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Geochemical Impacts From Permanganate Oxidation Based on Field Scale Assessments.

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Geochemical Impacts From Permanganate Oxidation Based on Field Scale Assessments

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by

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ABSTRACT

Geochemical Impacts From Permanganate Oxidation Based on Field Scale Assessments

by

Kelly Moore

In situ chemical oxidation (ISCO) using permanganate is a technology for treatment of organic hazardous wastes. This research is a review of 30 permanganate (MnO_4^-) ISCO sites to determine whether there are long term impacts on groundwater quality due to the introduction of the oxidant into the subsurface. A second objective is to determine if manganese concentration can be predicted by trends in specific pre and postoxidation monitored parameters (i.e., pH and oxidation reduction potential (ORP)). The final objective is to identify the effects of site and design conditions on groundwater conditions postoxidation Results indicate that (1) there are limited long term groundwater impacts due to oxidant introduction (i.e., water quality indicators begin to approach preoxidation levels by 2 years postoxidation), (2) manganese concentrations can be predicted and (3) site and design conditions have pronounced short term impacts on geochemical parameters (i.e., especially site media type, mass of oxidant injected, and initial ORP).

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CHAPTER 1

INTRODUCTION

In Situ Chemical Oxidation

In situ chemical oxidation (ISCO) is a remediation technology that has been used under a wide range of geological conditions for the destruction of hazardous contaminants in soil and groundwater. It involves the delivery of chemical oxidants into the subsurface to destroy contaminants. Common oxidants used include catalyzed hydrogen peroxide propagated (CHP) reactions, persulfate, ozone, and permanganate (MnO_4^-). Each of these oxidants works “best” on certain contaminants and under certain site conditions. Each of these oxidants is discussed in more detail in Chapter 2.

Permanganate is a common oxidant used for ISCO. It is a powerful oxidant (1.68V) that relies on direct electron transfer to oxidize contaminants. The primary redox reactions for permanganate are given in equations 1 through 3. In the pH range of 3.5 to 12, the half-cell reactions involve a 3-electron transfer, as shown in equation 2. In each of these three permanganate reactions, the manganese is reduced from Mn (VII) to Mn (II), Mn (IV), or Mn (VI). Manganese oxide solids form under typical environmental conditions (equation 2).

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{+2} + 4H_2O \quad \text{(for pH <3.5)} \quad (1)$$

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_{2(s)} + 4OH^- \quad \text{(for pH 3.5 to 12)} \quad (2)$$

$$MnO_4^- + e^- \leftrightarrow MnO_4^{-2} \quad \text{(for pH > 12)} \quad (3)$$

This research focuses on site and design conditions that affect post-ISCO geochemistry. Table 1 shows key site conditions; these parameters include soil permeability, soil heterogeneity, total organic carbon (TOC), Oxidation Reduction potential (ORP), and pH.

Table 1
Site Condition Parameters

Parameter	Importance
Permeability	Affects oxidant delivery
Heterogeneity	Affects oxidant distribution
TOC	Natural organic matter (NOM) reacts with permanganate
ORP	Correlates with oxidant movement
pH	By-products of H^+ and/or OH^- may result

Design conditions of importance include delivery approach, the mass of oxidant delivered, and the concentrations of oxidant delivered. They also include any technologies coupled with permanganate ISCO (e.g., bioremediation, soil vapor extraction, phytoremediation, other oxidants). Delivery approaches commonly used include multipoint injection wells, recirculation wells, and hydraulic fracturing. These are discussed more in-depth in Chapter 2.

The geochemical conditions that may be affected by these site and design conditions are metal concentrations, pH, and ORP. Metals (including chromium) can be oxidized and/or mobilized to more harmful forms. pH and ORP can be increased or decreased depending on site conditions and contaminants present. These potential effects are described in more detail in Chapter 2.

Problem Statement

ISCO has been used for more than 10 years to remediate hazardous waste sites contaminated by chlorinated solvents (e.g. PCE, TCE, DCE, VC, etc.). While the approach to using this technology has evolved, there are still issues associated with its use. For example, a large amount of oxidant is often delivered to destroy the contaminants. Sometimes the amount of oxidant injected is much higher than the demand for the oxidant in the subsurface. While there are several guidance documents available that recommend parameters to monitor when using permanganate ISCO, there has been little field research conducted to determine what happens to the excess oxidant post-ISCO and what happens to the subsurface geochemical properties post-ISCO. In general, most professionals who use ISCO theorize that at some time point post-ISCO, the subsurface geochemical properties return to pre-ISCO conditions. However, this has not been tested using field data.

Project Description

This research is a review of data from 30 contaminated sites in which permanganate (MnO_4^-) ISCO was used to remediate site contaminants. There are three key objectives of this research. The first objective is to determine whether there are long-term impacts on groundwater quality due to the introduction of permanganate into the subsurface (e.g., is manganese remaining in the subsurface too long). The second objective is to determine if manganese concentrations can be predicted by trends in specific pre and postoxidation monitored parameters (i.e., pH and ORP). The final objective is to identify the effects that site and design conditions have on parameter (manganese, chromium, ORP, and pH) levels postoxidation. Statistical analyses of site data over time and distance from delivery (including correlations and ANOVAs) were used to meet these objectives.

Significance

This research has several important benefits. First, very little research has been conducted on a field scale dealing with long-term impacts of permanganate ISCO. Most recommendations for parameters to monitor come from guidance documents that are based on theory or on laboratory experiments. This research will add evidence to support or refute the existing guidance by evaluating field data collected at 30 sites. Another benefit is the determination of impacts that permanganate can have on groundwater quality. When permanganate ISCO is administered, large quantities of permanganate are usually injected. However, very little research has been done to determine the long-term impact of this oxidant on groundwater quality. This research also identifies conditions and areas on which monitoring should be focused, thus potentially leading to reduced monitoring and maintenance costs.

CHAPTER 2

LITERATURE REVIEW

Hazardous Waste Remediation

Contamination of soil and groundwater by toxic chemicals is a global problem. The overall goal of remediating these contaminated sites is to reduce or, if possible, completely eliminate adverse impacts on environmental and public health. During the past 30+ years, over 500,000 contaminated sites have been reported in the United States (US EPA, 1997). The contaminants of concern (COCs) most associated with these sites are volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), and metals (Figure 1). VOCs commonly encountered include tetrachloroethene (PCE) and trichloroethene (TCE), which were widely used as dry cleaning solvents, and benzene, which was used as an industrial solvent before being discovered as a human carcinogen. SVOCs of concern include polyaromatic hydrocarbons (PAHs) and pesticides. Metals are often found at sites as cocontaminants (Evanko & Dzombak, 1997; Riley & Zachara, 1992; US EPA, 1994, 1997) (Figure 2). During the past 2 decades there have been many innovative methods and technologies developed to remediate contaminated sites. These include both *in situ* and *ex situ* methods. Examples include bioremediation, phytoremediation, and chemical remediation (Table 2).

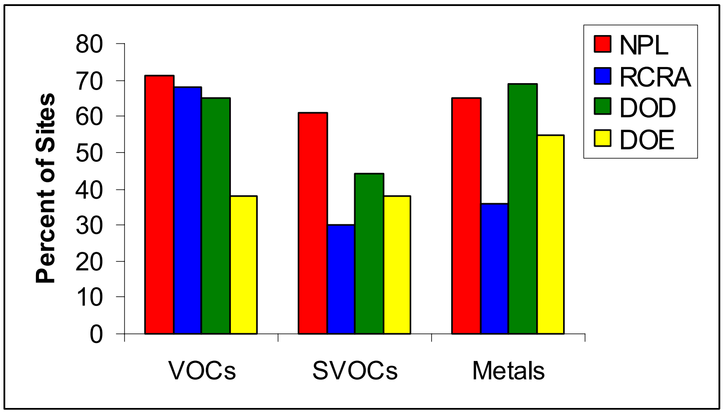

Figure 1 Common Contaminants Found at Hazardous Waste Sites (Adapted from US EPA, 1997). This figure shows the common contaminants found at several types of hazardous waste sites. NPL= National Priority List Sites, RCRA= Superfund Sites, DOD= Department of Defense Sites, and DOE= Department of Energy Sites. VOCs= Volatile Organic Compounds and SVOCs= Semi-Volatile Organic Compounds

