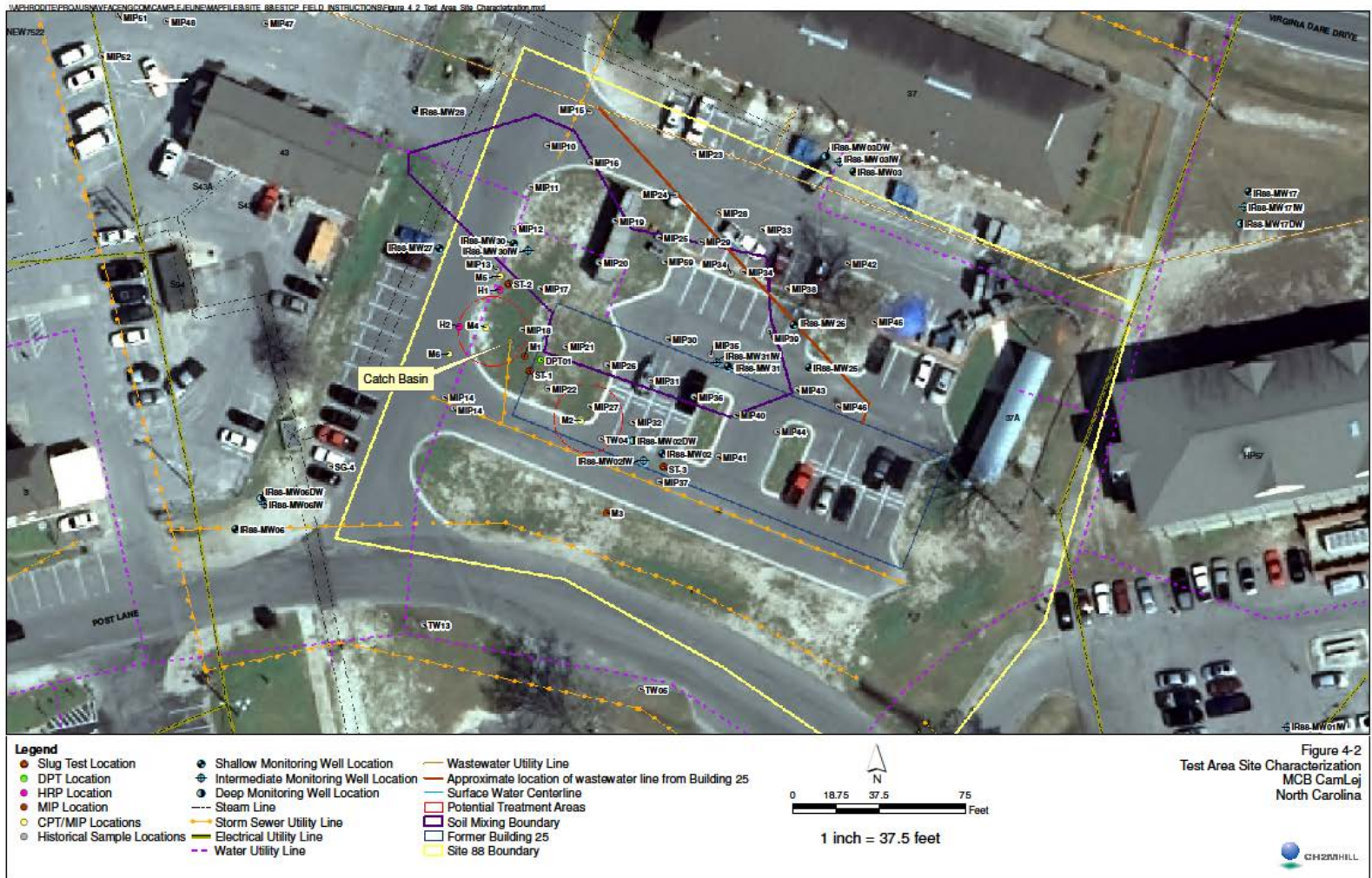


Figure 1. Test area at MCIEAST-MCB CAMLEJ, NC, OU 15, Site 88.

Site 88 is underlain by a thick sequence of coastal plain soils consisting of unconsolidated sands, silts, clays, and partially indurated shelly sands. Soils within the Surficial Aquifer are generally comprised of silty sands, ranging in thickness from 20 to 30 ft, which overlie a discontinuous layer of clayey silt or clay approximately 20 ft bgs. A clayey silt and clay confining layer, ranging in thickness from 4 to 10 ft, underlies the former location of Building 25 at a depth of approximately 20 ft bgs and extends westward as far as Building 3, whereupon it pinches out. Within the Castle Hayne Aquifer, a fine grained layer overlies massive beds of fine to medium grained sand with sporadic zones of partial cementation and shell fragments extending to a depth of roughly 180 ft bgs. At Site 88, the Castle Hayne Aquifer is divided into the upper Castle Hayne (25-80 ft), the middle Castle Hayne (80-130 ft), and the lower Castle Hayne (130-180 ft). A plastic clay layer, known as the Beaufort confining unit, was encountered beneath the Castle Hayne Aquifer.

The data collected during site characterization indicates alternating fine grained silty sand and sand to approximately 20 ft bgs in the vicinity of the test area. The fine grained sediments are underlain by a more dense silty clay and clay layer approximately 7 to 12 ft thick to a depth of approximately 30 ft bgs. Below this unit are alternating layers of silty sand and sand. The sands become more dominant with depth and fewer fines are present, generally between 40 to 60 ft bgs. The boring log for deep monitoring well 88-MW02DW, located adjacent to the test area, indicates that fine grained silty sand is again present between 60 to 88 ft bgs, which is underlain by a layer of partially cemented sand and shells exists from 88 to 90 ft.

4.2.2 Hydrogeology

The hydrogeologic setting at Site 88 is that of a two aquifer system, the Surficial Aquifer and the Castle Hayne Aquifer, with the two aquifers typically separated by a low permeability clayey silt aquitard (Duke, 1999). This low permeability unit is present under former Building 25 within the test area, and, as noted above, is discontinuous to the west of former Building 25.

In November 2009, depth-to-water measurements were taken across Site 88. In the vicinity of the test area, the water table was found to occur from 7.25 to 10.10 ft bgs. The depth to water in monitoring wells screened within the Upper Castle Hayne Aquifer in the vicinity of the test area, ranged from 14.46 to 15.62 ft bgs.

The water table surface of the surficial aquifer is highly variable, which is likely due in part to the heterogeneous nature of the shallow sediments, and also the anthropogenic effects relating to the soil mixing activities that occurred previously nearby. Shallow groundwater flow in the test area is to the southwest, with a horizontal hydraulic gradient of approximately 0.002 ft/ft. A downward vertical hydraulic gradient of approximately 0.25 ft/ft between the Surficial Aquifer and the Upper Castle Hayne Aquifer in the test area was calculated.

The Upper Castle Hayne Aquifer's groundwater flow pattern is less complex than that of the Surficial Aquifer, with groundwater flow generally to the west with an approximate horizontal hydraulic gradient in the vicinity of the test area of 0.0004 ft/ft. A downward vertical gradient of 0.0015 ft/ft between the Upper Castle Hayne and Middle Castle Hayne Aquifers within the test area was calculated, based on the November 2009 depth-to-water measurements.

A pneumatic slug test method was employed through direct push technology (DPT). Steel rod piezometers were installed in November and December 2009 at three locations across the test area, ST-1, ST-2, ST-3 as shown in Figure 1. Hydraulic conductivity was calculated using the Hvorslev method. The hydraulic conductivity values calculated at each slug test location are summarized in Table 3. The hydraulic conductivity in the Surficial Aquifer ranged from 1.5 ft/day to 5.2 ft/day, with an average hydraulic conductivity of 2.8 ft/day. The hydraulic conductivity in the Upper Castle Hayne Aquifer just below the confining unit ranged from 0.9 ft/day to 4.9 ft/day, with an average hydraulic conductivity of 2.5 ft/day.

4.3 CONTAMINANT DISTRIBUTION

Based on the chemical data gathered for Site 88, former Building 25 is the source of the chlorinated volatile organic compounds (VOC) that are currently observed in the groundwater within the shallow, intermediate, deep and very deep aquifer zones. The contaminants of concern (COC) for Site 88 are PCE and its anaerobic biodegradation daughter products TCE, *cis*-1,2-DCE, and vinyl chloride. Data obtained from groundwater samples collected as part of the remedial investigation (RI) in August 2007, indicate the maximum chlorinated VOC concentration within the shallow aquifer in the vicinity of former Building 25 and the test area, was reported at well IR88-MW02 with PCE and *cis*-1,2-DCE concentrations of 12,000 µg/L and 13,000 µg/L, respectively. Concentrations in the source area decrease significantly with depth.

During site characterization activities conducted in November and December 2009, membrane interface probe (MIP) profiling was conducted at six locations to delineate contaminant concentrations within the test area. MIP results indicate that the highest contaminant concentrations in the Surficial Aquifer exist from 16 to 18 ft bgs at location M1 (Figure 1), immediately above an apparent confining unit. MIP results in this area are indicative of DNAPL. Results suggest that contamination in the shallow zone extends approximately 45 ft to the southeast towards location M2 (Figure 1). MIP results consistently indicate higher contaminant concentrations throughout the Upper Castle Hayne Aquifer between 40 and 50 ft bgs at locations M1, M2, and M3 (Figure 1). Again, the highest contaminant concentrations were detected at location M1 from approximately 33 to 35 ft bgs, immediately below an apparent confining unit. In both the Surficial and Upper Castle Hayne Aquifers, contaminant concentrations appear to decrease significantly to the west.

Two groundwater and three soil samples were collected from a soil boring during characterization. Analytical results are summarized in Tables 4 and 5. PCE and *cis*-1,2-DCE were detected at maximum concentrations of 7100 micrograms per kilogram (µg/kg) and 10,000 µg/kg, respectively, in the soil sample collected immediately above the confining unit. Below the confining unit, PCE ranged from below the laboratory detection limit (720 µg/kg) to 1300 µg/kg and *cis*-1,2-DCE ranged from below the laboratory detection limit (5.2 µg/kg) to 22 µg/kg. PCE was detected in the groundwater sample collected immediately above the confining unit (14-16 ft bgs) at a concentration of 220,000 µg/L. Below the confining unit (33-35 ft bgs), PCE was detected at a concentration of 230,000 µg/L. These groundwater concentrations are indicative of DNAPL, which is consistent with observed site conditions described above and the results of the MIP data collected from M1 adjacent to DPT01. Site characterization results for the test area are summarized in Table 6.

Table 3. Hydraulic conductivity (k) calculated at each slug test location.

Location	Interval Depth (ft bgs)	Test	Conductivity Results (ft/day)	Average Conductivity (ft/day)
ST-1	33-35	1	4.9	4.6
		2	4.8	
		3	4.2	
	38-40	1	2.6	2.5
		2	2.5	
		3	2.5	
	43-45	1	9.8	9.8
		2	9.8	
		3	9.8	
ST-2	14-16	1	2.2	2.0
		2	1.5	
		3	2.1	
	33-35	1	0.9	1.0
		2	1.0	
		3	1.0	
		4	1.0	
	42-44	1	6.1	6.0
		2	6.1	
		3	5.9	
		4	5.9	
		5	6.0	
	47-49	1	10.7	10.9
		2	10.7	
		3	11.0	
		4	11.0	
	54-56	1	8.7	9.0
		2	8.7	
		3	9.1	
		4	9.4	
		5	9.2	
		6	9.2	
	61-63	1	2.3	2.8
		2	2.4	
3		2.8		
4		3.7		
ST-3	14-16	1	5.2	4.0
		2	2.7	
	33-35	1	1.5	1.5
		2	1.4	
	45-47	1	16.6	17.0
		2	16.4	
		3	18.1	
	54-56	1	8.2	7.4
		2	7.5	
		3	8.0	
		4	6.9	
		5	6.3	
	60-62	1	3.9	3.2
2		2.5		
ST-4 (offset from ST-1)	14-16	1	0.6	0.6
		2	0.6	
		3	0.6	
		4	0.5	

**Table 4. Analytical results for contaminants
(gas chromatography – mass spectroscopy [GC-MS]) in soils.**

Sample ID	DPT01-16-18	DPT01-33-35	DPT01-53-55
Sample Date	11/12/2009	11/12/2009	11/12/2009
VOCs (µg/kg)			
2-Butanone	49	14 U	10 U
Acetone	2300 U	48	40
Carbon Disulfide	14	14 U	10
Tetrachloroethene	7100	720 U	1300
Toluene	7.6	6.9 U	5.2 U
Trichloroethene	600	12	540 U
<i>cis</i> -1,2-DCE	10,000	22	5.2 U
<i>trans</i> -1,2-DCE	21	6.9 U	5.2 U
Vinyl chloride	38	6.9 U	5.2 U

U – Analyte not detected
trans-1,2-DCE = *trans*-1,2-dichloroethene

Table 5. Analytical results for contaminants (GC-MS) in groundwater.

Sample ID	DPT01-14-16	DPT01-33-35
Sample Date	11/12/2009	11/12/2009
VOCs (µg/L)		
Acetone	75,000	50,000 U
Tetrachloroethene	220,000	230,000
Trichloroethene	10,000 U	13,000 U
<i>cis</i> -1,2-DCE	10,000 U	13,000 U
Vinyl chloride	10,000 U	13,000 U

U – Analyte not detected

Table 6. Site characterization summary.

Depth Interval of Study Area	7 ft bgs to 18 ft bgs	33 ft bgs to 62 ft bgs
Predominant soil type	Sand	Sand
Fine-grained soil type	Silty sand (7 to 11 ft bgs) Sand (11 to 18 ft bgs)	Silty sand (33 to 40 ft) Sand (40 to 60 ft bgs)
Depth to water, ft bgs	7.5	15.5
Hydraulic conductivity, ft/day	0.5 to 5.2 Average: 1.8 Heterogeneity: 10.4 Vertical conductivity: 0.00013 Anisotropy: 13,846	0.9 to 18.1 Average: 6.6 Heterogeneity: 20.1
Hydraulic gradient, ft/ft	Horizontal: 0.002, southwest Vertical: 0.25, downward	Horizontal: 0.0004, west Vertical: 0.0015, downward
PCE concentration in groundwater, µg/L	220,000	230,000
PCE concentration in soil, µg/kg	7100 (16-18 ft bgs)	ND<720 (33-35 ft bgs) 1300 (53-55 ft bgs)
Depth interval with greatest mass of contaminant as indicated by MIP, ft bgs	16 to 18	33 to 35
Visual or analytical evidence of DNAPL?	Yes	No

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Two plots were used to implement the demonstration and achieve the project objectives. One was a control plot (permanganate only), and one was a SHMP + xanthan test plot (permanganate + SHMP + xanthan; hereafter referred to as permanganate + polymer) (Figure 2). An injection well was installed in the center of each test plot for substrate delivery. Multi-level sampling (MLS) wells were installed at various distances from the injection wells and screened at four depth intervals to monitor the water quality of the targeted zones. Injection operations were initiated sequentially, starting with the control plot and then the test plot. At the end of injection for each plot a DPT rig was mobilized to collect depth-discrete and continuous soil cores to characterize the presence/absence of permanganate and to provide subsamples for off-site analysis (as described in Section 5.5).