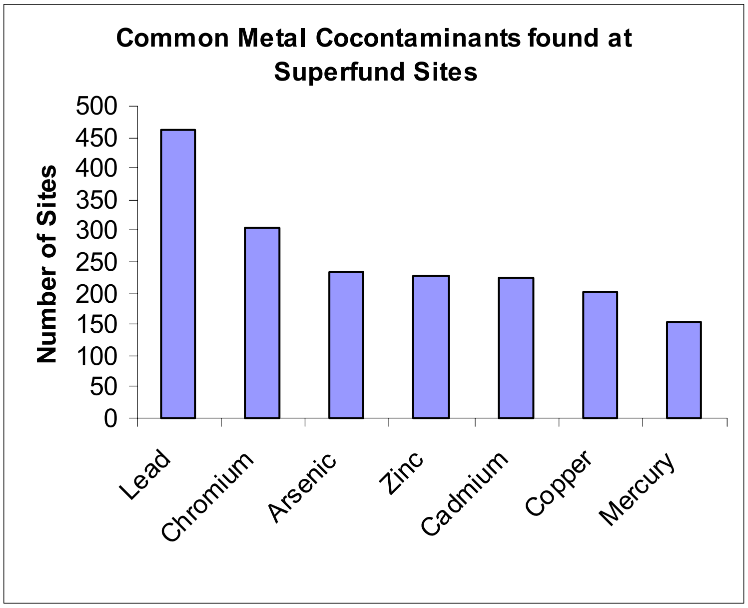

Figure 2 Metal Cocontaminants Most Commonly Found at Superfund Sites (Adapted from US EPA, 1997).

Table 2

Example Remediation Technologies

	Bioremediation/Natural Attenuation[1]	Phytoremediation[2]	Chemical Oxidation Remediation[3]
Defined	Use of microbial communities to remediate contaminants; These communities can be found naturally in the subsurface or introduced for a specific contaminant	Use of plants to uptake contaminants from the subsurface	Introduction of a chemical oxidant into the subsurface to destroy the contaminant
Effectiveness	Slow but effective in most cases; Usually coupled with another technology	Great potential especially for heavy metal remediation	Very effective in most cases; Can also be coupled with other technologies
Advantages	Inexpensive; Can treat a wide range of contaminants	Inexpensive	Wide range of contaminants can be treated; Fast
Disadvantages	Slow	Slow	Can be costly

Note: This table shows example remediation technologies. These are only a few examples; there are many other remediation techniques.

Sources: [1]Interstate Technology and Regulatory Cooperation (ITRC) (1999)
[2]Interstate Technology and Regulatory Cooperation (ITRC) (2001b)
[3]Interstate Technology and Regulatory Cooperation (ITRC) (2001a)

In Situ Chemical Oxidation

In situ chemical oxidation (ISCO) is a chemical remediation method used to alter and/or destroy organic contaminants that is increasingly being applied at hazardous waste sites. Usually an oxidant is injected into the subsurface in solution and relies on direct contact with the contaminant for the reaction to occur producing typically harmless end products (e.g., carbon dioxide and water) (Huling & Pivetz, 2006; ITRC, 2005; Siegrist et al., 1994). The successful implementation of ISCO requires effective techniques for delivering and dispersing chemical oxidants to the subsurface. ISCO also requires effective measuring and monitoring of key parameters to ensure that no adverse environmental or public health impacts occur due to the treatment procedure. The most common ISCO oxidants used are permanganate, ozone, catalyzed hydrogen peroxide propagated reactions (CHP reactions), and persulfate. Due to the different chemical characteristics of each oxidant, each has specific parameters that should be measured and monitored and each works "best" on certain contaminants and site characteristics (Table 3).

Table 3

Features of Commonly Used Oxidants

Features		CHP Reactions	Ozone	Potassium or Sodium Permanganate
Reagent Characteristics	Form	Liquid	Gas	Liquid or Solid
	Point of Generation	Offsite, Shipped Onsite	Onsite During Use	Offsite, Shipped Onsite
	Quantities Available	Small to Large	Small to Large	Small to Large
Oxidation In Situ	Delivery Methods	Wells, Injection Probes, Mixing	Sparge Wells	Wells, Injection Probes, Mixing, Fracturing
	Dose Concentrations	5 to 5 wt. % H_2O_2	Variable	0.02 to 4.0 wt. % MnO_4^-
	Single/Multiple Dosing	Multiple is Common	Multiple	Single and Multiple
	Amendments	Fe^{+2} and Acid	Often Ozone in Air	None
	Subsurface Transport	Advection	Advection	Advection and Diffusion
	Rate Reaction/Transport	High or Very High	Very High	Moderate to High
	Companion Technology	None Required	Soil Vapor Extraction	None Required
Oxidation Effectiveness	Susceptible Organics	BTEX, PAHs, Phenols, Alkenes	Substituted Aromatics, PAHs, Phenols, Alkenes	BTEX, PAHs, Alkenes
	Difficult to Treat Organics	Some Alkanes, PCBs	Alkanes, PCBs	Alkanes, PCBs
	Oxidation of NAPLs	Enhanced Oxidation Possible	Enhanced Degradation Possible	Enhanced Degradation Possible
	Reaction Products	Organic Acids, Salts, O_2, CO_2, Substantial Gas Evolution	Organic Acids, Salts, O_2, CO_2, Minimal Gas Evolution	Organic Acids, Salts, MnO_2, CO_2, Minimal Gas Evolution
Subsurface Effects on Oxidation	Effect of NOM	Demand for Oxidant	Demand for Oxidant	Demand for Oxidant
	Effect of pH	Most Effective at Acid pH	Most Effective at Acid pH	Effective over pH 3.5 to 12
	Effect of Temperature	Reduced Rate at Lower Temperature	Reduced Rate at Lower Temperature	Reduced Rate at Lower Temperature
	Effect of Ionic Strength	Limit Effects	Limit Effects	Limit Effects
Oxidation Effects on Subsurface	pH	Lowered if Inadequate Buffering	Lowered if Inadequate Buffering	Lowered if Inadequate Buffering
	Temperature	Minor to High Increase	Minor to High Increase	None to Minor Increase
	Metal Mobility	Potential for Redox Metals	Potential for Redox Metals	Potential for Redox/Exchange Metals
	Permeability Loss	Potential for reduction due to gas evolution and colloids	Potential for reduction due to gas evolution and colloids	Potential for reduction due to MnO_2 colloid genesis

Note: This table shows the features of oxidants commonly used for *in situ* chemical oxidation.
Source: Siegrist, Urynowicz, West, Crimi, & Lowe (2001)

There are two main advantages of using ISCO technologies over other conventional treatment technologies such as pump and treat. First, large volumes of waste materials are not usually generated and second, treatment is commonly implemented over a much shorter time frame (Cronk & Marvin, 2004; Nimmer, Wayner, & Morr, 2000). Both of these advantages often result in savings on material, monitoring, and maintenance.

Permanganate ISCO

Permanganate is delivered into the subsurface as either potassium permanganate, which is in powder form and is mixed on site, or as sodium permanganate, which is in liquid form. Contaminant destruction is the result of direct electron transfer. Permanganate has a longer half-life compared to more powerful oxidants. This means permanganate will persist in the subsurface longer than other oxidants. As a result it can migrate by diffusion and react with contaminants that other oxidants might not be able to reach (Siegrist, Urynowicz, & West, 2000). The primary redox reactions for permanganate are given in equations 1 through 3 in Chapter 1. In the pH range of 3.5 to 12, the half-cell reactions involve a 3-electron transfer, as shown in equation 2. In each of these three permanganate reactions, the manganese is reduced from Mn (VII) to Mn (II), Mn (IV), or Mn (VI).

Permanganate can be delivered into the subsurface by a variety of approaches. These approaches include multipoint injections, recirculation wells, and hydraulic fracturing (Figure 3). Recirculation wells involve adding the oxidant to extracted groundwater then reinjecting the oxidant containing groundwater into the subsurface, creating a recirculation cell between the injection and extraction wells (West et al., 1998;

West, Siegrist, Cline, & Gardner, 2000). Hydraulic fracturing involves connecting many preexisting fractures and flow pathways in the rock with a larger fracture. This larger, man-made fracture starts at the well and extends out as much as several hundred feet. The hydraulic fracture is formed when a fluid is pumped down the well at high pressures for short periods of time (hours). The high-pressure fluid exceeds the rock strength and opens a fracture in the rock. A propping agent, usually sand, is pumped into the fractures to keep them from closing when the pumping pressure is released (Murdoch, 1995; Murdoch, Wilson, Savage, Slack, & Uber, 1994; Siegrist, Lowe, Murdoch, & Struse, 1999). The multipoint injection approach involves injecting the oxidant through several injection wells in the target treatment zone. Usually these wells are spaced an even distance apart and are injected simultaneously at the same depth or over different depths (US EPA, 2007). Each of these is an effective approach for delivering the oxidant into the subsurface. Site characteristics usually dictate which approach will be most effective. For example, hydraulic fracturing has been frequently chosen as the approach to use for lower permeability media, such as those that are predominately tight clays (Siegrist et al., 1999).