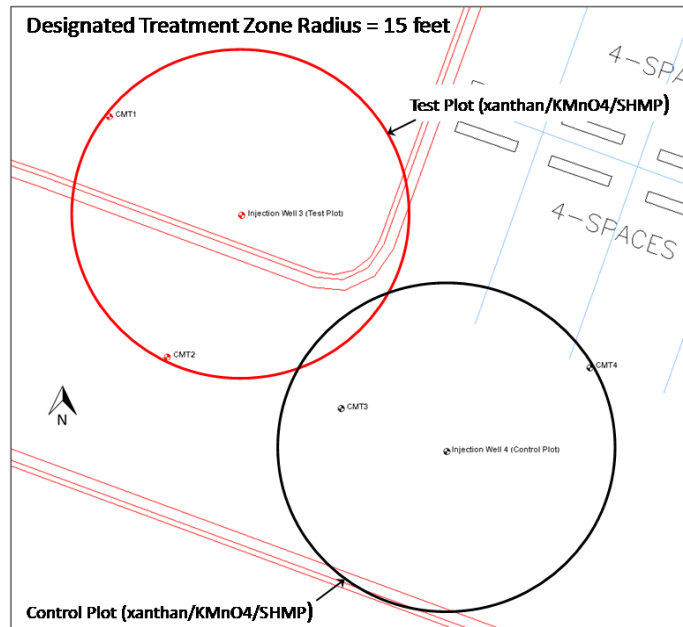


Figure 2. Layout of demonstration plots.

5.1.1 Control Plot

The control plot consisted of one injection well located at the center of the plot and two MLS wells installed around the perimeter of the plot at a distance of approximately 15 ft from the injection well. The injection well was screened from 35 to 55 ft bgs within the upper Castle Haynes formation. Both MLS wells were installed to sample the same depth interval of the injection well and included four sampling ports with this depth interval. Specific MLS well screens were installed to target individual stratigraphic units within this interval. Groundwater samples were collected from both MLS wells prior to, during and after injection operations. Additional groundwater and soil samples were collected 1-year post-treatment.

5.1.2 Polymer Test Plot

The test plot also included a single injection well located at the center of the plot (screened 35-55 ft bgs within the upper Castle Haynes formation) and two MLS wells. As was the case for the control plot, the two test plot MLS wells were installed at a distance 15 ft from the injection wells with four depth-discrete sampling ports. The depths and screen lengths of the MLS wells sampling ports will be determined in the field based on site stratigraphy. Similar to the control plots, the MLS well screens targeted individual isolated stratigraphic units and/or zones with unique permeability. Again, groundwater samples were collected from both MLS wells prior to, during and after injection operations. Additional groundwater and soil samples were collected 1-year post-treatment.

5.1.3 Process Control and Injection System

As detailed in the project's Final Technical Report, an automated process/flow system was constructed to allow unmanned 24-hour injection operations. For the polymer-amended ISCO (PA-ISCO) formulation demonstrated, this 24-hour injection capability was necessary to provide a consistent subsurface fluid viscosity. A schematic diagram of the process/flow system used to deliver sodium permanganate (NaMnO_4), xanthan gum, and SHMP to the demonstration plots is presented as Figure 3. The dosing equipment consisted of standard off-the-shelf construction materials (e.g., polyvinyl chloride [PVC] piping, flexible hoses with cam lock fittings, and poly tanks), inline mixing and monitoring equipment, and basic controls for automated 24-hour operation and shutdown capability. All equipment was contained within individual secondary containment basins. The injection flow system designed to allow for an injection rate between 0.5 and 10 gallons per minute (gpm) under a 50 pounds per square inch gauge (psig) backpressure at the wellhead. The various chemical metering systems were designed to maintain a set dosing rate regardless of the rate of injection. The rate of injection was fixed at 6 gpm for both demonstration plots as a basis for direct comparison of sweep-efficiencies with and without polymer.

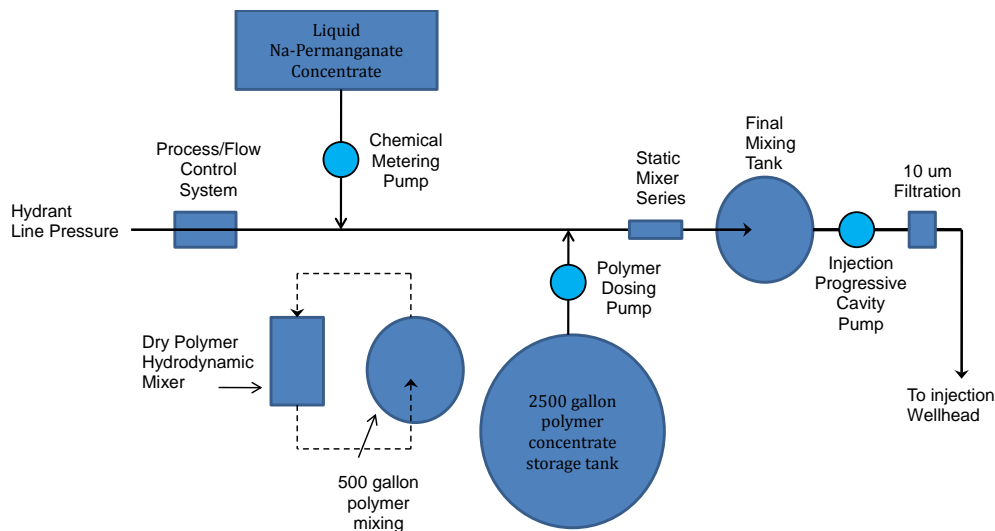


Figure 3. Schematic of the PA-ISCO demonstration process equipment.

5.1.4 Post-Treatment Operations

Post-treatment operations consisted of collecting soil samples (detailed in Section 5.5) and groundwater samples to characterize the subsurface distribution of the injected permanganate solutions and additional groundwater quality parameters used to further evaluate this novel PA-ISCO technology. The first post-treatment sampling event occurred within 8-12 hours post-injection (both plots) and the final sampling event took place approximately 1-year post treatment.

5.2 BASELINE CHARACTERIZATION

Baseline characterization activities took place in two parts: (1) preliminary site screening activities and (2) sampling activities that took place during the well field installation after the site was selected for the demonstration. Both activities allowed an assessment of pre-treatment site conditions that contributed to implementation design calculations

5.2.1 Baseline Soil Sampling

During well installation, baseline cores were collected from each plot to characterize pre-treatment conditions. Soil samples were analyzed for VOCs, natural oxidant demand, total organic carbon (TOC), grain size distribution, pH, oxidation/reduction potential (ORP), cation exchange capacity (CEC), and manganese content. Baseline sampling allowed for collection of media used for treatability studies described in Section 5.3 and provided reference data to compare changes in groundwater quality due to the demonstration, as discussed in Section 5.7.

5.2.2 Baseline Groundwater Sampling

Prior to implementation of the demonstration, groundwater samples were collected from each MLS well within each plot to measure pre-treatment water quality using the low-flow sampling techniques that are standard for MCIEAST-MCB CAMLEJ. Data are discussed in Section 5.7

5.2.3 Potable Water Injection Testing

Step-injection tests were performed using the two central injection wells (i.e., IW3 and IW4) to evaluate the initial hydraulic properties of each plot and to optimize injection flow rates used during the demonstration. In these tests, potable water was injected at a constant volumetric rate while the well pressure response was monitored and recorded using an in-well pressure transducer (Level Troll 500, In-Situ, Inc.). Injection continued until the pressure response to injection stabilized. Thereafter, the rate of injection was increased and the pressure within the well was again monitored and recorded until the pressure response stabilized. This procedure continued until stable pressure responses were collected at 5-6 flow rates. Calculated transmissivities were observed to be similar for both demonstration plots, suggesting a similar degree of permeability heterogeneity exists between these test plots. This result is significant for this demonstration in that the similar heterogeneity condition provides a good basis for comparing sweep-efficiencies between the control and test plots. The results of this hydraulic testing are presented in Tables 7 and 8, in which transmissivity and hydraulic conductivity are calculated at each flow rate condition.

Table 7. Results of the step-injection hydraulic testing (test plot, IW3).

Q (gpm)	P (PSI)	P (ft)	T (ft ² /day)	K (ft/day)	K (cm/sec)
0	0				
4	1.94	4.47	172.10	6.88	2.43E-03
6	3	6.92	166.94	6.68	2.36E-03
10	5.3	12.22	157.49	6.30	2.22E-03
15	8.1	18.68	154.57	6.18	2.18E-03
22.2	11.8	27.22	157.03	6.28	2.22E-03

Note: P (ft) is the pressure head in feet of water. K determined using 25 ft as the saturated thickness (b), as $K = T/b$.
PSI = pounds per square inch

Table 8. Results of the step-injection hydraulic testing (control plot, IW4).

Q (gpm)	P (PSI)	P (ft)	T (ft ² /day)	K (ft/day)	K (cm/sec)
2	1.3	3.00	128.41	5.14	1.81E-03
3.2	2.1	4.84	127.19	5.09	1.79E-03
5	3.4	7.84	122.75	4.91	1.73E-03
7	4.8	11.07	121.72	4.87	1.72E-03
10	6.6	15.22	126.47	5.06	1.78E-03
15	10.2	23.53	122.75	4.91	1.73E-03

Note: P (ft) is the pressure head in feet of water. K determined using 25 ft as the saturated thickness (b), as $K = T/b$.

5.3 TREATABILITY STUDY RESULTS

The objectives of the Treatability Study were to:

1. Determine an optimal solution formulation for demonstrating polymer-enhanced delivery and sweep-efficiency improvement at our selected test site.
2. Collect rheological and transport related data needed to support implementation design.
3. Test our proposed polymer/oxidant mixing strategy at the bench-scale prior to scaling up this strategy at the field scale.

5.3.1 Solution Formulation

Evaluations that were conducted and described in the ER-200912 Treatability Study Report, which relate to the solution formulation are briefly described below.

- Evaluation of polymer/oxidant solution viscosities as a function of applied shear rate for several polymer/oxidant solution mixtures to understand the effect of permanganate salinity and oxidation on solution viscosity. Results indicated that for a given xanthan gum concentration, initial solution viscosities were not greatly sensitive to permanganate concentration within a range of 500 – 5000 milligrams per liter (mg/L) permanganate.
- Measurement of the viscosity/shear rate function over time. Results indicated that the most rheologically stable combination of xanthan gum and permanganate were those for 500 mg/L permanganate, regardless of the xanthan concentration. However, a 500 mg/L permanganate concentration was determined to be too low for the oxidant demand of

the Castle Hayne sediments (i.e., sediment oxidant demand averaged 0.8 grams per kilogram [g/kg]). The use of the conceptual design for ISCO (CDISCO) design tool (developed under ESTCP Project ER-200623, In Situ Chemical Oxidation for Groundwater Remediation: Technology Practices Manual) suggested that a 5000 mg/L permanganate concentration was optimal to meet at 15 ft radius objective within 5 days of operation in the field (scheduling and budget constraint).

- One-dimensional column tests were also performed to characterize the potential for permeability reduction as a result of polymer entrapment and/or manganese dioxide plugging, which is important to understand when selecting the injection rate. Although permeability reduction within the Castle Hayne's sediments was not significant, the addition of SHMP helped to further minimize permeability reduction. Based on these results, SHMP was included in the polymer/oxidant solution during field-scale implementation at a concentration of 5000 mg/L.
- Treatability tests were performed to evaluate the ability of SHMP to control MnO₂ generated as a result of permanganate oxidation of PCE and results indicated 5000 mg/L SHMP was favorable for the 5000 mg/L permanganate and the site-specific conditions. Transport evaluations in columns packed with site media and conducted with and without SHMP verified that SHMP decreased MnO₂ deposition and minimized pressure build-up within the media.

5.3.2 Estimating Maximum Injection Pressures

The maximum allowable injection pressure for the upper Castle Hayne Formation was estimated using matrix failure calculations by first calculating the pressure required to initiate formation damage. Injection operations within both test plots would be operated below this maximum pressure condition. For the site-specific conditions, the maximum injection pressure for the upper Castle Hayne aquifer was determined to be 68 PSI (gauge pressure applied at the wellhead). A 40% factor of safety was applied to account for potential well completion irregularities and errors associated with the selection of the soil friction angle. This reduces the maximum injection wellhead pressure to 50 PSI. Therefore, the injection system and all associated plumbing for this demonstration was designed to accommodate, at most, a 50 PSI backpressure at the wellhead.

5.3.3 Optimizing Injection Flow Rates and Polymer Concentration

To provide the best comparison of sweep-efficiency between the control plot and the test plot, the injection flow rate in both plots should be the same. Therefore, our objective here was to optimize the injection rate for the polymer-amended solution (i.e., test plot) first. Based on the analyses and calculations performed, we determined a 1000 mg/L xanthan gum solution (containing 5000 mg/L NaMnO₄) could be injected into the upper Castle Haynes formation at a maximum rate of 6 gpm before meeting the maximum formation pressure estimated in Section 5.2.3.

However, preparing a concentrated polymer solution in the field with which to meter in a 1000 mg/L solution into the process control system was determined to be impractical. Furthermore, a 1000 mg/L xanthan solution would provide a range of fluid viscosities that were in excess of the optimal range needed to demonstrate sweep-efficiency improvement at this site (i.e. between 10

and 30 centipoise [cP]). Utilizing equations that relate the porous media equivalent shear rate to the Darcy velocity, it was determined that a 500 mg/L xanthan gum solution injected at a rate of 6 gpm provided the ideal range of fluid viscosities within the radius of influence (ROI) of the test plot. At 6 gpm, it was additionally determined that a 1 pore volume (PV) injection would require 5 days (the PV of each demonstration plot was estimated to be approximately 59,000 gallons or 8000 cubic feet [ft³]), which was additionally optimal for our demonstration time frame. Therefore, the results of these calculations and those performed during our treatability study work indicated that the optimal solution formulation for this demonstration would contain a 500 mg/L xanthan gum concentration, 5000 mg/L NaMnO₄, and 5000 mg/L SHMP.

5.4 FIELD TESTING

Field operations commenced on October 20, 2010, with the delivery of the process control (skid-mounted, pre-constructed) and mixing systems (also skid mounted), NaMnO₄ concentrate, xanthan gum, and SHMP. The process/control system and each additional sub-system was connected on site and tested prior to initiating injection operations. A portable diesel generator supplied power for the electronic systems and overhead lighting was rented to allow operations at night.

5.4.1 Control Plot Operations

Control plot operations began on October 28, 2010, following step-injection testing. The permanganate chemical metering pump was set to dose the 40% sodium permanganate concentrate at a rate that provided a 5000 mg/L permanganate concentration leaving the process system. At startup and throughout the 5-day injection period, liquid samples were collected from a sampling port located on the injection wellhead manifold. Permanganate concentration was measured on site using a portable ultraviolet-visible spectrophotometer (UV/Vis) (HACH DR/2010). Solution standards were prepared on site prior to injection operations to calibrate the UV/Vis spectrophotometer. Samples were collected from additional points along the process and injection system during the initial phases of injection to help fine tune the rate of dosing at the metering pump. The rate of injection was fixed at 6 gpm. Control plot injection was terminated on November 2, 2010, which constituted a 5-day (or 1 PV) injection duration.

Prior to startup and throughout the injection period, groundwater samples were collected at the two multi-level monitoring well locations positioned at the edge of the test plot using low-flow sample collection methods. Water quality parameters and permanganate concentrations at each of the four depth intervals were monitored throughout the injection period.

5.4.2 Test Plot Operations

Mechanical problems with the gear pump used to recirculate and prepare the xanthan gum/SHMP concentrate solution necessitated a delay of further field activities until the pump could be repaired. Field staff remobilized to the site on December 5, 2010, to initiate test plot operations. Test plot operations began with the preparation of the xanthan gum/SHMP concentrate solution. This concentrate was prepared within the 500 gallon polymer mixing tank and then transferred into the 1500 gallon poly storage tank. The working volume of each batch prepared was 350 gallons. Water was added to the batch tank via a dedicated bypass line on the process control skid and a volumetric totalizer was used to measure the volume of water added.

Xanthan gum and SHMP were introduced as dry powders to the stainless steel hopper that was mounted upon the hydrodynamic mixing unit. A total of 14.6 pounds of xanthan gum, and 87.5 pounds of SHMP powder, were introduced per batch to provide a concentrated solution containing 5000 mg/L xanthan gum and 30,000 mg/L SHMP. These powdered components were weighed on site using a top-loading scale. Once the dry xanthan and SHMP were added to the batch, the hydrodynamic mixer continued to re-circulate the concentrated solution within the batch tank for a period of 1.5 hours before the batch was transferred to the 1500 gallon storage tank. A total of three concentrate batches were prepared prior to initiating injection operations to provide enough fluid for overnight injection. Additional 350 gallon batches were then prepared daily during the course of injection operations.

The polymer dosing pump (progressive cavity pump) was set for a 1/10 dilution of the polymer concentrate solution, providing a 500 mg/L xanthan gum and a 3000 mg/L SHMP solution upon exiting the process flow system. As was the case for the control plot, the NaMnO₄ concentrate was metered down to deliver a 5000 mg/L concentration upon exiting the process flow system. The rate of injection of the PA-ISCO fluid formulation was set at 6 gpm, in keeping with the rate used for the control plot.

Test plot injection was initiated on December 8, 2010. As was the case for the control plot, samples of injected fluid were collected from the injection wellhead manifold throughout the injection period and analyzed for permanganate concentration. In this case, the samples were also measured for solution viscosity using a portable viscometer (Brookfield LVDV-E). Viscosity standards were prepared on site using various dilutions of the polymer concentrate solution. Test plot injection ended on December 13, 2010, for a 5-day (or 1 PV) injection.

5.5 SAMPLING METHODS

Post-treatment samples were collected following standard methods of sampling and analysis. Samples were collected for each continuous multichannel tubing (CMT) well and from each port within the CMTs. Groundwater samples were collected from each plot during and immediately post-treatment. A total of 12 DPT sediment cores were collected per demonstration plot. These sediment cores were collected at 5-ft intervals between 20 and 60 ft bgs. This coring interval contained the lower portion of the silty clay upper confining unit, the upper Castle Hayne Formation, and the upper portion of the cemented sands that acted as a lower confining unit within the upper Castle Hayne. The sediment cores were additionally logged for sediment stratigraphy and the presence and absence of permanganate (i.e., purple color and/or MnO₂ staining). A photographic example of the sediment cores collected is presented in Figure 4.

As shown in Figure 5, these cores were collected along three transects centering on the injection well in both demonstration plots. This approach provided a means of investigating the lateral distribution of injected permanganate and served to allow a volumetric assessment of sweep-efficiencies between the two demonstration plots. DPT sediment coring began within 12 hours of injection cessation and continued for up to 3 days post-injection.

One year post-treatment, an additional round of groundwater samples was collected from each well depth. Also, three DPT cores were collected for each plot at a distance approximately 5, 10, and 15 ft from injection (shown as A, B, and C for the test plot and X, Y, and Z for the control plot in Figure 5).



Figure 4. Sediment cores used to vertically characterize the presence or absence of permanganate within the control plot.

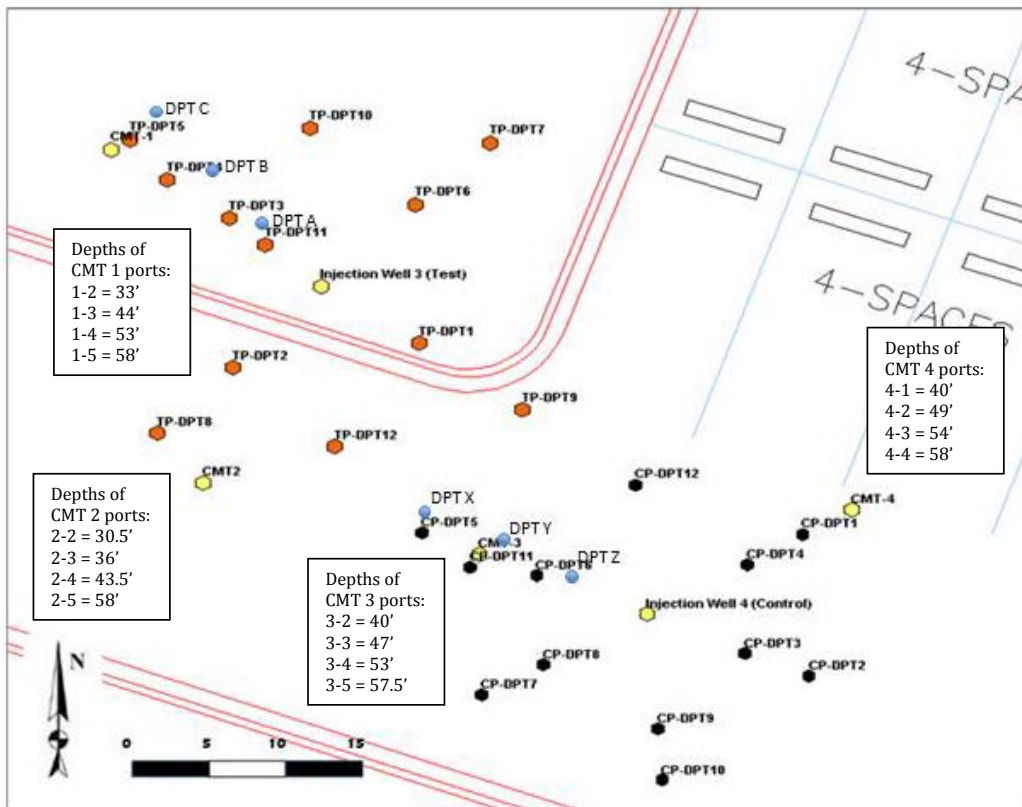


Figure 5. Location of DPT cores.

CP-DPT indicates control plot cores. TP-DPT indicates test plot cores. DPT A, B, and C are 1-year post-treatment cores collected for the test plot and DPT X, Y, and Z are 1-year post-treatment cores collected for the control plot.

5.6 SAMPLING RESULTS

5.6.1 Permanganate Distribution and Sweep Efficiency

Sediment stratigraphy and permanganate presence or absence data collected during the DPT coring events were compiled and reconstructed in cross-sections for each investigation transect to better visualize the distribution of permanganate. A map showing the locations of these transect cross-sections is provided as Figure 6. One representative cross-section each for the control plot and test plot are presented in Appendix B as Figures B-1 and B-2.

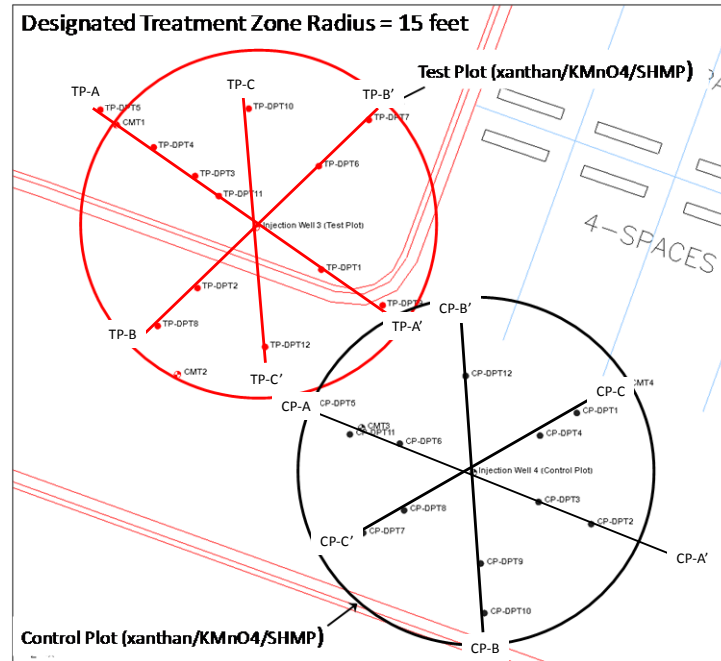


Figure 6. Location of DPT transects.

The permanganate presence or absence data and the permanganate and MnO_2 concentration data collected during each post-injection coring event were used to produce a three-dimensional (3D) dataset representing the 3D distribution of permanganate at the end of injection operations. This dataset was input into the Groundwater Modeling System (GMS) (v. 8.1) software package. DPT location coordinates were determined from distance measurements taken in the field during the coring event and utilizing triangulation calculations from the known locations of nearby monitoring wells. Ordinary kriging of the permanganate dataset was then used to provide a 3D volumetric representation of the distribution of permanganate within both demonstration plots. In both cases the experimental variogram was a general semivariogram utilizing 8 lags with a 2 ft separation distance. GMS could not provide a cylindrical grid space. Therefore, a square (or cube) grid space (dimensions: $X=28$ ft, $y=28$ ft, $z=-35$ ft) was used to represent the control volume for each demonstration plot. Ordinary kriging of the permanganate data was used to populate the grid volume. The results of this kriging procedure are presented as isosurface projections in Appendix B as Figures B-3 and B-4.

Control Plot Results: In the absence of polymer addition, it was anticipated that the injected permanganate solution would follow paths of least resistance associated with the higher

permeability sands. However, upon examining the control plot cross-sections it is clear that injected permanganate also penetrated the less permeable finer sands and silty sands within the treatment zone. This result negates meaningful statistical correlation between the presence of permanganate and media permeability based on media textural classification for this site. Closer examination of the DPT boring logs, however, indicated that the presence of permanganate within the upper Castle Hayne formation sediments is more closely related to the vertical location of sediments that were observed in the core borings to be “loose and saturated”. These sediments were observed to be very fluid and, in many cases, were found to be positioned between more densely compacted sediments of similar grain size (i.e., textural category) within the collected cores and appear to have provided preferential flow paths for injected fluid propagation. The occurrence of variable density depositional facies is typical of the Tidewater region of the Atlantic Coastal Plain and appears to be a common feature of the upper Castle Hayes sediments in the area of the demonstration site.

The distribution of permanganate becomes more vertically discontinuous with distance from the injection well and after a 1 PV injection, permanganate occurred within distinct depth intervals at a distance of 11 ft from the point of injection. In transect cross-section CPB-CPB', a more vertically continuous occurrence of permanganate was observed at boring CP-DPT12. It is likely that the bulk of the injected permanganate followed this preferential flow path to the north of the control plot and outside the control plot boundary in the vicinity of CP-DPT12.

In the absence of polymer addition the injected permanganate did not extend to the eastern, southern, and western edges of the control plot volume. Rather, it appears that the injected permanganate preferentially flowed toward and exited the control volume to the north during the injection period. These results speak to the degree to which permeability heterogeneity can control the distribution of injected fluids within even a moderately heterogeneous aquifer such as the upper Castle Hayne. Mitigating this type of preferential flow on the subsurface distribution of injected remedial fluids is a key function of viscosity-modification via polymer amendment.

Integration of the isosurface contours within the grid domain (for permanganate concentrations >0 mg/L) provided the total volume swept within the control volume. This swept volume divided by the total volume of the simulation domain provides the sweep efficiency for the permanganate treatment in the absence of polymer addition. The volumetric sweep efficiency for the control plot injection was thus determined to be 33%.

Test Plot Results: The subsurface distribution of permanganate within the test plot is significantly more uniform and vertically continuous for the polymer-amended fluid, suggesting a more uniform displacement front during injection. Also, contrary to the results of the control plot, the distribution of permanganate is observed to be less dependent on the locations of loose and saturated sediments. It appears, then, that the addition of polymer to the permanganate fluid formulation mitigated the bypassing of strata within the heterogeneous aquifer, regardless of the degree of compaction of the sediments, and contacted more of the soil within the treatment volume.

The addition of polymer to the injected permanganate solution provided improved sweep efficiency compared to the control plot injection. While some preferential flow is observed

within portions of the test plot volume, the overall distribution of permanganate was greatly improved. The sweep efficiency for the test plot injection was determined to be 67%, or a 109% improvement over the control plot injection (i.e., no polymer case).

5.6.2 VOCs in Soil and Groundwater

PCE concentrations in groundwater changed very little relative to the initial concentration over the duration of delivery and 1-year post-treatment in the test plot. It is likely that the concentrations did not change during delivery because permanganate did not reach CMTs 1 and 2 during the 5-day delivery period (although it was found within 1-2 ft upon coring). PCE concentrations in the control plot decreased some during delivery in CMT-3, and the decreases generally correspond with the arrival time of the permanganate signature in those well ports. The TCE pattern (or lack thereof) is similar to the PCE, in general.

Both the test and control plots show lower VOCs concentrations in soil core samples in areas where permanganate is present relative to those where permanganate is not present. In both plots, the effectiveness of treatment generally decreased with distance from injection. This is anticipated in ISCO treatment because the distances closer to injection receive, overall, a greater number of PVs of oxidant solution for a longer duration than those distances on the periphery. In comparing the results of the two plots, it is important to note that the test plot was more significantly contaminated than the control plot prior to treatment. The test plot experienced twice the sweep efficiency of the control plot and the overall treatment effectiveness in the test plot is greater. Example data are shown in Appendix B as Figures B-5 for the test plot and Figure B-6 for the control plot.

Because the demonstration/validation was conducted at the pilot scale over a short delivery period (as per scope, project duration, and funding), we did not anticipate complete concentration and/or mass reduction for this particular plot. The site media had a relatively high organic carbon fraction ($f_{oc}=0.02-0.07\%$), with the potential for the majority of contaminant mass to be associated with the solid phase, which in turn serves as a source for groundwater contamination. Also, because of the high organic carbon content, the media exerted a significant demand for the oxidant. At the full scale, these site characteristics would typically call for multiple injections of oxidant to address desorbed mass as the sorbed phase re-equilibrates with the aqueous phase. Furthermore, these conditions call for delivery of multiple PVs of solution, requiring a longer injection duration than was practicable for this demonstration. The primary focus of the design, implementation, and subsequent monitoring for this demonstration/validation was the enhanced delivery of the oxidant via viscosity modification by the addition of water soluble polymers. While contaminant treatment effectiveness was captured in the performance criteria set for the demonstration, these criteria were established prior to site selection and characterization.

5.6.3 Groundwater Quality

Numerous groundwater quality parameters were measured in both soil and groundwater samples over time. There was little change in pH with treatment in either the test or the control plot. The oxidation-reduction potential, total solids, and conductivity values corresponded with arrival of permanganate in the control plot, where arrival occurred at different sampling times for each depth, indicating the preferential flow of the permanganate. In the test plot, these geochemical

signatures of permanganate oxidation were not measured in groundwater from the test plot indicating that the oxidant's influence did not span the 15 ft between the injection and monitoring wells. Oxidant, however, was found just 1-2 ft from the monitoring wells in the soil cores.

Based on the differences in ORP, conductivity, and total solids concentrations of both the test and control plots, and the fact that permanganate was observed in soil cores collected only 1-2 ft from the CMTs of the test plot, it is apparent that the oxidant travel with polymer present is retarded overall relative to the preferential travel without polymer present. This is expected. The more viscous polymer solution travels more uniformly and through a greater percentage of the total volume of the subsurface due to the lack of preferential flow and movement into the less permeable layers. These data support the findings of increased sweep efficiency with the use of polymer.

Chromium is often of interest at ISCO sites due to its redox-sensitive nature and higher toxicity in its oxidized form. Extremely small, statistically insignificant increases were measured in chromium (Cr) at shallow depths in the test plot. More significant increases were measured in CMT 3 (control plot) at each depth, generally corresponding with the movement of permanganate front through the screened interval. The transient increase of chromium in groundwater in close proximity to injection, which persists only as long as the elevated redox potential (Eh) provided by the oxidant persists, is consistent with other permanganate oxidation sites (Moore, 2008). Because the permanganate injected into the test plot did not reach CMT 1 and 2, we are unable to compare the effect in the test and control plots.

Cations in the control plot, specifically sodium (Na^+) (included in both sodium permanganate and sodium hexametaphosphate), follow the same general trend as the ORP, total solids, and conductivity values, where concentrations increase with arrival of oxidant in the well at different times for the discrete sampling depths. In the test plot, there was little change in the cation concentrations, similar to the ORP, total solids, and conductivity values.

There is little change in anion concentrations with respect to time in the test plot, like the cation data. The control plot data show spikes in concentrations of sulfate that generally correspond with the arrival of permanganate and sodium. It is likely that a naturally reduced form of sulfate is being oxidized and mobilized by the permanganate. There is very little change in either the chloride or phosphate concentrations in either plot over time. While increases in chloride concentrations would be anticipated with oxidation of PCE and TCE, it is likely the small amounts generated from the low concentrations of oxidation-produced chloride relative to the high natural chloride concentrations of this coastal system are insignificant.