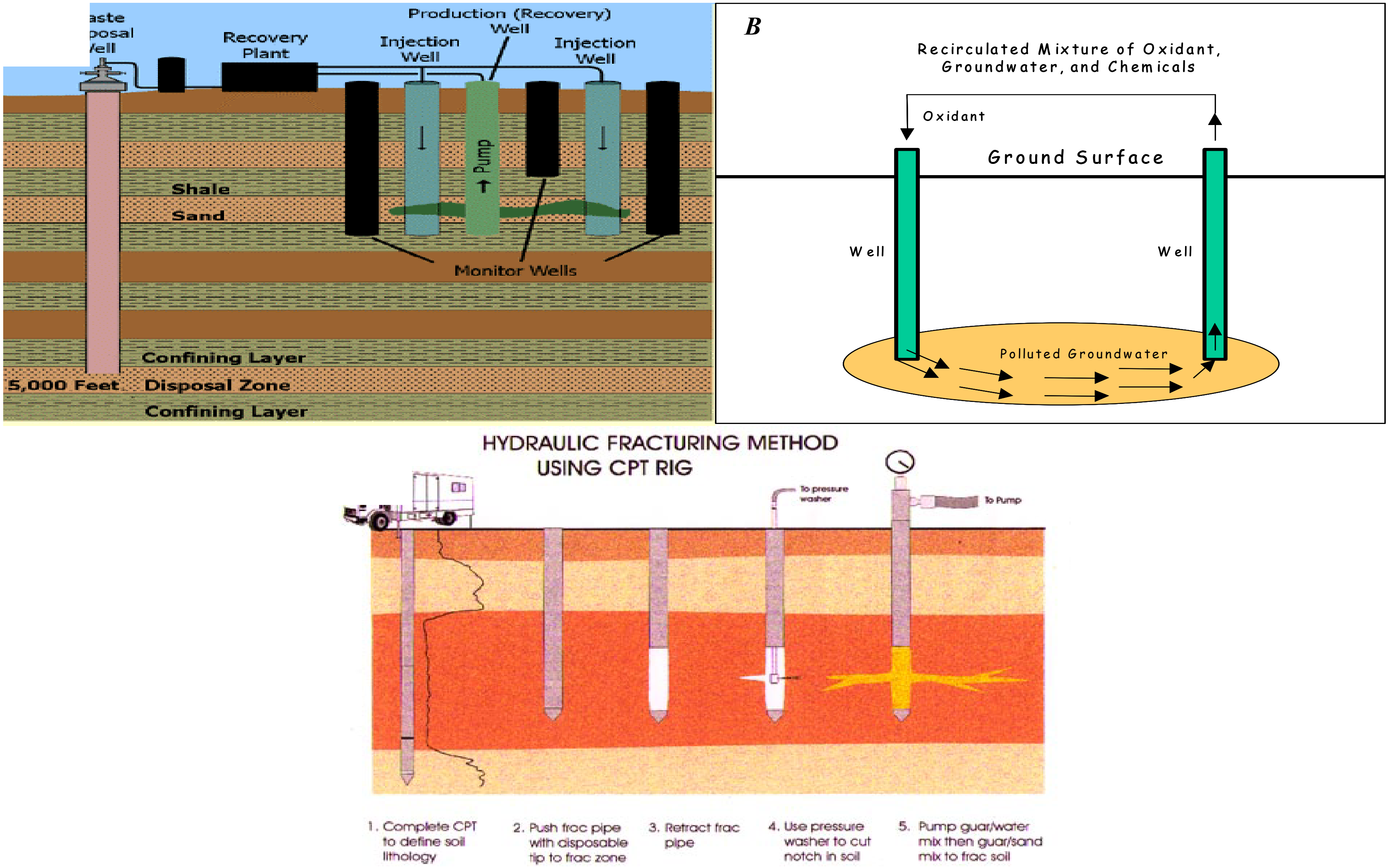

Figure 3 Examples of ISCO Delivery Approaches: (A) injection well (Reprinted with permission from TNRCC, 2002), (B) recirculation well (Adapted from US EPA, 2001) and (C) hydraulic fracturing (Reprinted with permission from GDT, 2003).

Effects on the Subsurface

ISCO is a groundwater remediation technology that has been used for at least 10 years. Although it has been shown to effectively degrade some important COCs, its use can also affect groundwater quality. These effects are partially due to the site and design conditions present at the site. Site conditions include media type (i.e., permeable or impermeable and homogeneous or heterogeneous), initial ORP, initial pH, and initial total organic carbon (TOC). Design conditions include delivery approach, mass of oxidant delivered, concentration of oxidant delivered, and any technology coupled with permanganate ISCO (i.e., applied before, concurrent with, or after ISCO).

Site media type dictates what delivery approach should be used and the amount of oxidant needed to destroy contaminants; media type can also have pronounced impacts on parameters. For example, permeability can affect the ability to deliver oxidant to the contaminated zone and can also affect geochemical parameters. Studies have shown that more permeable and homogenous media result in easier movement of constituents through the subsurface (Oberle & Schroder, 2000); these constituents can be contaminants and/or metals (including manganese and chromium). According to Soel, Zhang, and Schwartz (2003), homogenous high permeability pathways commonly facilitate a large flux of treatment chemicals, thus oxidizing more chemicals and producing more byproducts (i.e., manganese). This can lead to higher concentrations of manganese and other associated byproducts in groundwater. Media type can also affect the pH and ORP of the system. Heterogeneous media can cause large variations in ORP at sites. This is due to the potential for contaminant entrapment due to heterogeneous pathways (Saenton, Illangesekare, Soga, & Saba, 2002). ORP levels at these areas will be much lower due to limited or no interaction with the oxidant. Therefore, measuring ORP levels could indicate heterogeneous or impermeable pathways. One main affect of site media is the impact on movement and flux of oxidant and groundwater pathways. This in turn affects advection, dispersion, and dilution of groundwater.

Initial ORP and pH levels are other site conditions that can affect geochemical conditions. These influence one of the main concerns associated with permanganate ISCO use, the potential to mobilize metals (including chromium and manganese). As stated earlier, metals can be naturally occurring or be present as cocontaminants. Metals can also be added to the subsurface during permanganate ISCO due to impurities in permanganate (Table 4). These metals can be mobilized from the soil and enter the groundwater where they can greatly affect its quality by exceeding drinking water standards (Crimi, 2002; Crimi & Siegrist, 2003; Evanko & Dzombak, 1997; Huling & Pivetz, 2006; Siegrist et al., 2001). One of the most important metals that can be affected is chromium. Numerous studies have shown that permanganate can oxidize trivalent chromium to the more harmful hexavalent chromium due to high ORP in the subsurface. Studies have also shown that manganese dioxide solids, a byproduct of permanganate oxidation, can oxidize chromium. For example, Eary and Rai (1987) studied the kinetics involved in the oxidation of trivalent chromium to hexavalent chromium by reaction with manganese dioxide (a byproduct of permanganate oxidation) and found that the trivalent chromium reacts directly with the manganese dioxide to produce hexavalent chromium not by catalyzed reaction with oxygen at the manganese dioxide surface. Other studies including Moes, Peabody, Siegrist, and Urynowicz (2000) and Li and Schwartz (2000) support these findings. Hexavalent chromium is a problem at ISCO sites due to the potential to migrate off site and cause adverse impacts to environmental and public health. According to the Agency for Toxic Substances and Disease Registry (ATSDR) (2000), ingestion of hexavalent chromium causes numerous adverse health effects including respiratory, cardiovascular, hepatic, renal, reproductive, and developmental effects. It has also been linked to several forms of cancer including lymphoma, liver, bladder, renal, and others (ATSDR, 2000). Other metals of importance due to their redox potential or their likelihood of being at contaminated sites include lead, arsenic, zinc, cadmium, copper, and mercury.

Table 4
Example Impurities Found in Permanganate

Impurity (mg/kg of product)	$KMnO_4$	$NaMnO_4$
Arsenic	4	4
Cadmium	0.1	0.1
Chromium	7.5	5
Copper	2	0.1
Lead	1	0.7
Mercury	0.05	0.03
Zinc	6	0.4

Note: This table shows metal impurities found in permanganate. Potassium permanganate has more impurities than sodium permanganate.
Source: Personal Communication, Carus Chemical Company, 2008.