5.6.4 Deposition and Fate of Manganese

Of particular interest to this demonstration is the influence of SHMP and xanthan polymer on the fate of manganese. A specific objective related to the use of SHMP is to avoid the deposition of MnO_2 within the treated area that could be anticipated to cause preferential flow under conditions where high contaminant concentrations are present. While we wouldn't anticipate such preferential flow with the contamination levels measured for this demonstration, we can

expect to see the influence and impact of SHMP on MnO₂ for the purpose of extrapolating results to other systems.

Very little change is measured in dissolved manganese (Mn) over time in the test plot. For the pH and ORP conditions of these systems, we expect Mn to be predominately present as MnO₂ and not dissolved Mn, therefore results are not surprising, particularly with the strong evidence shown by other geochemical parameter measurements that the oxidation signature did not transport beyond the treatment area within the test plot. In the control plot, like other measured geochemical parameters, such as Na⁺ and conductivity, we see spikes in Mn. These spikes, which correspond with observations of permanganate's purple color, again, demonstrate the preferential flow of permanganate in the control plot.

Manganese extraction data for example test plot and control plot cores, respectively, are presented in Figures 7 and 8. Water extractable cations are loosely bound and readily exchangeable (i.e., mobile), and barium(Ba)-extractable cations are more strongly associated with the soils. Exchange with Ba occurs when the system is overwhelmed by a very high concentration of another cation or by exchange for a more strongly sorbing cation. The Mn as MnO₂ was determined through dissolution of the solids using hydroxylamine hydrochloric acid with nitric acid.

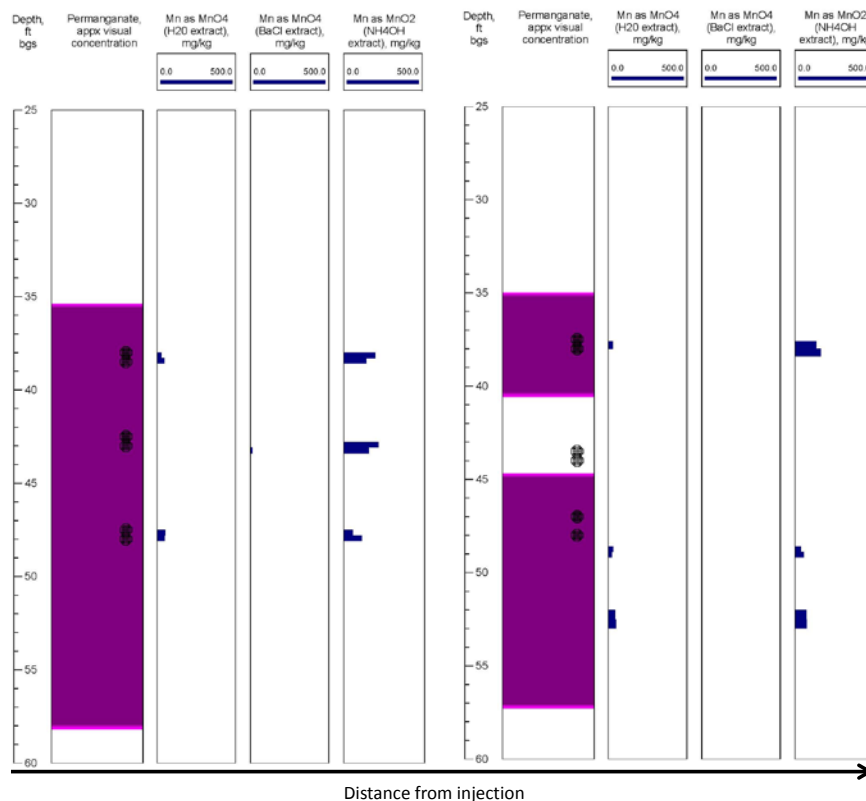


Figure 7. Manganese as water-extractable, Ba-extractable, and as MnO₂ for example test plot cores post-treatment with distance from injection.

Dots on the permanganate distribution plot indicate locations where MnO₂ samples were collected; where no MnO₂ concentrations are shown in the MnO₂ concentration log, results are below detection (0.01 mg/kg).

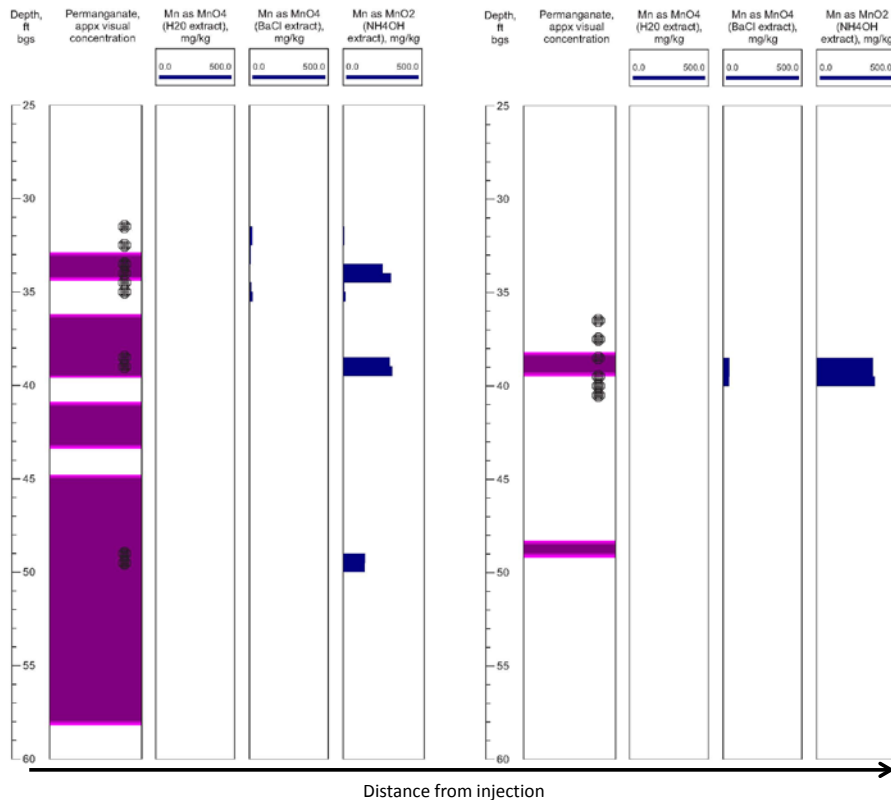


Figure 8. Manganese as water-extractable, BA-extractable, and as MnO₂ for example control plot cores post-treatment with distance from injection.

Dots on the permanganate distribution plot indicate locations where MnO₂ samples were collected; where no MnO₂ concentrations are shown on the MnO₂ concentration log, results are below detection (0.01 mg/kg).

Where Mn as MnO₂ concentrations are high due to permanganate reaction (e.g., depth interval 35-40 ft in the test plot [Figure 7] and depth interval 38-39 ft in the control plot [Figure 8]), the Mn was nearly 100% as MnO₂. Where MnO₂ was low and permanganate was not detected (interval 40-45 ft in the test plot [Figure 7] and the intervals just above and below the 38-39 ft interval in the control plot [Figure 8]), the percentage as MnO₂ was significantly less, typically between 25 and 50%.

In general, the mass of Mn as MnO₂ and total mass of Mn extracted per mass of media are similar for the test and control plots that were most exposed to permanganate. An objective for the use of SHMP was to maintain MnO₂ solids suspended in the aqueous phase. Because of this, and also because we do not see higher concentrations of total solids (indicative of MnO₂) in the groundwater measured in the CMTs of the test plot relative to the control, we cannot conclusively demonstrate that SHMP helps to keep MnO₂ suspended in this demonstration. The viscosity of the xanthan polymer, we believe, “holds” the MnO₂ within the bulk solution, which did not reach the monitoring wells. Therefore, we also cannot say the SHMP did not keep MnO₂ suspended. The coring and extraction method does not differentiate soil-associated and pore water-associated MnO₂. With the xanthan polymer included in the injection, it is difficult to assess the benefit of SHMP for inhibiting MnO₂ particle deposition, although we do suggest its use with xanthan polymer based on results of the treatability work conducted, which indicated

less pressure increase in transport studies with polymer + SHMP than with polymer alone. We cannot extrapolate the findings to the field as we did not conduct a test with polymer and no-SHMP, however we do anticipate scalable results. SHMP not only supports suspension of MnO_2 particles, it will similarly affect any particles carrying a negative charge, thereby inhibiting their deposition and potential build-up of pressure and preferential flow.

The mass of Mn per mass of media generally decreases with distance in both the test and control plots (Figure 9). This result is expected for both plots regardless of the presence of polymer because areas closer to injection are exposed to a greater total mass of Mn as permanganate. The effect is more pronounced in the test plot where delivery was more uniform and where closer distances experienced greater permanganate exposure, as opposed to the preferential flow in the control which favored specific depths and traveled further in some layers than others.

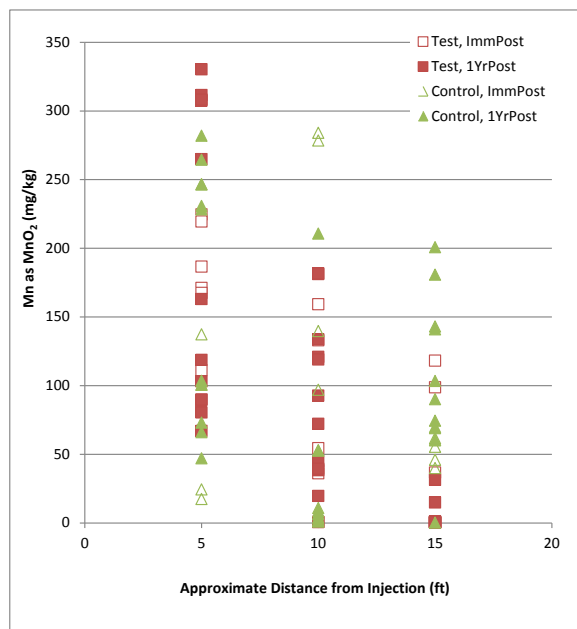


Figure 9. Mn as MnO_2 with distance from injection for test and control plots immediately post-treatment (Test, ImmPost and Control, ImmPost, respectively) and 1 year post-treatment (Test, 1YrPost and Control, 1YrPost, respectively).

The Mn-related results actually point to more interesting influences of the polymer than those on Mn itself. Results point to the influence of viscosity on the movement of dissolved or suspended solutions (retaining them relative to surrounding water), indicating the polymer could be valuable in other contexts as an amendment delivery agent. For example, the relatively high natural demand of permanganate in these test and control plots resulted in relatively rapid loss of permanganate over time, however in a media with lower natural demand, we could expect permanganate to persist chemically – higher solution viscosity could also help to retain the permanganate spatially. Results also point to the influence of the polymer solution on media cation exchange. While this influence is less understood, improved understanding could provide guidance on how the polymer could be used to influence metals behavior in the subsurface. For example, if the polymer leaves behind a higher CEC over time, its use could translate to increased removal of metals species over time. This could add significant value in a combined remedies approach that is designed to influence both organics and metals species for a given site.

5.6.5 Fate of Polymer

As discussed in several other sections, the polymer appears to retain the geochemical signature of oxidation (solids, Mn, anions, cations, etc.), likely due to the solution viscosity. We see evidence of greater movement of the polymer-amended permanganate into lower permeability layers relative to the permanganate control plot relative to permanganate itself, geochemistry, and Mn (as MnO₂ and as otherwise extracted). This section more closely examines measured viscosity in groundwater and results of sodium characterization toward understanding the fate of the polymer.

Calculated polymer concentrations based on viscosity measurements calibrated to xanthan polymer concentration are shown in Figure 10. One-year post-treatment we see polymer in these monitoring wells located approximately 15 ft from the injection well. Viscosity was retained longer than initially anticipated. It was anticipated that the polymer would dissipate within 1-week post-treatment based on the results of initial treatability studies; however, the laboratory studies were conducted in systems where permanganate was in excess and remained in excess throughout the tests. In the presence of permanganate, some slow reaction with xanthan polymer occurs, resulting in decreased viscosity over time. In the field, the permanganate reacted more quickly than the lab studies because of the oxidation of the soil, which had a relatively high natural demand. This resulted in reduced permanganate concentrations within the treatment volume relative to the treatability test, and explains the observed viscosity retention 1-year post-treatment. Therefore, dissipation of polymer and viscosity appears to be occurring primarily through dilution at the edges of the treated zone. Additional time series data would enable the determination of whether polymer concentrations are increasing at the well, indicating the bulk of polymer is still retained within the test plot, or whether concentrations are decreasing and have moved primarily away.

Polymer Concentration Based on Viscosity Measurement			
Date	Well	Port #	Concentration (mg/L)
11/3/2011	1	2	1.73±0.64
11/3/2011	1	3	1.97±1.4
11/3/2011	1	4	9.03±1.34
11/3/2011	1	5	BDL
11/3/2011	2	2	6.99±0.99
11/3/2011	2	3	3.87±1
11/3/2011	2	4	16.96±1.04

Figure 10. Polymer concentration as indicated by viscosity measured 1-year post-treatment in CMT 1 (Well 1 in table) and CMT 2 (Well 2 in table) with depth as designated by the port number.

Sodium (from sodium permanganate and from sodium hexametaphosphate) concentrations help to understand the fate of the polymer as well. Sodium in the control plot shows the preferential flow of oxidant solution in this area, with the bulk passing through the well during delivery. One year post-treatment, concentrations were back to ambient levels. The test plot showed little change in measured sodium concentrations during delivery, which is consistent with the fact that permanganate was not observed in these wells. It is also consistent with the supposition that the

viscous polymer retains the oxidation geochemical signature and travels as a slug that had not arrived in the well by the end of delivery. One year post-treatment we also see somewhat higher concentrations in CMTs 1 and 2, but it is still an order of magnitude lower than the highest concentrations measured in CMTs 3 and 4. It is possible that, based on these data, the sodium in the test plot passed out of the CMT 1 area and that ambient conditions returned within 1 year. It is also possible that the bulk of the polymer solution remains intact in the test plot and the Na measured 1-year post-treatment is just the front of sodium being released from the viscous solution. Measurements of sodium via extraction associated with solids help to clarify which of these possibilities is most likely. Sodium extraction data for test plot samples collected immediately post-treatment (left) and for samples collected one year post-treatment (right) are presented in Figure 11. One year later, sodium concentrations in the test plot are similar to, or even higher than, those for samples collected immediately post-treatment at the distance of approximately 5 ft, which is closest to injection. The concentrations in the farther distances (10 and 15 ft) are lower than those for samples collected immediately post-treatment. This is an indication that the polymer is actually retreating rather than being flushed from the treated area.

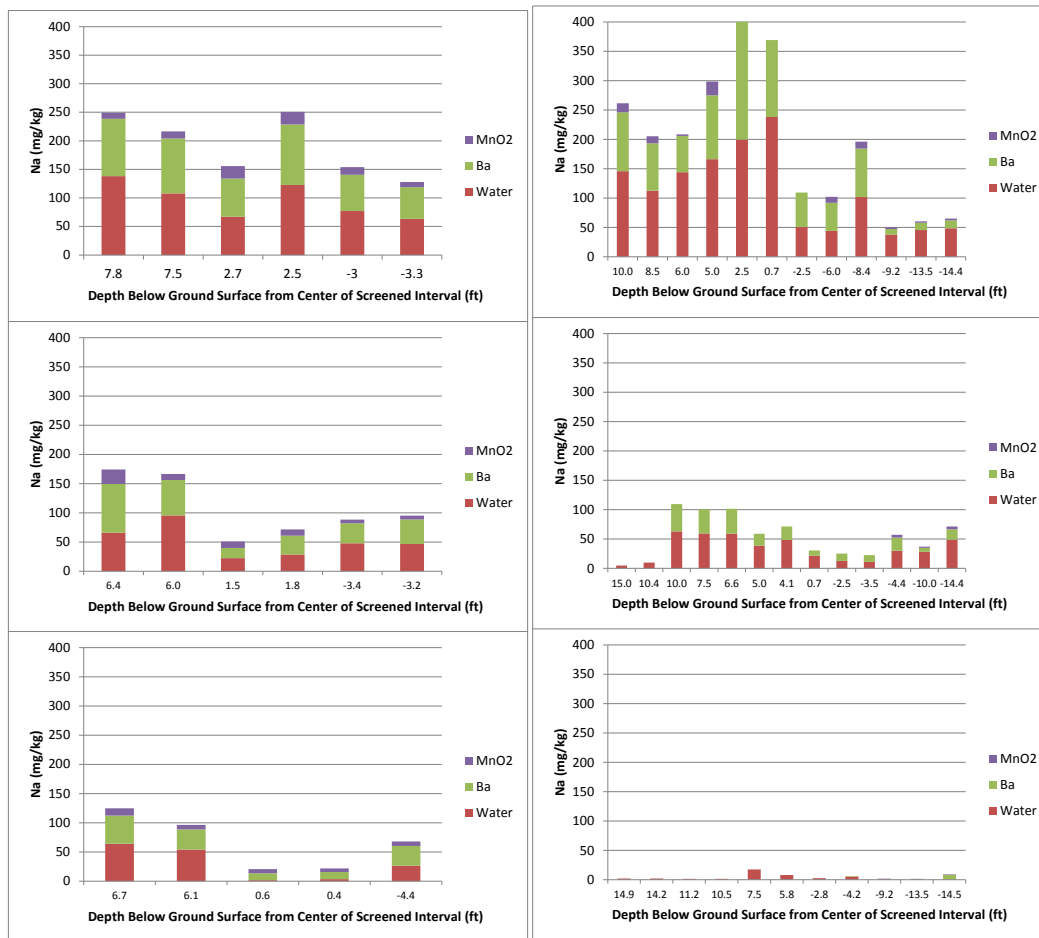


Figure 11. Sodium as water-extractable, Ba-extractable, and associated with MnO₂ solids structure for the test plot cores collected immediately post-treatment (left) and 1-year post-treatment (right) with respect to depth (relative to the center point of the screened interval).

Charts designated (A) are for cores approximately 5 ft from injection, (B) are approximately 10 ft from injection, and (C) are approximately 15 ft from injection.

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6.0 PERFORMANCE ASSESSMENT

The performance criteria, data requirements, success criteria, and results for the demonstration/validation of polymer-amended ISCO are presented in Table 9, which are further described in the following subsections.

Table 9. Performance Objectives

Performance Criteria	Data Requirements	Success Criteria (with use of polymer)	Results
Quantitative Performance Objectives			
Increased penetration of oxidant into lower permeability layers/strata	<ul style="list-style-type: none"> - Examination of soil cores for evidence of permanganate or MnO₂ - If LPM of thickness appropriate for discrete groundwater sampling is present, then MnO₄⁻/MnO₂ concentrations measured in groundwater over space and time 	<ul style="list-style-type: none"> - 50% longer distance of permanganate penetration into lower permeability layers/strata - 25% higher permanganate concentration at expected time of arrival in each monitoring well - Demonstrated improvement in vertical sweep efficiency within lower permeability layers/strata - Demonstrated improvement in overall vertical sweep efficiency in test plot 	Objective met
Decreased flow bypassing (increased lateral sweep efficiency) of areas of high contaminant mass	<ul style="list-style-type: none"> - Examination of soil cores for evidence of permanganate or MnO₂ in media with high contaminant concentration - Soil core extractions for MnO₂ and measurements of MnO₄⁻ and MnO₂ in groundwater over time and distance - Soil core extractions for contaminant with distance 	<ul style="list-style-type: none"> - 50% lower mass of MnO₂ in given mass of media (indicative of inhibition of deposition that can increase bypass) - 25% greater mobile MnO₂ concentration at given time point in monitoring well - 50% lower mass of contaminant in high concentration cores 	Objective partially met; sweep was improved, however not specifically associated with high contaminant mass
Evaluate long-term potential for and short-term occurrence of contaminant rebound	<ul style="list-style-type: none"> - Contaminant concentrations in groundwater over time and distance - Contaminant concentrations in soil cores pre- and post-treatment 	<ul style="list-style-type: none"> - Data collected and are representative of test plots - Post-treatment groundwater monitoring results remain below baseline concentrations 	Objective partially met
Improved contaminant treatment effectiveness	<ul style="list-style-type: none"> - Contaminant concentrations in groundwater over time and distance from injection - Contaminant mass in soil over time and distance 	Statistically significant reduction in contaminant mass as compared to a control plot	Objective met
Qualitative Performance Objectives			
Decreased impact of MnO ₂ on injection pressure	Injection well pressure over time	No increase in injection pressure attributable to MnO ₂	Objective met
Improved understanding of impacts of polymers on groundwater quality	pH, ORP, key metals, solids concentrations, conductivity, bioactivity	Note differences	Objective met

6.1 INCREASED PENETRATION OF OXIDANT INTO LOWER PERMEABILITY LAYERS/STRATA

The penetration of oxidant into lower permeability layers/strata was assessed by logging lithology and the distribution of permanganate in soil cores collected immediately post-treatment and comparing these for the control (permanganate only) and test plots (permanganate plus polymer). The project team evaluated the distance permanganate penetrated lower permeability strata and calculated the sweep efficiency of the oxidant using geostatistical methods. Also, groundwater monitoring wells screened over different lithologic units captured the movement of permanganate through different layers, and these data were compared for the control and test plots.

Soil core and groundwater data demonstrate improved, more uniform distribution of permanganate through the polymer test plot relative to the control plot through multiple lines of evidence including permanganate concentrations and numerous geochemical parameters monitored. Sweep efficiency with delivery of one PV of oxidant solution to the control plot (permanganate only) was 33%, whereas sweep efficiency in the test plot with polymer was 67%.

6.2 DECREASE FLOW BYPASSING OF AREAS OF HIGH CONTAMINANT MASS

This objective was selected prior to selecting the project's site, and relates to the use of SHMP for control of MnO₂ byproduct. Where contaminant mass is high (i.e., NAPL), SHMP can prevent the deposition of MnO₂ around areas where oxidant contacts contaminant where preferential flow can then occur. It was determined that assessment of sweep efficiency with polymer was a higher priority criterion than MnO₂ control, therefore site selection and demonstration design was focused on appropriate conditions for assessing sweep (e.g., heterogeneity distribution and overlying semi-confining layer). While contamination in the area where this demonstration was performed was indeed present, concentrations were not high enough to specifically assess this criterion therefore findings are inconclusive. MnO₂ distributions in soil were measured post-treatment. Similar concentrations of MnO₂ were measured in the control and test plot, however, we believe the viscous polymer solution in the test plot holds the geochemical signature, including MnO₂ solids, therefore we would not be able to detect a difference until the polymer-treated plot is fully restored to pre-treatment conditions (i.e., viscosity dissipated and MnO₂ "released"). Sweep efficiency was improved with polymer as discussed above, however its relationship to contaminant mass is not established.

6.3 EVALUATE LONG-TERM POTENTIAL FOR AND SHORT-TERM OCCURRENCE OF CONTAMINANT REBOUND

Rebound assessment was made by evaluating groundwater concentrations over time in each of the control and test plots, as well as post-treatment soil concentrations. Approximately one calculated PV was delivered to each the test and control plot for demonstration purposes. MCIEAST-MCB CAMLEJ sediments in our test area have a high natural demand for oxidant, as determined during treatability evaluations, and a high organic carbon content to which contaminants can be strongly sorbed. While a 1 PV flush is sufficient to assess differences in permanganate distribution, which is the project's focus, we would not expect 100% treatment

within these pilot scale plots, making this a challenging success criterion. This objective was partially met.

Measured groundwater concentrations show the influence of preferential flow through the control plot as a function of lithology during treatment. A decrease in concentration corresponds with the arrival of permanganate in the wells at different times for different depths. Contaminant concentrations rebounded, however, likely because upgradient groundwater re-entered the plot and/or remaining sorbed mass in the untreated layers re-equilibrated with the aqueous phase. In the test plot, however, evaluation of VOCs is inconclusive because evidence indicates that the polymer remains in the plot and is slowly “releasing” the geochemical signature of oxidation. We suspect preferential flow around the test plot due to presence of polymer. If this is the case, measurements in the well are stagnant until polymer dissolves and ambient flow is returned. This is not a negative result; simply inconclusive. Theory and our understanding of ISCO based on many years of practice and thousands of applications indicate that where oxidant and contaminant meet, reaction occurs. Soil core data do show low to no VOCs in permanganate-impacted soils, while VOCs remain at pre-treatment levels in unaffected soils. The test plot experienced twice the sweep of the control plot and the overall treatment effectiveness in the test plot is greater.

To achieve more effective treatment at the full-scale, multiple injections and PVs would be necessary, as it would for most ISCO sites. The advantage of the polymer-addition is that by improving the sweep efficiency, greater contact can be achieved between the oxidant and the existing contaminant with fewer PVs and fewer mobilizations. Polymer-addition mitigates the effects of preferential flow and promotes penetration of oxidant into lower permeability geomeia (Silva et al., 2012). In the absence of polymer-addition, where preferential flow exists, there is a diminished return on the injection of multiple PVs as the injected fluids will largely continue through the same preferred pathways, and while beneficial to treat sorbed mass, rebound can occur by back diffusion out of lower permeability zones.

As described in Section 8.4, the more effective mode of PA-ISCO treatment would involve a multiple PV treatment strategy that would take advantage of the physics of viscosity-modified fluid transport processes to maximize sweep-efficiency in heterogeneous geomeia. However, if a multiple injection strategy is employed, the timing of re-injection events would not be critical to remnant viscosity (if any) of the previous treatment. This is to say that the remnant viscosity need not completely dissipate prior to another injection. Nonetheless, it could be advantageous to utilize components of the post-treatment geochemical signature to base the timing of subsequent treatments (e.g., absence of permanganate, presence of by-products and rebounding contaminant) from samples collected at monitoring well locations positioned within the treatment area.

6.4 IMPROVED CONTAMINANT TREATMENT EFFECTIVENESS

As mentioned above, because efficiency of sweep was greater in the test plot than in the control plot, a greater mass of media was contacted by permanganate in the test plot. Where permanganate did reach contaminant, low to non-detect concentrations of the VOCs were measured. A statistical analysis of treatment effectiveness was not possible because of the few number of cores collected pre-treatment, which were limited to the injection well and CMT installation locations to preferential movement of polymer/permanganate to the surface. High

concentrations of contaminant remained in the test plot at the 44-45 ft interval where permanganate movement into this interval was limited by the short injection duration. Most other depths, particularly those closer to injection where permanganate presence was nearly uniform were treated effectively, which is significant because the extent of contamination, in terms of both concentration and spatially with depth, was greater for the test plot than for the control. While the control plot had less contamination initially, there were more intervals unaffected by oxidant and left untreated.

6.5 DECREASED IMPACT OF MnO₂ DEPOSITION ON INJECTION PRESSURE

Either deposition of MnO₂ due to reaction with natural media and/or contaminants or the introduction of viscous polymer that has the potential to sorb onto soils could result in increased pressure. Because of the relatively low contaminant concentrations associated with the solids and also because we used SHMP to alleviate polymer sorption and MnO₂ deposition (benefits described in Section 5.3.1 based on treatability study results), we did not anticipate a significant increase in pressure. No increase in injection pressure occurred in either the test or the control plot above that provided in the design calculations.

6.6 PERFORMANCE OBJECTIVE: IMPROVED UNDERSTANDING OF IMPACTS OF THE ENHANCED DELIVERY APPROACH ON GROUNDWATER QUALITY

Because the use of polymers with oxidant has not been evaluated in the field, it would be generally beneficial to improve the understanding of potential effects of polymer addition on groundwater quality. We collected extensive data on geochemical parameters of the soils and groundwater, as described in Section 5.7 of the final report. Key findings include:

- Polymer apparently retains the geochemical signature of oxidation, including solids generated, metals (including Mn and Cr), and anions (including sulfate).
- Polymer appears to “retreat” from the leading edge following application rather than flush through the treated area, which can result in a slower “release” of the geochemical signature. Results up to 1-year post-treatment are showing the beginning of this release. Both operational and treatment performance monitoring approaches should be adapted accordingly when applied at the full scale.
- Treatment using xanthan with SHMP results in a higher cation exchange capacity in soils around the “fringe” of treatment. The cause of this effect is unclear and warrants further study as it can possibly be manipulated to affect metals naturally present or present as co-contaminants.

7.0 COST ASSESSMENT

This section presents the results of an additional costs assessment to implement PA-ISCO. These costs are focused on the costs above and beyond those commonly associated with permanganate ISCO treatments that are well understood. A cost model that was developed to demonstrate the additional costs associated with PA-ISCO application is described in Section 7.1; Section 7.2 presents an assessment of the additional cost drivers for PA-ISCO technology; and Section 7.3 presents the results of an analysis of the cost model.

7.1 COST MODEL

A cost model was developed to assist remediation professionals in understanding the costs associated with including polymer-amendment for permanganate ISCO treatment. The cost model identifies the major cost elements specific to the inclusion of polymer-amendment at a site similar to the demonstration site described in this report. Excluded are costs typical of regular permanganate treatment, with the purpose of focusing on the excess costs of including polymer.

A summary of the costs associated with this first pilot-scale field demonstration of PA-ISCO is presented in Table 10. The cost model was developed for a template site of similar scale and site characteristics observed during this demonstration. These characteristics are presented in Table 11. Cost elements and data that were tracked during this first field demonstration focus on those that are above-and-beyond the costs of the typical permanganate-only ISCO approach. Specifically excluded from consideration are the costs associated with pre-remediation activities (e.g., characterizing contaminant distribution using membrane interface probe, risk determination and related needs), treatability testing specific to the optimization of permanganate concentrations, and post-treatment decommissioning. Also excluded are costs associated with well installation (including multi-level screened monitoring wells) and investigation derived waste (e.g., contaminated soil cuttings and well development water) characterization and disposal.

As this field demonstration was led by University employees and associates, actual labor costs were based on student wages. To provide a more realistic cost model, the labor costs presented in Table 10 were based on an assumed loaded hourly rate of \$85 for a typical mid-level Geologist /Scientist/Laboratory Technician and a \$100 hourly rate for a typical Project Engineer.

It is important to remember that PA-ISCO is a new and novel technology and the costs associated with this first field demonstration should be expected to be higher. PA-ISCO costs are expected to decrease as additional implementation experience is gained during future applications. This is true of most novel groundwater remediation technologies when they were first being evaluated.

7.1.1 Cost Element: Site Characterization

Site characterization is required for permanganate ISCO to assess a site's hydraulic properties, contaminant distribution and degree of contamination, and natural oxidant demand to determine dosage requirements and other design parameters necessary for successful in situ treatment. The

same is true for PA-ISCO. However, additional site characterization activities are required, including:

1. Discrete vertical characterization of permeability to assess the need for polymer amendment or to optimize polymer concentrations for maximal sweep efficiency improvement.
2. Injectivity testing to determine the maximum injection pressure and the averaged hydraulic conductivity of the formation.
3. Collecting depth-discrete soil and groundwater samples to assist treatability testing related to assessing the potential for permeability reduction.