Site pH also can affect metal mobility. ISCO conditions have the potential to increase or decrease groundwater pH (Siegrist et al., 1999; Siegrist et al., 2000). In an unbuffered system, Case (1997) found that the pH rapidly dropped to pH 2 or 3 during permanganate oxidation of high concentrations of TCE. Siegrist et al. (1999) also observed decreasing pH during permanganate oxidation of a silty clay soil with low concentrations of TCE. However, other studies have observed increases in pH (Crimi & Siegrist, 2003; Nelson, Parker, Al, Cherry, & Loomer, 2001). pH can vary depending on site conditions and contaminants present. For example, oxidation of PCE and TCE will lower the pH by release of H^+ (i.e., 8 moles of H^+ per 3 moles of PCE and 1 mol of H^+

per 1 mol of TCE), whereas oxidation of DCE and VC raises the pH by release of OH^- (i.e., 2 moles of OH^- per 3 moles of DCE and 7 moles of OH^- per 3 moles of VC (Huling & Pivetz, 2006). Changes in pH can result in mobilizing metals or changes in the number of soil microbes, cation exchange capacity, water holding capacity, etc. (ITRC, 2005). A final site condition that affects geochemical parameters is initial TOC. The organic carbon content of the subsurface will directly affect the mass of oxidant to be delivered. The TOC of a site is correlated with the amount of natural organic matter (NOM) and the natural oxidant demand (NOD) of the site (Huling & Pivetz, 2006). Permanganate is rapidly consumed by NOM and reduced inorganic species, which then compete with contaminants for permanganate and are referred to as the NOD (Li & Schwartz, 2000). NOD will compete with the COCs for the permanganate and will continue to do so until the permanganate or the NOD is exhausted. Treatability studies and/or push pull tests are usually required to assess the extent of NOD and its potential effect on permanganate or target contaminant oxidation (Mumford, Lamarche, & Thomson, 2004; Watts & Teel, 2006). TOC directly affects ORP due to oxidation of organic carbon by permanganate. TOC also affects metals (manganese and chromium) by providing sorption sites. Under normal conditions (reducing conditions) organic matter will absorb metals; however, under ISCO conditions the organic matter can react with the oxidant thus allowing metals to mobilize (Huling & Pivetz, 2006).

The approach chosen to deliver the oxidant can greatly impact geochemical parameters. As stated earlier in the chapter, common approaches used are multipoint injection wells, recirculation wells, and hydraulic fracturing. The chosen delivery approach is related to the media type present and usually dictates the concentration of oxidant delivered. For example, recirculation wells usually involve a slow injection of low concentration permanganate. In theory, this type of delivery would have less short term impacts and more long term impacts, whereas injection probes (used in multipoint injection wells) usually inject a large amount of higher concentration permanganate over a shorter period of time. In theory, this type of delivery would have a greater short-term impact and less of a long-term impact. However, very little research has been done to support or to refute these theories.

The mass and concentration of oxidant delivered can also affect geochemical parameters. These are strongly dependent on the natural oxidant demand (NOD) of the system (i.e., constituents that compete with contaminants for permanganate). The higher the NOD, the more oxidant needed to satisfy the demand. More oxidant injected results in a higher system ORP and more subsurface impacts (Siegrist et al., 2000). These impacts can lead to greater byproduct formation, metal mobility, and changes in system pH.

Coupled technologies involve any technology used with the permanganate ISCO to help remediate the site contaminants. As discussed earlier, common technologies coupled with permanganate ISCO include soil vapor extraction (SVE), bioremediation, phytoremediation, and other oxidants. Each technology can have an effect on geochemical parameters. However, no studies have considered ISCO specific versus coupled technology effects.

Guidance Documents

When discussing what parameters should be measured and monitored during ISCO, guidance documents appear ambiguous (Table 5). For example, Interstate Technology and Regulatory Cooperation (ITRC) guidance documents recommend monitoring and measuring a large number of parameters, while Department of Energy (DOE) guidance documents recommend monitoring much fewer. In theory it is a good idea to monitor the maximum amount of parameters, but for most private companies that have cost restraints, it is impossible to monitor large numbers of parameters. Therefore most companies will chose to monitor a limited number of parameters listed in the guidance document or be directed toward particular ones by regulatory agencies. In some cases the parameters selected may be the most important parameters, but in other cases important parameters may not be selected.

Table 5

Guidance Document Recommendations for ISCO Monitoring

	Guidance Document				
Parameters	ITRC 2001[1]	ITRC 2005[2]	GWRTAC[3]	ESTCP[4]	DOE[5]
PH	X	X	X	X	X
DO	X	X	X	X	
ORP			X	X	X
Conductivity	X	X		X	
COD	X	X			
TOC		X			X
Alkalinity	X	X			X
Hardness		X			
Turbidity		X			
Temperature		X	X	X	X
Total Solids		X			
Bioactivity		X			
Manganese		X		X	
Chromium	X	X		X	
Cadmium		X		X	
Lead	X	X		X	
Nickel		X		X	
Iron		X		X	
Sodium	X	X			
Potassium	X	X			
Calcium	X	X			
Magnesium	X				
Aluminum		X			
Arsenic		X			
Antimony		X		X	
Selenium	X				
Vanadium	X				
Uranium	X				
Molybdenum	X				
Thallium				X	
Nitrate	X	X			
Sulfate	X	X			
Chloride	X				
Ammonia		X			
Phosphate		X			

Sources: [1] Interstate Technology and Regulatory Cooperation (ITRC) (2001)
[2] Interstate Technology and Regulatory Cooperation (ITRC) (2005)
[3] Yin, Y. and H.E. Allen (1999)
[4] Environmental Security Technology Certification Program (ESTCP) (1999)
[5] Innovative Technology Summary Report (1999)

According to guidance, in all ISCO projects it is important to know which metals are present in the soil and groundwater because, as discussed earlier, this treatment technology can oxidize some metals, including iron, chromium, and selenium, to a more soluble form, thereby increasing their migration potential (Crimi & Siegrist, 2003; Li & Schwartz, 2000; Moes et al., 2000). Also, as discussed earlier in the chapter, in an oxidized state, some metals, including chromium, are more harmful than in their original state. ISCO can also affect metals by decreasing the available natural organic matter (NOM) (Huling & Pivetz, 2006). Under normal circumstances NOM will absorb metals; however, under ISCO conditions NOM can react with the oxidant thus allowing metals to mobilize (Huling & Pivetz, 2006). Therefore, knowing which metals to monitor can reduce the likelihood of deleterious effects. According to guidance issued by the Interstate Technology Regulatory Cooperation (ITRC, 2001), the initial investigation should include the following metals: chromium, uranium, vanadium, selenium, lead, and molybdenum. However, in 2005 the ITRC revised the metals that should be monitored to barium, cadmium, chromium, copper, iron, lead, and selenium. These are the most important metals to monitor due to their toxicity, redox sensitivity, and persistence in the environment.

More guidance recommended analyses include total dissolved solids (TDS), major anions (chloride, sulfate, nitrate, fluoride), and major cations (calcium, sodium, magnesium, potassium, manganese). These analyses are useful to determine baseline levels and to track changes in mineral composition due to oxidant treatment (ITRC, 2005). It is important to track the changes in mineral composition because the mineral composition of a soil not only helps define the soil texture but also affects the chemical and physical properties of the soil, i.e., cation exchange capacity, pH, Eh, and water holding capacity. These analyses are also helpful in identifying oxidant distribution and effectiveness.

Other parameters that the Interstate Technology and Regulatory Cooperation (ITRC, 2005) recommends measuring and monitoring include pH, ORP, and dissolved oxygen (DO). As discussed earlier in the chapter, the baseline pH values are useful in determining the suitability of an oxidant's effectiveness as shown in equations 1-3 in Chapter 1. The pH should be measured periodically during treatment to monitor changes. This monitoring is important because, as discussed earlier, the pH of the soil and groundwater has major impacts on the activities that occur in the soil, i.e., mobilizing of metals, change in number of soil microbes, cation exchange capacity, water holding capacity, etc. The redox potential can be used to determine oxidant movement in the field. Positive values of redox reflect oxidizing conditions and generally coincide with the oxidant movement.

According to these guidance documents, permanganate treatment requires the measuring and monitoring of several other parameters not measured for other ISCO treatments. A key parameter of interest is the manganese groundwater concentration. As stated earlier, the Secondary Drinking Water Standard created by the US EPA for groundwater manganese concentrations is 0.05 mg/L. Secondary Drinking Water Standards protect aesthetic properties of water including odor, color, and taste. Background measurements of manganese concentrations should be collected to establish existing conditions prior to injection of permanganate. The potential for manganese oxide precipitation and permeability loss in soils should also be considered. As discussed earlier in the chapter, this permeability loss can affect the water holding capacity, cation exchange capacity of the soil, and more importantly fluid flow paths (Huling & Pivetz, 2006).