Table 10. Cost Model for PA-ISCO.
(16 days total characterization and injection)

Cost Element	Data Tracked During Demonstration	Costs		
Site characterization	Vertical characterization of permeability (DPT – pneumatic slug testing and or cone penetrometer test [CPT] pore pressure dissipation tests plus data analysis <u>performed concurrent with soil sampling</u>)	Subcontractor	\$4500	
		Field geologist	\$2040	
		Engineer/scientist analysis	\$400	
		Injectivity testing (2 field days plus analysis)	Geologist	\$1360
	Soil sampling – treatability testing	Subcontractor	\$1500	
		Geologist	\$680	
		Sample shipping	\$800	
Treatability testing	Labor, materials, and analytical costs for batch experiments, transport experiments, and data analysis	Lumped costs	\$4300	
Materials costs	Polymer Costs	Xanthan gum	\$3200	
		SHMP	\$1180	
	Polymer mixing equipment		\$20,000	
	Process Control system*		\$54,000	
Installation/ decommission	Process Control system subcontractor	Subcontractor (fee)	\$5000	
	Shipping of equipment	To and from site	\$10,000	
	Labor	Project engineer	\$2400	
	Labor	Project scientist	\$2040	
Operation and maintenance	Labor – initial polymer concentrate preparation	Project scientist (8 hours prior to injection operations)	\$680	
	Labor – daily polymer preparation	Project scientist (4 hours per day for 4 days)	\$1360	
	Equipment rental (generator and overhead lighting)	Total per 7 day preparation and injection duration	\$3000	
Total			\$118,440	

* See discussion of the Process Control System in Section 7.1.3

Table 11. Cost Analysis Design Basis for Template Site MCIEAST-MCB CAMLEJ, NC.

Design Parameter	Units	Quantity
<i>Target Treatment Area Dimensions and Hydrogeology</i>		
Total depth	ft bgs	60
	m bgs	18.3
Depth to water	ft bgs	12
	m bgs	3.7
Treatment depth interval	ft bgs	28-60
	m bgs	8.5-18.3
Treatment zone radius	ft	15
	m	4.6
Total treatment area	ft ²	706.5
	m ²	65.7
Total treatment volume	ft ³	22,608
	m ³	640.7
Average hydraulic conductivity	ft/day	6.2
	m/day	1.9
Horizontal groundwater gradient	ft/ft	0.002
Average porosity assumed	--	0.35
Treatment PV	gallons	59,187
	ft ³	7,913
	m ³	224
Sediment bulk density (dry)	kg/m ³	1800
Total soil mass in treatment volume	kg	1,153,223
<i>Injection Design</i>		
Number of injection points		1
Injection point ROI	ft	15
	m	4.6
Design concentration of NaMnO ₄	mg/L	5000
Design concentration of SHMP	mg/L	3000
Design concentration of xanthan gum	mg/L	500
Number of PVs injected	--	1
Number of monitoring wells	--	2
<i>Per PV Chemical Demands</i>		
Mass of MnO ₄ required	kg	1121
	lb	2466
Mass of xanthan gum required	kg	112
	lb	246
Mass of SHMP required	kg	670
	lb	1474

Therefore, the cost model for this cost element reflects these additional costs. For this demonstration a DPT rig was used to perform depth-discrete slug testing to vertically characterize hydraulic conductivity of the treatment zone. Additional hydraulic testing methods were attempted utilizing pore pressure dissipation tests via high-resolution piezocone but these attempts were largely unsuccessful for the site subsurface conditions. Soil and groundwater samples were collected during the single site characterization event that included hydraulic profiling and well installation for the demonstration. Injectivity testing was performed using a step-injection test mode utilizing the injection well installed for the demonstration and the

process control system constructed for the demonstration. Labor and subcontractor costs for the site characterization efforts were tracked as presented in Table 10.

7.1.2 Cost Element: Treatability Test

While oxidant demand tests to determine the rate and extent of permanganate interaction with natural subsurface media are recommended whether or not polymer amendments are added, the use of polymer requires additional testing that involves increased labor, materials, and analytical costs. Additional testing includes the determination of optimal xanthan and SHMP concentrations to use on a site-specific basis at the batch scale, characterization of concentration-specific rates of reaction of xanthan, and permanganate (albeit slow), and, ideally, one-dimensional (1D) transport evaluations to assess potential impacts to conductivity and flow. Costs were tracked on a per site basis and will apply to a demonstration of any scale as they appear in Table 10, which again are those costs additional to those of a typical permanganate ISCO project.

7.1.3 Cost Element: Material Cost

Materials costs specific to PA-ISCO that were tracked during this demonstration included polymer chemical costs, the cost of the polymer mixing equipment, and the cost of a process control system (PCS) capable of monitoring and maintaining polymer dosing and injection flow rate for automated 24-hour operation.

The importance of 24-hour injection relates to the physics of viscosity enhancement and its effect on sweep efficiency improvement as described in detail by Silva et al. (2012). Briefly, the mechanism of sweep improvement involves the maintenance of viscous cross-flow potentials between strata of variable permeability. Therefore, a steady and continuous flow condition must be maintained during treatment to maintain solution viscosity at design levels to maintain cross-flow potentials. Additionally, automated 24-hour injection was a necessity for this site because the project team was not able to staff overnight operations on base.

The PCS designed and constructed for this pilot demonstration possessed a somewhat higher degree of complexity than would be necessary for a more typical permanganate ISCO operation and this degree of complexity is reflected in the cost of the PCS. However, significant cost savings were realized by eliminating the need to staff overnight monitoring of the injection operation. The PCS included separate flow-control, chemical dosing, and injection modules each of which were electronically monitored and linked to a telemetry alarm system. Each of these systems and associated electronics were mounted on a steel skid to minimize on-site installation costs. An additional skid-mounted system housed fluid homogenization and filtration modules.

The polymer mixing equipment purchased for this demonstration was a skid-mounted hydrodynamic mixing system with a stainless steel dry chemical hopper and recirculation pump. A polymer concentrate was made on site prior to and during injection and transferred to a 2500 gallon storage tank. Capital equipment costs for this system are presented in Table 10. However, costs savings related to polymer concentrate solution preparation could be realized by sourcing a pre-made concentrate solution, of sufficient volume, that could be trucked to the site and

contained within a large liquid product tanker trailer throughout the injection period. This would obviate the equipment and labor costs related to on-site polymer concentrate preparation.

Polymer chemical costs were tracked on a mass used per treatment PV basis. The polymer mixing and PCS costs were tracked as a lump sum for the demonstration, and were implemented on a cost per PV basis during the cost analysis presented in Section 7.3.

7.1.4 Cost Element: Installation

Installation costs tracked during this demonstration relate to those associated with the PCS subcontractor supplying a technician to install the PCS and associated systems. Subcontractor costs to decommission the PCS system at project end were rolled into these costs. Additional labor costs were tracked for project personnel on site to assist with the installation and testing of additional system components, including poly tanks, the polymer mixing equipment, and wellhead injection manifolds to record injection pressure response.

Because equipment was used under rental terms, PCS equipment shipping costs were also tracked, and the costs presented in Table 10 include costs associated with shipping all project components to and from the site.

7.1.5 Cost Element: Operation and Maintenance

Polymer-specific operations and maintenance (O&M) costs tracked during this pilot demonstration included additional labor costs associated with polymer mixing and preparation of polymer concentrate solution. These costs were tracked on a person-hour basis for the demonstration. The initial mixing and concentrate preparation required one field person for 1 day (8-hours) prior to injection to prepare enough polymer concentration to supply uninterrupted overnight injection. Once PA-ISCO fluid injection initiated, polymer concentrate batches were prepared daily requiring 4 person-hours per day. These costs are represented in Table 10. However, the daily labor costs of polymer concentrate preparation could be rolled into normal daily O&M costs for any in situ groundwater remediation technology. Additionally, costs savings related to polymer concentrate solution preparation could be realized by sourcing a pre-made concentrate solution, of sufficient volume, that could be trucked to the site and contained within a large liquid product tanker trailer throughout the injection period.

Equipment rental costs included in Table 10 include the rental of a diesel generator (supplying power to run the PCS and polymer mixing equipment), overhead lighting for evening operations, and fuel costs. This equipment was rented for a period of 6 weeks during this demonstration. However, rental costs presented in Table 10 are specific to the 2-week period in which the equipment was specifically used during injection and post-injection sampling.

7.2 COST DRIVERS

The cost to implement PA-ISCO is related to the use of permanganate oxidant and the degree of permeability heterogeneity and will vary significantly from site to site. The key cost drivers specific to PA-ISCO application are listed below, along with a brief discussion of their impact.

7.2.1 Operational Costs

- **Preparation of Polymer Solutions** – As discussed in Section 7.1.5, costs associated with the preparation of the polymer concentrate, using the methods and equipment employed in this demonstration, would rise with increasing scale of remediation. These scaled costs relate to labor needed to prepare the concentrate solutions on site, as the costs of the mixing equipment would be independent of scale. However, as discussed in Section 7.1.5, we suggest that if a prepared polymer concentrate solution could be sourced and trucked to the site in large liquid product tanker trailers, the costs of this service could offset the cost of on-site preparation and obviate the need for the polymer mixing equipment.
- **Continuous Injection** – Costs associated with providing injection equipment that would provide continuous 24-hour injection is currently required for PA-ISCO treatments. This cost would be a one-time cost per implementation and would be fixed regardless of the scale of the implementation.

7.2.2 Nature and Extent of Contamination

- **Depth and extent of the treatment zone** – As with any in situ remediation technology, chemical costs will increase with increasing treatment volume. Similarly, costs associated with well installation (increased number of wells) and the treatment duration will increase.
- **Presence of NAPL** – If polymer sweeps less permeable strata containing NAPL that is not swept by a non-viscous amendment, there is a potential for the PA-ISCO solution to mobilize this NAPL. This has less to do with the viscosity of the PA-ISCO fluid, but rather that the enhanced viscosity promotes access to lower permeability geomeedia that could contain NAPL. However, there is also the potential that PA-ISCO would provide a means of treating this hydraulically isolated NAPL zone that would otherwise not be treated by traditional ISCO application.

7.2.3 Aquifer Geology and Hydrogeology

- **Vertically averaged hydraulic conductivity** – Relates to the rate of injection achievable and the concentration of polymer needed to achieve the same degree of sweep efficiency improvement. A site with a lower average permeability will require a slower rate of injection and longer treatment duration to maximize sweep efficiency improvement.
- **Implementation within confined and unconfined aquifers** – The present PA-ISCO demonstration was performed in a locally confined aquifer as described in Section 3 of this report. Application within an unconfined, water table aquifer is entirely feasible. The limiting factor would be a shallow water table condition, which would limit the rate of injection possible and necessarily increase the duration of treatment. Careful implementation design is recommended for this application scenario.
- **Degree of heterogeneity** – The principal function of PA-ISCO technology is to mitigate the effects of permeability heterogeneity on sweep efficiency within the treatment zone

during injection. However, the degree of permeability heterogeneity can affect the duration of treatment for PA-ISCO, in that longer injection durations will be required to maximize sweep efficiency improvements as the degree of heterogeneity increases. While the relative location of high and low permeability strata is not a significant factor in the effectiveness of PA-ISCO, the degree of permeability contrast can result in increased number of injected PVs required to maximize sweep efficiencies. Generally, as the degree of permeability contrast between the bulk media and the target lower permeability zone increase, so does the injection duration.

7.3 COST ANALYSIS

The primary objective of this first pilot demonstration was to evaluate sweep efficiency improvement for a polymer-amended permanganate solution and learn from the results of this test to better understand the efficacy of the technology for future full-scale application. As a result, the PA-ISCO formulation was not designed to completely remediate the treatment volume, which complicates a comparative analysis of the life cycle costs of PA-ISCO treatment versus traditional permanganate ISCO.

To facilitate this cost analysis, it was assumed that a 2 PV PA-ISCO treatment, utilizing the same polymer and oxidant concentrations, would provide maximal sweep efficiency improvement to contact 100 % of the PV within the template site described in Table 11. It is further assumed that this 2 PV treatment would provide sufficient oxidant to overcome both the initial instantaneous and slower natural oxidant demand contributions and achieve 100% treatment efficiency. Under this scenario, and utilizing the sum of the costs identified in Table 10, the additional cost of PA-ISCO (i.e., costs in addition to the normal cost of traditional permanganate ISCO implemented in the same manner) would be \$118,440 or \$185/cubic meter (m^3).

Approximately 9% of costs (\$11.3 K) were associated with high level site characterization. The ability to assess the applicability of PA-ISCO relies on understanding permeability distribution, and thus this high level of site characterization is warranted. It is good practice, however, to conduct high level site characterization for any in situ remediation effort toward improved overall cost-effectiveness.

Roughly 56% (or \$69K) of the total cost was related to the purchase, shipping, and subcontractor labor associated with the process control system used in this pilot demonstration. The requirement of 24-hour injection for PA-ISCO necessitates a similar equipment purchase and therefore would be a fixed cost, regardless of the scale of implementation. However, the unit cost of this equipment would decrease with increasing scale of implementation (e.g., increased number of injection locations within a larger treatment volume or multiple PA-ISCO implementations at additional sites). As PA-ISCO develops, we would expect this equipment, along with the polymer mixing equipment at \$20K (17% of total cost), to become available for rent, with the total costs normalized over multiple sites over multiple years. If, for example, the equipment is purchased by a vendor and wants to realize a return on investment within 2 years, and we assume the equipment can be applied to a minimum of six sites per year, \$89K (75%) of the total costs described in Table 10 would be reduced to approximately \$7.5K. Thus, total costs of PA-ISCO above and beyond traditional ISCO are estimated as \$36,940, or \$58/ m^3 (or \$44/cubic yard [yd^3]). Again, because these equipment costs are fixed regardless of scale and

these numbers are applied to this relatively small pilot-scale test, we can expect a significant decrease in cost per treated volume with increasing scale.

In a recent review of traditional ISCO application at over 200 individual sites, the average unit cost of ISCO was found to be \$123/m³ (Krembs et al., 2010). Therefore, the unit cost of PA-ISCO (estimated as \$181/m³ or 138.5/yd³) is competitive with traditional ISCO, particularly considering the potential benefit.

The active remediation timeframe for injection of 2 PVs of amendments is estimated at 10-12 days based on the duration of this 1 PV demonstration. Based on analyses reported in Section 5.7.1 of the final report, a permanganate-only plot would require approximately 6 PVs and 1-month or more field time; and theory dictates that while sweep would be improved without polymer in 6 PVs, there would still be significant preferential flow. Assuming 100% contact, the cost savings of PA-ISCO at a minimum are the costs associated with approximately 20 days of field time. A conservative estimate of field costs at \$800/day for labor and travel (hotel, per diem, etc.) translates to a savings of \$16K, or \$25/m³ (\$19/yd³) in the case presented here, which is approximately 40% of the estimated costs associated with use of PA-ISCO above and beyond traditional ISCO (assuming rented equipment with total costs normalized over 2 years and multiple sites, as discussed above). For a worst case scenario, PA-ISCO costs \$33/m³ (\$25.2/yd³) above traditional ISCO for the same benefit as traditional ISCO.

If we assume PA-ISCO achieves treatment goals and results in site closure within 5 years of implementation, but ISCO without polymer does not reach treatment goals because of incomplete sweep (resulting in 30 years of long-term monitoring), the costs saved using PA-ISCO include 25 years of monitoring costs. Assuming a cost of approximately \$50K per year for long-term monitoring, a simple estimate of the associated cost savings indicates savings of up to \$1.25 million per site.

8.0 IMPLEMENTATION ISSUES

8.1 POTENTIAL ENVIRONMENTAL ISSUES

8.1.1 Regulatory Issues

For this pilot demonstration, an underground injection control (UIC) permit application was completed and submitted to the North Carolina Department of Environment and Natural Resources, although it was not mandated because of MCIEAST-MCB CAMLEJ's status as a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) site (and the intent of the regulation was followed). At full-scale, a UIC permit will be required in most jurisdictions for the injection of permanganate oxidant and for the extraction and re-injection of PA-ISCO fluids and contaminated groundwater if implemented as an inter-well recirculation mode of in situ treatment. Regulatory requirements for permanganate treatment are well known. Xanthan gum, the polymer used in this demonstration is a food grade biopolymer. It is therefore expected that acquiring a UIC permit should not be difficult.