While monitoring guidance exists, site data are also needed to understand what to monitor (i.e., theoretical changes vs. real changes). By comparing collected site data from each site with each other and guidance documents, this research began by trying to determine which parameters are critical to monitor when using a certain design approach at a site with certain characteristics and which design approach works best for which site types. However, once data were collected it was determined that there was not enough data available to accomplish this goal (See Table 9). Although this research is not able to create a protocol, it will determine the affects site and design conditions have on geochemical parameter values. This determination will aid remediators by having a focused approach for monitoring (i.e., at certain site conditions metal concentrations are more likely to be high; therefore, focused monitoring will need to occur).

CHAPTER 3

METHODS

General Approach

For this research data were collected from 30 permanganate ISCO sites to (1) determine whether there are long term impacts on groundwater quality due to the introduction of permanganate into the subsurface, (2) determine if manganese concentrations can be predicted by trends in specific pre and postoxidation monitored parameters, and (3) determine the effects site and design conditions have on parameter levels. Data were categorized based on site and design conditions. It was also interpolated to establish common times and distances for each site. Data were analyzed using several statistical methods.

Case Studies

Data sets were collected from 30 sites in which permanganate ISCO was used to remediate site contaminants. Sites were selected where pilot scale or full scale ISCO studies were conducted at least 1 year prior to the beginning of this study. Three criteria were evaluated for inclusion. First, sites were required to have well documented pre and postoxidation data that included concentrations of metals (especially manganese and chromium), some geochemical information (i.e., pH and ORP), and background information on the site (i.e., background concentrations, site history, etc). Second, sites must have had well documented ISCO system design (i.e., delivery methods, concentration of oxidant used, and mass of oxidant delivered). Third, only sites containing full reports (including adequate QA/QC sections) from state and federal agencies and those from peer-reviewed sources were used. Detailed information including location, COCs, oxidant mass, oxidant concentration, media type, etc on each site can be found in Appendix A.

Organization of Data

Once a site was selected, a letter (A-δ) was assigned to take the place of the actual site name in order to protect client confidentiality. The information (parameter concentrations, oxidant mass and concentration, media type, well collection depths, etc.) was then organized into excel books. Each site was placed into a separate excel book with a different workbook sheet for each monitoring date (pre-ISCO, <4 weeks post, 4-24 weeks post-ISCO, 24-52 weeks post-ISCO, and 52-104 weeks post-ISCO). Parameters placed in the spreadsheets included manganese concentrations, pH, ORP, TOC, and chromium. Each monitoring well at each site was then assigned X, Y, and Z coordinates based on groundwater flow direction, the distance from the target treatment zone (TTZ), and well depth (Figure 4). The X and Y assigned coordinates were then used in ArcGIS 9.0 (ESRI, 2006) to obtain 2D interpolated concentrations of parameters at chosen distances from TTZ (X = 0 feet, 10 feet, 20 feet, 30 feet, 50 feet, and 100 ft) over chosen time points (pre-ISCO, <4 weeks postoxidation, 4-24 weeks postoxidation, 24-52 weeks postoxidation, and 52-104 weeks postoxidation), as described below. X, Y, and Z coordinates were used in a mathematical equation (described below) to obtain a 3D interpolation of parameter values. Both 2D and 3D interpolations were performed to check for consistency. These interpolations were done with the goal of having common distances to analyze for sites where monitoring locations are highly variable.

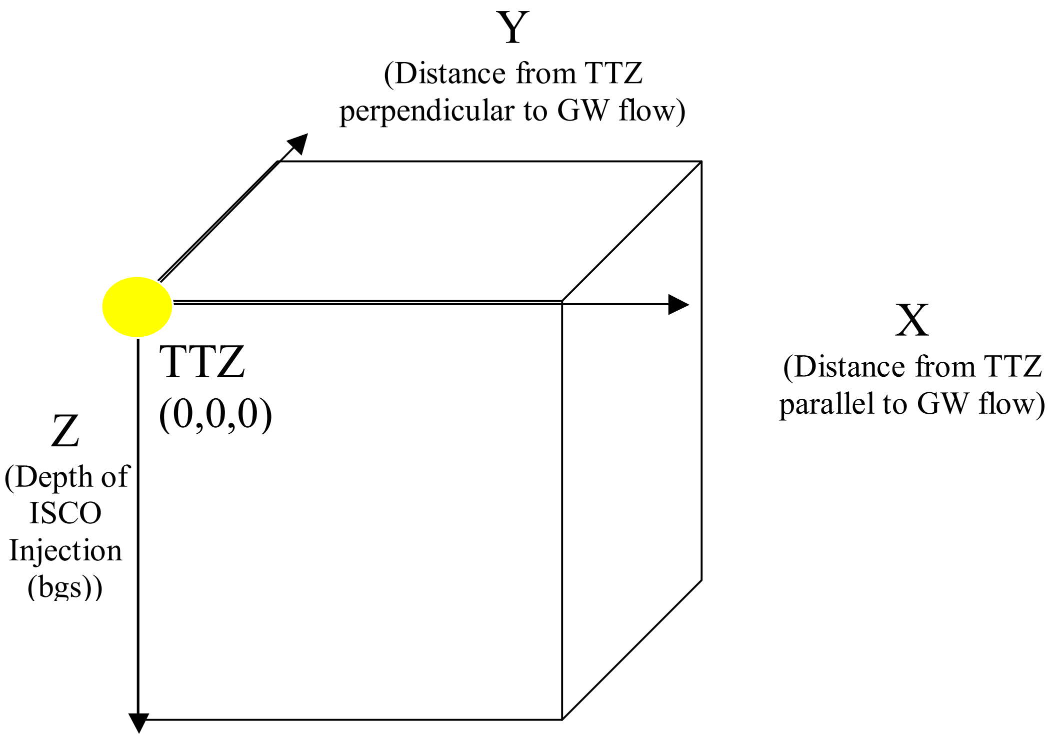

Figure 4 Diagram of Locations of X,Y, And Z Coordinates.
Note: GW= Groundwater; bgs= Below Ground Surface

Interpolation of Data

Due to the variability among monitoring wells from site to site (i.e., number, location, depth, etc.); an interpolation of data was performed to obtain parameter values at common distances and times. A simplified linear equation (equation 4) was used to find interpolated values based on the assigned X, Y, and Z coordinates (personal communication, Catherine Chen, February 23, 2008). For each site the Y_0 at each distance was set as 0. A Y of 0 was chosen to follow the flow of the groundwater vector. The X_0s of each site were chosen as 10 ft, 20 ft, 30 ft, 50 ft, and 100 ft. These are the distances from the TTZ with the groundwater flow vector. These distances were chosen based on feasibility of data and site groundwater velocities (Table 43). The Z_0s were chosen based on the actual depth below ground surface (bgs) at which the oxidant was injected. For the interpolated numbers see Appendix B. Time ranges were chosen based on the most common time points site remediators performed postoxidation monitoring.

$$\text{Unknown Concentration} = \frac{\sum \text{known concentration}/d^2}{\sum 1/d^2} \qquad (4)$$

$$\text{Where } d = \sqrt{(X-X_0)^2 + (Y-Y_0)^2 + (Z-Z_0)^2}$$

ArcGIS 9.0 (ESRI, 2006), a geographic information system produced by ESRI, was used to create 2D interpolation maps of sites to compare with these 3D interpolations. ArcGIS 9.0 contains several programs including ArcMap 9.2. This program was used to interpolate the data over distance and time. The assigned coordinates for each monitoring well of each site were downloaded into ArcMap 9.2. Once downloaded a 2D interpolation analysis using the X and Y dimensions was run on each parameter. Once the program had created a 2D interpolation map, distances from the TTZ were measured. As stated earlier, distances chosen were X = 0 feet, 10 feet, 20 feet, 30 feet, and 50 feet from TTZ. Therefore, for each site parameter a 2D interpolation map was created for each monitoring time point category. For example ArcMap 9.2 interpolation maps see Appendix C. These 2D interpolated parameter concentrations were compared with the 3D interpolated values to look for consistency. The 3D interpolated values were placed into a spreadsheet to be statistically analyzed using Microsoft Excel (2007) and MiniTab 12 (1998).