8.1.2 Air Discharge

The PA-ISCO process described herein will not normally result in the discharge of chemicals to the atmosphere.

8.1.3 Wastewater Discharge

The PA-ISCO process described will not normally result in the generation of wastewater streams. In this first pilot demonstration of PA-ISCO technology, PA-ISCO fluids were delivered to the subsurface as an injection-only mode of treatment, which did not generate a wastewater stream. Some small quantities of wastewater may be generated during well installation and groundwater sampling events and must be managed as they would be for other investigation derived waste.

8.1.4 Waste Storage, Treatment, and Disposal

The PA-ISCO process described will not normally result in the generation of significant waste streams. Some waste may be generated during well installation and groundwater sampling and must be managed as they would be for other investigation derived waste. If NAPL areas are targeted for treatment, it is possible that the waste generated will be hazardous and would need to be managed as such.

8.2 END-USER ISSUES

Potential end-users of this technology include responsible parties for sites contaminated by TCE, PCE and potentially other chlorinated solvents. End-users will have an interest in the technology because it can potentially improve the treatment of groundwater aquifers in situ by the improved contact between the contaminant and the injected remedial fluid resulting from improved sweep efficiencies within heterogeneous aquifer environments. PA-ISCO can therefore improve the effectiveness of treatment over traditional permanganate ISCO application. End-users and other stakeholders may have concerns regarding: (1) applicability of the PA-ISCO to sites with more

than one-order-of-magnitude variation in hydraulic conductivity/permeability, (2) the effectiveness of the technology in reducing concentrations of target compounds within lower permeability media; (3) potential negative impacts of permanganate and its reaction byproducts in the environment (concern with ISCO in general and not specific to PA-ISCO); and (4) potential negative impacts of xanthan gum on subsurface hydraulics.

Previous SERDP-funded research that contributed to this pilot-scale implementation demonstrated that a one or two-order of magnitude variability in media permeability is not a limitation to sweep efficiency improvement via polymer amendment. Rather it is the permeability contrast between adjacent strata that governs the rate of sweep, and therefore the number of PVs required to achieve 100% sweep efficiency. The technology is best implemented within sands, silty sands, and silts where the permeability contrasts between these media categories are less severe. Polymer amendment will not drive remedial fluids into clays, wherein the larger polymer molecules will filter out of solution and the viscousifying effect diminishes. However, this does not mean that polymer amendment cannot treat contaminants accumulated within clayey sediments. As observed during this field demonstration, the viscosity of the injected PA-ISCO solution was found to persist within the treatment zone in excess of a year following initial treatment. The low horizontal hydraulic gradient at this site, coupled with the viscosity of the injected solution, appears to have hydraulically isolated the PA-ISCO treatment zone. This result should not be necessarily viewed as a negative consequence of polymer amended fluids. Rather, future remediation designs could be tailored to take advantage of this viscosity retention and hydraulic isolation to sequester permanganate, or other remedial fluids, within the zone of treatment to provide a source continued long-term treatment of contamination within emanating from low-permeability media (e.g., clays, and clayey silts) that were not swept during the initial polymer-amended treatment.

Additionally, the viscosity of the PA-ISCO fluid, and the retention of this viscosity post-treatment, was shown to have sequestered the geochemical signature of ISCO (including metals, which may be of concern at some sites). The expected slow dissipation of viscosity post-treatment could result in slow, low-concentration release of the geochemical signature, preventing “slugs” of high concentrations of metals of concern from passing through monitoring wells.

8.3 PROCUREMENT ISSUES

There are no significant procurement issues related to the purchase of permanganate and/or xanthan gum biopolymer, as there are a number of permanganate and xanthan gum biopolymer vendors in existence. Also no significant procurement issues were encountered for the purchase of the polymers and polymer mixing equipment. However, the end-user should be cognizant of the need for this type of specialized polymer mixing equipment to ensure proper hydration of these dry polymer products to avoid injectivity issues.

8.4 DESIGN ISSUES

Based on the results of the PA-ISCO pilot demonstration conducted at MCIEAST-MCB CAMLEJ (Site 88), the following potential design issues should be considered in future applications of PA-ISCO:

- Daylighting of PA-ISCO Fluids:** Daylighting is a common undesirable occurrence with in situ remediation and, therefore, any condition which may increase it is of design concern. It is a requirement of PA-ISCO, and other polymer-amended remedial fluid applications, that the solutions possess enhanced viscosity. Injection of fluids of increased viscosity naturally evokes concerns over the daylighting of injected fluids at or near the point of injection due to the higher required injection pressures. In this demonstration, however, solution viscosities injected did not exceed 30 cP (or 30 times the viscosity of water, which is half the viscosity of vegetable oil). Additionally, the polymer used to provide viscosity enhancement possessed shear-thinning rheological character, in which the apparent viscosity of the fluid decreases with increasing hydrodynamic shear (or with increasing pore water velocities). As a result, the location of lowest viscosity would be at the location of greatest pore velocity, or immediately adjacent to the injection well during injection. In fact, pore fluid velocities near the injection well during this pilot demonstration were high enough to provide a near-well fluid viscosity very close to that of water. The purposeful use of a shear-thinning viscous fluid mitigates the potential for daylighting. Daylighting becomes more of a concern for shallow water table aquifers, which could require lower injection flow rates resulting in elevated PA-ISCO fluid viscosities.
- Delivery Volume and Injection Duration:** The purpose of polymer amendment is to improve the subsurface distribution of injected remedial amendments during in situ treatment. However, throughout this project and prior SERDP-funded work in this area (SERDP Project ER-1486) it has become clear that while polymer amendment can greatly improve the distribution of injected fluids in heterogeneous aquifers, achieving maximal sweep-efficiency improvements most often will require injection of more than a 1 PV injection. The number of PVs required depends on the maximum permeability contrast between strata within the treatment volume (Silva et al., 2012).
- Mode of PA-ISCO Treatment:** For this first pilot demonstration of PA-ISCO, the mode of introducing fluids utilized an injection-only mode. This has been a common mode of treatment for traditional permanganate ISCO treatments because of the reduced field time and overall costs of treatment. While we have successfully demonstrated significant sweep efficiency improvement (105% sweep improvement relative to a traditional permanganate injection), we have also estimated that achieving 100% sweep of the demonstration PV would require as much as a 2 PV injection. This could be a limitation of PA-ISCO application because many practitioners don't recognize or respond to the importance of injection volume in their ISCO designs, or the design of any treatment system involving the delivery of liquid amendments, in general. PA-ISCO, however, improves the efficiency of treatment by decreasing the total number of pore necessary to achieve sweep. Without polymer, preferential flow will continue and we can expect limited movement into the lower permeability layers regardless of how many PVs are delivered. With polymer, movement into lower permeability media will continue. In general, the challenge of high injection volumes for site treatment using any liquid amendment, particularly those with fast reaction rates, could be overcome by implementing the technology in a recirculation mode of treatment (e.g., divergent line-drive well pattern involving a center line of injectors and lines of extraction wells on

either side), whereby multiple PVs could be introduced to provide maximal sweep efficiency improvement while reducing the duration of treatment.

- ***Permeability Reduction Associated with Xanthan Biopolymer:*** Polymer amendment not only provides mobility reduction to improve subsurface sweep efficiency, but can also temporarily reduce the permeability of the media it is being injected into as a result of filtration and entrapment of these large polymer molecules within narrow pores and pore pathways. Transport experiments utilizing site aquifer sediments should be conducted as a part of a Treatability Study work scope to evaluate the potential for and degree of permeability reduction as a part of responsible remediation design. The degree of polymer permeability reduction will increase as the media permeability decreases, and the effects of significant polymer permeability reduction could result in lower injection flow rates and an increased potential for daylighting, as described previously. In the present case, including SHMP to the PA-ISCO formulation reduced the potential for permeability reduction (see Table 5-6) as described in Section 5.3.1 of this report.
- ***Sorbed-Phase Contamination:*** It is widely recognized that ISCO typically requires multiple injections to treat contamination associated with the solid-phase as it diffuses into the treatment PV following initial treatment.
- ***Equipment to Prepare Xanthan Gum Concentrates:*** For this first field demonstration, xanthan gum and SHMP were purchased as dry powdered product and concentrates of these polymers were prepared on-site. Operational and equipment costs associated with preparing these solutions in the field were manageable at the scale of this demonstration, but could become difficult as the scale of the treatment increases. In future applications it may be more appropriate to purchase these polymers as prepared aqueous solutions that could be trucked to the site in large tanker trailers. This action would mitigate labor costs associated with PA-ISCO application and eliminate the need for the relatively expensive (~20% of the total equipment cost) hydrodynamic mixing equipment purchased for this demonstration.

9.0 REFERENCES

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APPENDIX A
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APPENDIX B
SUPPORTING FIGURES

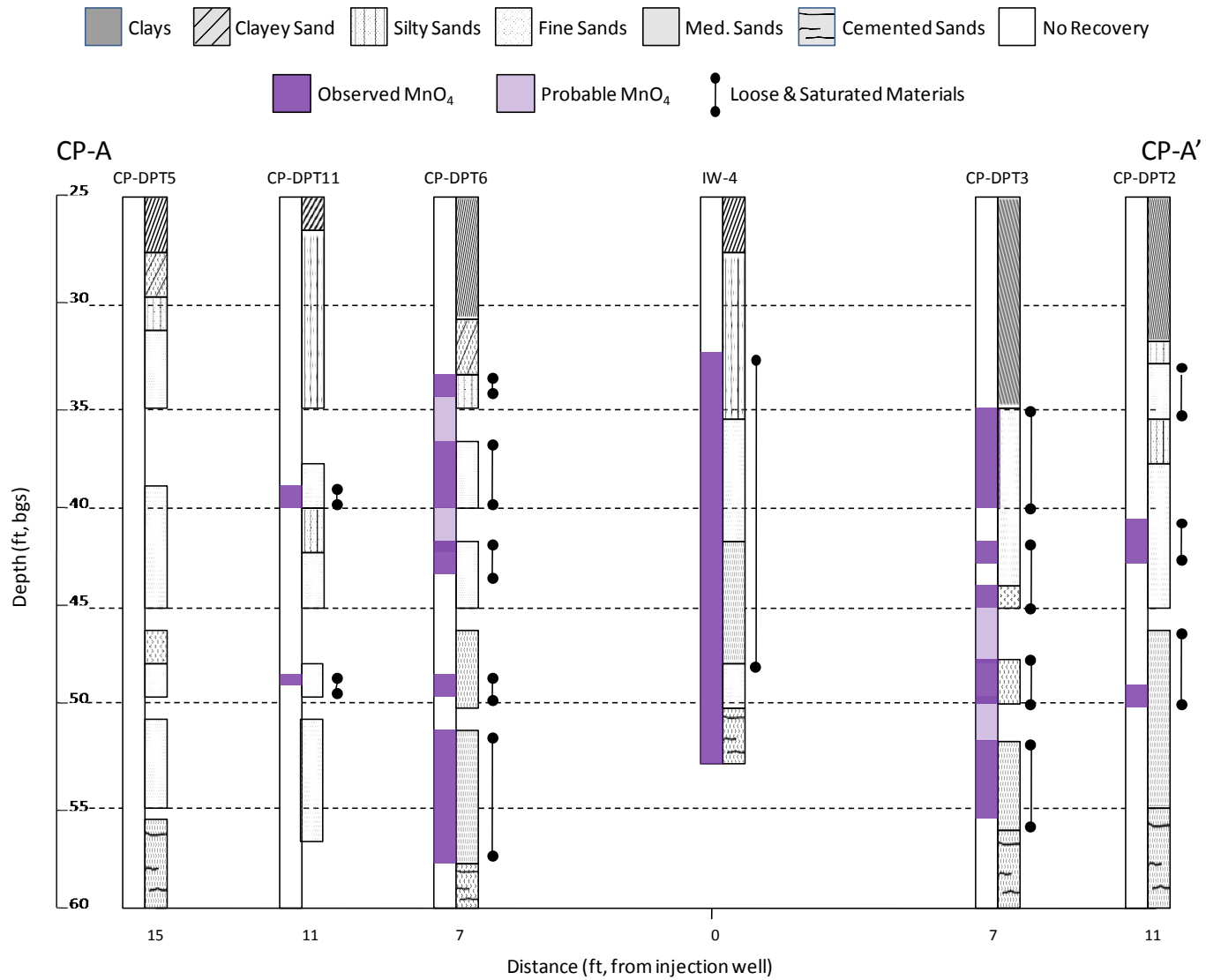


Figure B-1. General stratigraphy and distribution of permanganate observed within the control plot (along Transect CP-A-CP-A').

APPENDIX B (continued)
SUPPORTING FIGURES

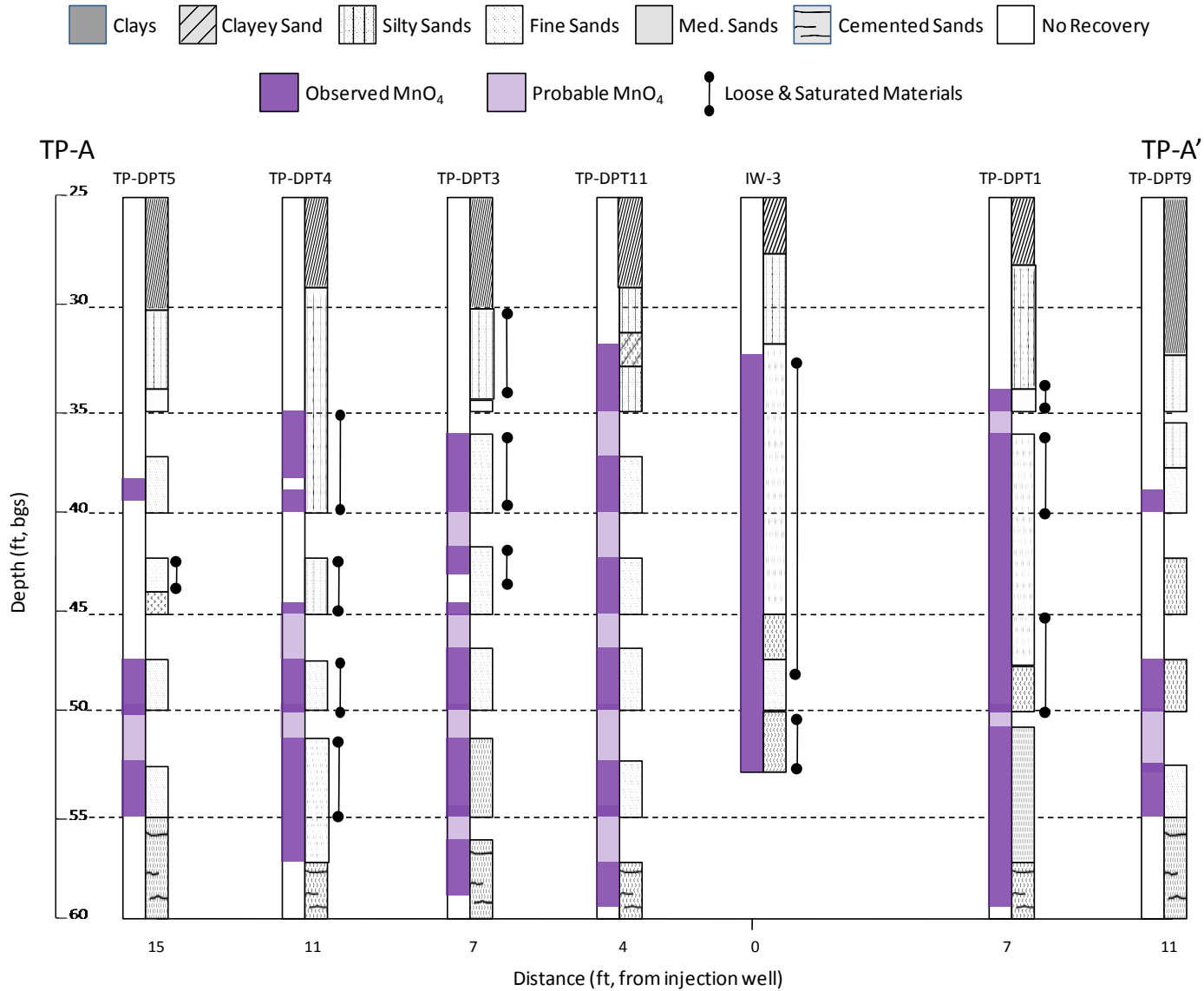


Figure B-2. General stratigraphy and distribution of permanganate observed within the test plot (along Transect TP-A-TP-A').

APPENDIX B (continued)
SUPPORTING FIGURES

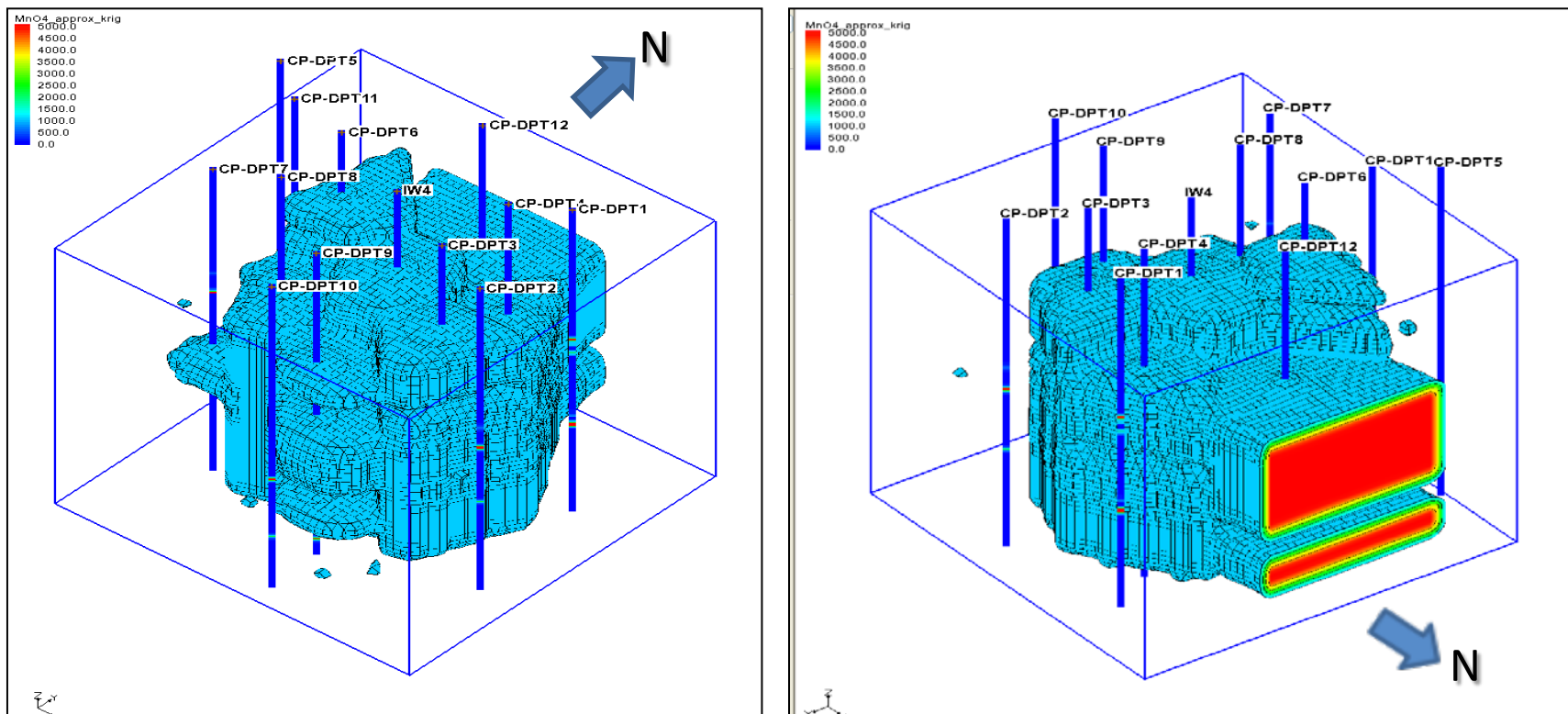


Figure B-3. Results of ordinary kriging of the post-injection permanganate data representing the distribution of permanganate within the control plot after a 1 PV injection.

Integrated sweep efficiency (volume contacted by permanganate divided by total volume) was 33%

APPENDIX B (continued)
SUPPORTING FIGURES

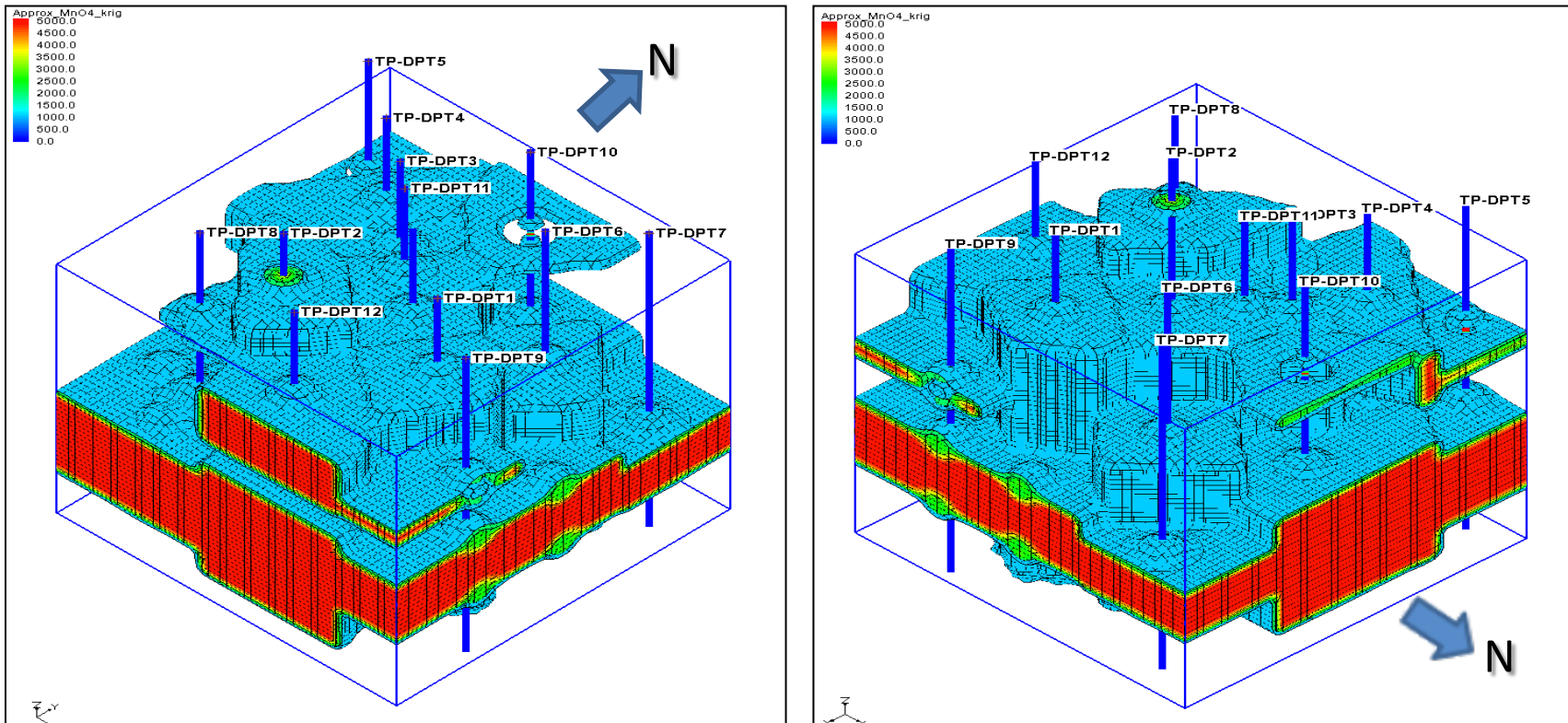


Figure B-4. Results of ordinary kriging of the post-injection permanganate data representing the distribution of permanganate within the test plot after a 1 PV injection.

Integrated sweep efficiency (volume contacted by permanganate divided by total volume) was 67%.

APPENDIX B (continued)
SUPPORTING FIGURES

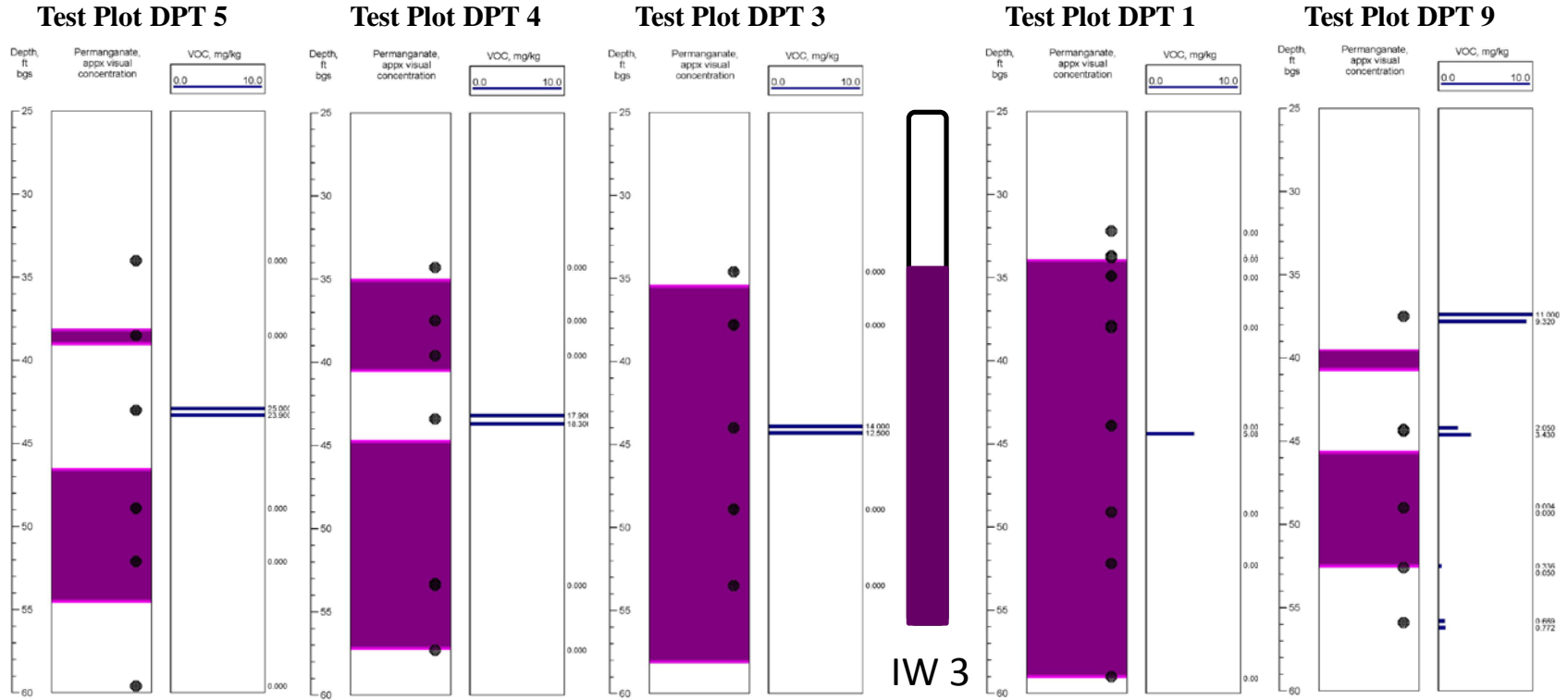


Figure B-5. Soil VOCs concentrations (TCE and PCE) along with permanganate distribution for transect TP-A-TP-A' (Figure 5-5).

Dots on the permanganate distribution plot indicate locations where VOCs samples were collected; where no VOCs concentrations are shown on the VOC concentration log, results are below detection (0.05 mg/kg).

APPENDIX B (continued)
SUPPORTING FIGURES

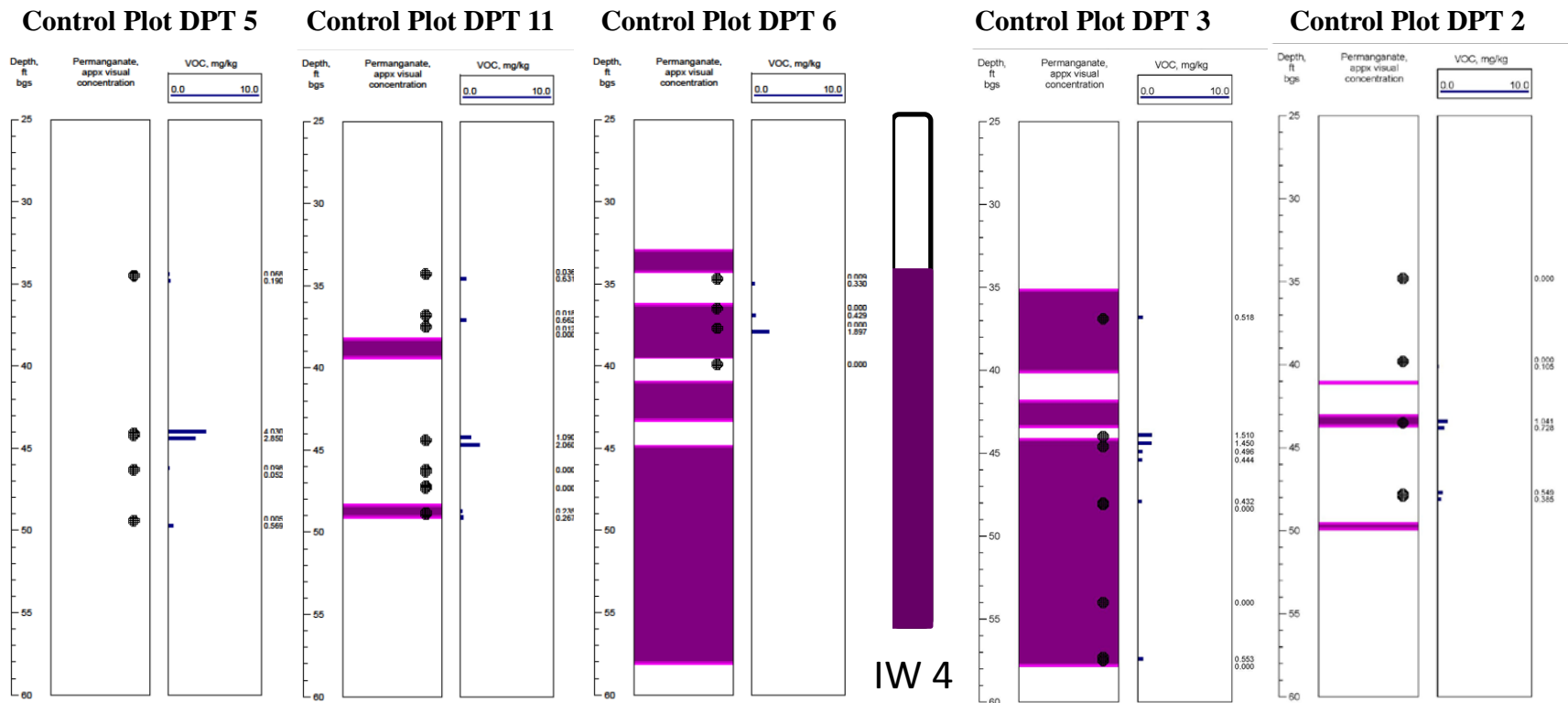


Figure B-6. Soil VOCs concentrations (TCE and PCE) along with permanganate distribution for transect CA-CA' (Figure 5-5).

Dots on the permanganate distribution plot indicate locations where VOCs samples were collected; where no VOCs concentrations are shown on the VOC concentration log, results are below detection (0.05 mg/kg).



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