Statistical Analyses

In preparation for statistical analyses, a spreadsheet was created. An example of the spreadsheet is shown in Table 6. The spreadsheet included site name (A-δ). It also included several categorized parameters based on design conditions (Table 7) and site conditions (Table 8). The spreadsheet also included parameter concentrations per time and distance. For more information on these parameters, see Chapter 1. Site and design conditions were chosen based on their potential impacts on site geochemical parameters and overall remediation outcomes. Ranges were chosen based on observed values at sites or through literature.

Table 6

Example Statistical Spreadsheet

	Site Conditions					Design Conditions			
	ORP	pH	TOC	Hetero	Perm	Delivery Approach	Mass	{ }	Coupled
A	0	-1	NM	0	0	-1	High	Med	0
B	0	0	NM	0	-1	1	High	Low	-1
C	-1	0	NM	-1	0	0	High	Med	1
D	1	0	0	-1	0	1	N/A	N/A	0
E	0	0	NM	0	0	0	N/A	High	-1
F	-1	0	NM	0	-1	1	Low	N/A	1
G	0	0	NM	0	0	1	Med	Med	0
H	1	0	NM	0	-1	1	N/A	Low	0
I	-1	0	NM	0	-1	1	N/A	N/A	0
J	0	0	NM	0	0	1	High	High	0
K	0	0	NM	N/A	N/A	N/A	N/A	N/A	0
L	1	0	-1	-1	0	1	High	Med	0
M	0	0	NM	0	-1	1	Med	High	1
N	1	0	-1	0	0	1	Low	Med	-1
O	1	0	0	-1	0	1	Med	High	0
P	1	-1	0	-1	0	1	Low	Low	0
Q	1	0	1	-1	-1	1	Low	High	0
R	1	0	1	-1	0	1	Low	High	-1
S	1	0	NM	N/A	N/A	1	N/A	N/A	0
T	1	0	0	N/A	N/A	1	N/A	N/A	-1
U	-1	0	0	-1	0	1	N/A	N/A	0
V	-1	0	1	-1	0	1	Med	Low	0
W	0	0	NM	0	0	1	Low	High	-1
X	-1	0	NM	0	0	1	Low	Med	0
Y	0	0	NM	0	0	-1	High	Low	0
Z	1	0	0	0	0	1	Med	Low	0
α	-1	0	NM	-1	0	1	Low	Low	1
β	-1	0	NM	-1	0	0	N/A	N/A	1
χ	-1	0	NM	-1	0	1	N/A	N/A	1
δ	1	0	0	-1	0	1	Med	N/A	1

Note: This table shows categorical values for each site used in this research. ORP= Oxidation Reduction Potential, TOC= Total Organic Carbon, Hetero= Heterogeneity, Perm= Permeability, Mass= Mass of Oxidant Delivered, { }= Concentration of Oxidant Delivered, and Coupled= Use of Coupled Technologies.

Table 7

Design Condition Variables and Categorical Value

Variable	Categorical Value
Delivery Approach	• Recirculation Well = -1 • MultiPoint Injection Wells = 0 • Hydraulic Fracturing = 1
Mass of Oxidant Delivered	• High (> 500 mg/kg) = -1 • Medium (100 – 500 mg/kg) = 0 • Low (< 100 mg/kg) = 1
Concentration of Oxidant Delivered	• High (> 9%) = -1 • Medium (2.5 – 9%) = 0 • Low (< 2.5%) = 1
Coupled Technology	• Pre-ISCO = -1 • None = 0 • Post-ISCO = 1

Table 8

Site Condition Variables and Categorical Value

Variable	Categorical Value
Total Organic Carbon (TOC)	• Low levels (<1 mg/L) = -1 • Medium levels (1-10 mg/L) = 0 • High levels (>10 mg/L) = 1
Oxidation Reduction Potential (ORP)	• Negative values = -1 • Near zero levels = 0 • Positive levels = 1
pH	• <6 = -1 • 6-8 = 0 • >8 = 1
Heterogeneity	• Homogeneous *(spatial variations in permeability of less than three orders of magnitude) = 0 • Heterogeneous *(spatial variations in permeability of more than three orders of magnitude) = -1
Permeability	• Permeable *(hydraulic conductivity > 10^{-7} m/s) = 0 • Impermeable *(hydraulic conductivity < 10^{-7} m/s) = -1

Note: (*) Represents information obtained from The National Science Academy (2001).

Before running analyses on the interpolated data, each parameter was tested for normality using the Kolmogorov-Smirnov Goodness of Fit Test. The data that were found to be nonnormal were transformed. The chosen transformation was a log transformation. A log transformation was chosen as the first transformation because plotted concentration data appeared to be logarithmic with the bulk of data centralized toward the lower concentration ranges. This produced normal data for all variables where transformation was necessary; therefore, no other transformations were required.

Several statistical analyses were performed on the data. To take into account various confounding factors, these analyses were run using a 75% confidence interval where applicable. The first analysis performed was a Pearson's correlation analysis. This analysis was run to determine if there was a positive correlation between (1) post-ISCO dissolved manganese concentrations and both pre- and post-ISCO ORP values, (2) post-ISCO dissolved manganese concentrations and post-ISCO pH values, (3) post-ISCO dissolved manganese concentrations and post-ISCO chromium concentrations, (4) post-ISCO dissolved manganese concentrations and mass of oxidant delivered, and (5) post-ISCO dissolved manganese concentrations and concentration of oxidant delivered. Next, analysis of variance (ANOVAs) was run on the data to determine if parameter values were affected by time (e.g., do levels return to pre-ISCO levels over time) and distance (e.g., do changed levels migrate downgradient for the TTZ) from TTZ. ANOVAs were also used to determine if there was a significant change in parameter levels at different site and design conditions and to determine if there were significant interactions between these site and design conditions. Parameters analyzed using ANOVAs were manganese, ORP, pH, and chromium. These were run at a 75% confidence interval with an alpha of 0.25.

Quality Assurance and Quality Control (QA and QC)

To ensure the quality of this research, a quality assurance and quality control plan was created and implemented. First, data were copied from the actual data set and entered into an Excel spreadsheet. Once this was completed for each site, two nonparticipating and noninvolved persons compared data entered to actual data for 10 randomly chosen sites to verify data were correctly transferred to the excel file. Second, data were copied and pasted into worksheets based on monitoring time point. Once this was completed for each site, one nonparticipating and noninvolved person compared copied and pasted data to the data recorded in the master spreadsheet for 10 randomly chosen sites. Third, data from monitoring time spreadsheets were copied and pasted into a separate spreadsheet for interpolation. Once again, an unbiased person checked 10 randomly chosen sites for consistency. Fourth, an equation for 3D interpolation was put into the interpolation spreadsheet. Once the data were interpolated, two nonbiased persons looked at each part of the equation of 10 randomly chosen sites for correctness. Fifth, once the interpolation was completed, a 2D interpolation was done using ArcGIS 9.2. The 2D and 3D values were compared for consistency. Finally, once the interpolation was done the interpolated numbers were put into a spreadsheet for statistical analysis. Two people once again compared the entered interpolated values with the interpolated values from the original spreadsheet of 10 randomly chosen sites for consistency. This check for consistency will help ensure quality results.

Limitations

Limitations due to data or lack of data are possible. First, data sets were obtained from reports that contained QA and QC sections and laboratory results. However, this research relies on the assumption that these QA and QC standards were followed and that laboratory analyses were run by certified laboratories. If this assumption is not true, results obtained could be invalid. There could also be limitations due to the lack of data for certain parameters or variables. For example, more data are available for permeable sites than for impermeable sites. And more data are available for manganese than for chromium. Therefore, some analyses are run using a limited number of values. These results could be skewed based on the data available. To counteract this limitation, some of the analyses are discussed qualitatively rather than quantitatively.

There could also be limitations due to the interpolations of values. Interpolation uses the parameter values at surrounding wells to create an estimated value based on surrounding concentrations. This process is not always accurate and involves an amount of uncertainty. The chosen interpolation method could also create some limitations. A simplified linear equation was used to perform 3D interpolations as opposed to numerical modeling. This simplified equation does not consider dilution, dispersion, hydraulic gradient, or other hydrological features. The use of numerical modeling would have produced values with less uncertainty involved. However, because analyses were run on data from all 30 sites combined, it was determined that the uncertainty involved with the simplified linear equation would not greatly affect the project outcome.

Human errors could result in invalid results. A QA and QC protocol was created and followed for this research. However, only 10 out of 30 sites were chosen to be tested for consistency. Therefore, it is possible that sites not chosen could contain errors. These errors could translate into invalid or misleading results.

CHAPTER 4

RESULTS

Descriptive Statistics of Sites

Figures 5–8 describe the 30 sites used for this research. Figure 5 shows the contaminants of concern found at the sites. The majority (>75%) of sites were contaminated by VOCs. Sites were also contaminated with SVOCs, metals (i.e., arsenic and lead), BTEX (i.e., benzene, toluene, ethylbenzne, and xylene), and others (i.e., dioxins, pesticides, and furans). Figure 6 shows the location of each of the 30 sites. Sites used in the research were located in 15 of the 50 states. The greatest number of sites (seven) was located in Tennessee. Figure 7 shows the media type found at the sites. Forty percent of sites consist of heterogeneous mostly permeable media, while 33% of sites have homogeneous mostly permeable media. There are also homogeneous and heterogeneous impermeable media found at sites. Figure 8 shows the number of sites that used coupled technologies. Six sites used other technologies before ISCO (i.e., soil vapor extraction, bioremediation, surfactants, etc.). Six sites used other technologies after ISCO (i.e., bioremediation, phytoremediation, other oxidants, etc.). Eighteen sites did not couple ISCO with another technology. Table 9 shows the sizes of the TTZs at sites. The size categories (small, medium, large) were chosen based on the size relation site to site. Sites categorized as small contained TTZs that ranged from 5 ft by 20 ft to 20 ft by 20 ft. Medium sites were chosen as those that had TTZs that ranged from 21 ft by 21 ft to 75 ft by 75 ft. Large sites are those that had TTZs larger than 75 ft by 75 ft. Finally, Table 10 shows the parameters monitored at each site with respect to guidance document recommendations. It is important to note that several parameters were only monitored at one time point or at only one well.

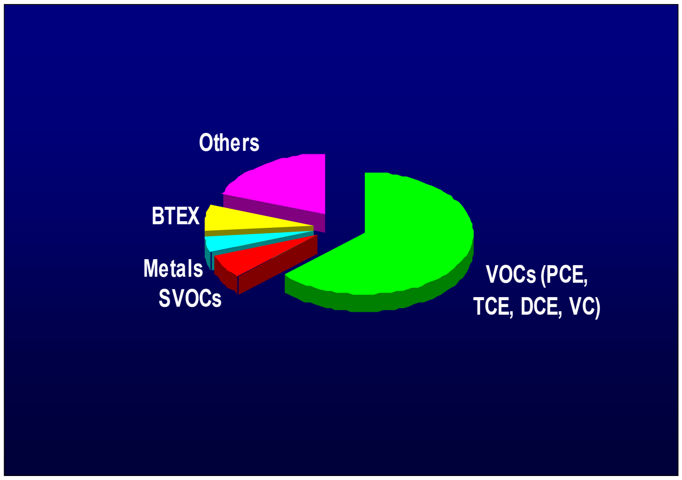

Figure 5 Contaminants of Concern at Sites Used For This Research. It is important to note to each site was not always contaminated with only one contaminant. Many sites were contaminated with two or more contaminants.

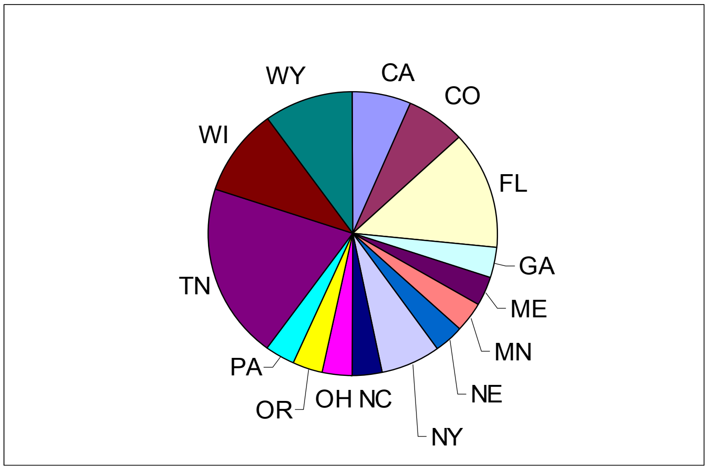

Figure 6 State Locations of Sites Used For This Research.

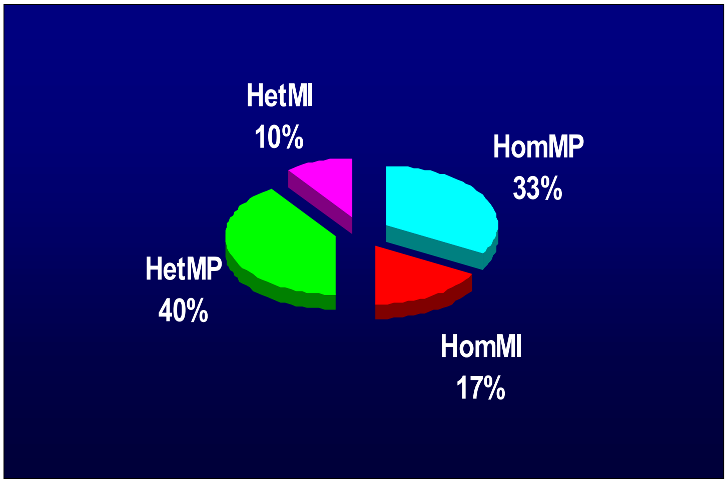

Figure 7 Media Types Found at Sites. This figure shows the percentage of each media type found at sites used for this research. 40% of sites are heterogeneous mostly permeable (HetMP), 33% are homogeneous mostly permeable (HomMP), 17% are homogeneous mostly impermeable (HomMI), and 10% are heterogeneous mostly impermeable (HetMI).

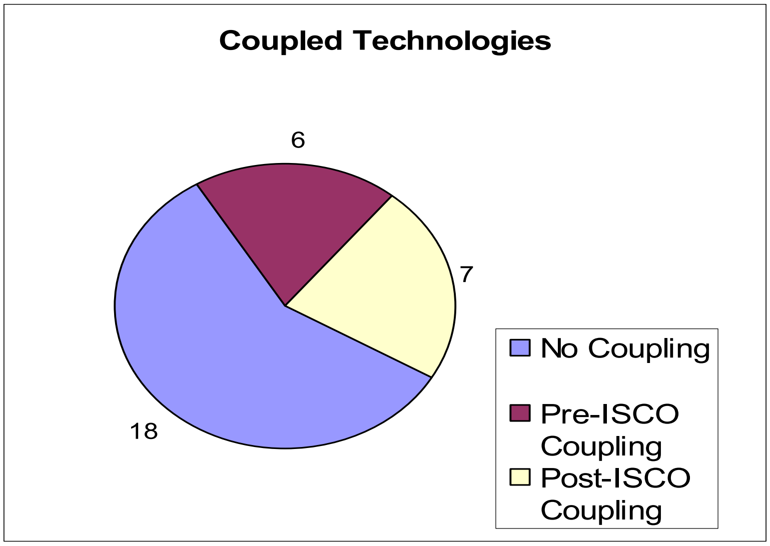

Figure 8 Numbers of Sites with Coupled Technologies. This pie chart shows the number of sites containing coupled technologies. These technologies are broken down into precoupling, postcoupling, or no coupling.

Table 9

Size of Target Treatment Zone at Sites Used for This Research

Size TTZ	# Sites	% Sites
Small	14	47
Medium	11	37
Large	5	16

Table 10

Parameters Monitored at Sites Used for This Research

	Site																													
Parameter	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	W	X	Y	Z	α	β	χ	δ
pH	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X
DO	X		X	X	X		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X				X			X	X
ORP	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X	X	X	X	X	X
Cond	**X**	**X**	**X**		**X**	**X**			**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	X	X		X	X	**X**			X				X	X
COD				X																										
TOC				X										X	X	X	X	X		X	X	X				X				X
Alkalinity	X			X						X		X		X	X	X	X	X		X	X									
Hardness	X											X																		
Turbidity	X		X			X				X										X		X								
Temp	X		X		X	X			X	X	X	X	X	X	X	X	X	X		X	X	X			X					
Total Solids	X											X									X					X				
Bioactivity																					X									
Manganese	X	X	X	X	X	X	X		X	X		X		X	X	X	X	X			X		X	X		X	X	X	X	
Chromium	X	X	X	X			X		X			X				X					X		X			X	X	X		
Cadmium	X		X	X																						X	**X**	X		
Lead	X		X	X												X					X					X	**X**	X		
Nickel	X		X																		X									
Iron	X		**X**	**X**	X							**X**	**X**	**X**	**X**	X	X	X		X	X	**X**				**X**		X	X	
Sodium			X	X						X		X									X					X				
Potassium	X		X							X		X									X					X				
Calcium	X		X							X											X					X			X	
Magnesium	X		X							X											X					X				
Aluminum	X		X																		X									
Arsenic	X			X												X					X					X	X	X		
Antimony	X		X	X																										
Selenium			X																							X	X	X		
Vanadium	**X**		X																											
Uranium																														
Molybdenum	X																													
Thallium	X		X	X																	X									
Nitrate				**X**						**X**		**X**	**X**	**X**	**X**	**X**	**X**	**X**		**X**	**X**	**X**								
Sulfate				X								**X**		X	X	X	**X**	**X**		**X**	X	X				**X**				
Chloride		X	**X**	X	**X**				**X**	**X**	X	**X**			X	**X**	X	X		**X**	X	X				**X**				
Ammonia																														
Phosphate																														

Note: Blue Highlighted parameters are those that were monitored only once or only at one monitoring well.

Qualitative Evaluation

Two variables (delivery approach and initial TOC) were analyzed quantitatively (Tables 11 and 12), but are discussed qualitatively. Of the 30 sites used for this research, 26 sites delivered oxidant using multipoint injection wells, 2 sites used recirculation wells, and 2 sites used hydraulic fracturing to deliver oxidant into the subsurface. Only 11 of the 30 sites measured an initial TOC level. Due to the lack of data for these two variables, they will be discussed qualitatively. Permanganate levels are also briefly discussed qualitatively. These were observed to determine the effect they had on ORP values (i.e., if ORP values drop once the permanganate was exhausted).

Table 11

ANOVAs at Monitoring Time Points for Site Delivery Approach

	Delivery Approach							
	Mn		pH		ORP		Cr	
	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value
T0	2.99	0.549	0.76	0.733	1.38	0.264	1.79	0.890
T1	1.85	0.165	2.47	0.092	8.55	4.76×10^{-4}	0.28	0.606
T2	3.52	0.037	0.09	0.908	0.98	0.381	2.8×10^{-3}	0.958
T3	0.02	0.985	0.02	0.985	5.49	6.93×10^{-3}	N/A	N/A
T4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Note: T0= pre-ISCO, T1=<4 weeks postoxidation, T2=4-24 weeks postoxidation, T3=24-52 weeks post-ISCO, T4= 52-104 weeks post-ISCO. N/A= no data available

Table 12

ANOVAs at Monitoring Time Points for Site Total Organic Carbon

	TOC							
	Mn		pH		ORP		Cr	
	F Value	p Value	F Value	p Value	F Value	P Value	F Value	p Value
T0	0.96	0.662	0.12	0.528	18.43	2.87×10^{-4}	0.83	0.523
T1	1.54	0.054	0.22	0.253	23.12	4.38×10^{-5}	1.23	0.085
T2	2.31	0.051	0.18	0.439	14.86	2.44×10^{-4}	N/A	N/A
T3	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
T4	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

Note: T0= pre-ISCO, T1=<4 weeks postoxidation, T2=4-24 weeks postoxidation, T3=24-52 weeks post-ISCO, T4= 52-104 weeks post-ISCO. N/A = no data available.

Quantitative Statistics

Normalization

Before any statistical analyses were run, data were checked for normality using the Kolmogorov-Smirnov Goodness of Fit Test. pH and ORP values were determined to be normal (0.345 and 0.340) (i.e., values obtained were greater than 0.1). However, the manganese and chromium concentrations were not normal (0.005 and 0.023) (i.e., values obtained were much less than 0.1). A log transformation was performed on the nonnormal data and the Kolmogorov-Smirnov Goodness of Fit Test was performed again. Results from the normality test showed that the transformed concentrations were now normal (0.340 and 0.350). Therefore, no other transformations were used.

Manganese

Pearson's Correlation Analyses. Several Pearson's correlation analyses were run on the transformed manganese concentrations. Correlation analyses use coefficients ranging from –1 to 1 to describe the relationship between two variables. Coefficients close to 1 represent a strong positive correlation and a coefficient close to –1 represents a strong negative correlation. For this research manganese correlation analyses included (1) dissolved manganese and both pre- and post-ISCO ORP, (2) dissolved manganese and post-ISCO pH, (3) dissolved manganese and chromium, (4) dissolved manganese and mass of oxidant delivered, and (5) dissolved manganese and concentration of oxidant delivered. As Table 13 shows, manganese shows positive correlation with initial and post-ISCO ORP, as well as with the mass of oxidant delivered. Manganese also shows a slightly positive correlation with pH, chromium, and concentration of oxidant delivered; however, this is not a strong correlation.

Table 13
Pearson's Correlation Analyses for Manganese

Variables	Correlation Coefficient
Manganese and Initial ORP	0.76
Manganese and Postoxidation ORP	0.88
Manganese and pH	0.59
Manganese and Chromium	0.49
Manganese and Mass Delivered	0.62
Manganese and Concentration Delivered	0.56

<u>ANOVAs.</u> ANOVAs were run to determine if there were significant ($\alpha = 0.25$) differences in (1) manganese concentrations over time, (2) manganese concentrations over distance, and (3) manganese concentrations based on site and design conditions. Time and distance ANOVA results can be seen in Table 14. According to these results, manganese concentrations are beginning to approach pre-ISCO conditions at monitoring time point T4 (52-104 weeks post-ISCO). These results also show that manganese concentrations inside the target treatment zone (D0) are significantly ($\alpha = 0.25$) different from manganese concentrations outside the target treatment zone. This suggests that impacts are localized in the target treatment zone. Site and design condition ANOVAs run based on time monitoring points (<4 weeks post-ISCO, 4-24 weeks post-ISCO, 24-52 weeks post-ISCO, and 52-104 weeks post-ISCO). Results for each time monitoring point can be seen in Tables 15-19. Table 20 shows a summary of significant variables found in these analyses. Tables 20-25 show results from ANOVA results run on manganese concentrations at each distance from TTZ. Table 26 shows a summary of significant variables found in these analyses. These results show that the only significant impacts are seen inside the target treatment zone (D0).

Table 14

Manganese Concentration ANOVAs for Time and Distance

Manganese (n=20)						
	Average (mg/L)	Average (mg/L)	Range (mg/L)	Range (mg/L)	F Value	p Value
T0 vs. T1	T0= 1.32	T1= 10.29	T0= 0.002-7.22	T1= 0.104- 79.79	268.44	1.94×10^{-7}
T0 vs. T2	T0= 1.32	T2= 10.22	T0= 0.002-7.22	T2= 0.040- 124.84	64.09	4.34×10^{-5}
T0 vs. T3	T0= 1.32	T3= 5.74	T0= 0.002-7.22	T3= 0.039- 26.46	1942.87	7.74×10^{-11}
T0 vs. T4	T0= 1.32	T4= 2.41	T0= 0.002-7.22	T4= 0.280- 20.95	17.75	0.030
D0 vs. D1	D0= 10.14	D1= 7.34	D0= 6.24-83.25	D1= 0.0065- 23.59	122.98	1.88×10^{-7}
D0 vs. D2	D0= 10.14	D2= 5.76	D0= 6.24-83.25	D2= 0.0071- 25.30	112.70	9.45×10^{-6}
D0 vs. D3	D0= 10.14	D3= 5.57	D0= 6.24-83.25	D3= 0.0058- 26.46	95.44	9.11×10^{-6}
D0 vs. D4	D0= 10.14	D4= 5.49	D0= 6.24-83.25	D4= 0.0068- 25.96	278.03	2.81×10^{-7}
D0 vs. D5	D0= 10.14	D5= 5.75	D0= 6.24-83.25	D5= 0.0096- 22.53	100.07	4.75×10^{-6}

Table 15

Manganese ANOVAs at Monitoring T0 (Pre-ISCO)

Manganese T0 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	0.55	0.511
Permeability	0.91	0.124
Initial ORP	0.84	0.225
Design Approach		
Mass	0.86	0.425
Concentration	0.88	0.441
Coupling	0.94	0.391

Table 16

Manganese ANOVAs at Monitoring T1 (< 4 Weeks Post-ISCO)

Manganese T1 (n=13)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.48	0.227
Permeability	4.24	0.043
Initial ORP	30.04	7.55×10^{-10}
Design Approach		
Mass	2.06	0.138
Concentration	1.44	0.246
Coupling	4.05	0.022

Table 17

Manganese ANOVAs at Monitoring T2 (4-24 Weeks Post-ISCO)

Manganese T2 (n=11)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.84	0.180
Permeability	2.35	0.130
Initial ORP	4.39	0.017
Design Approach		
Mass	14.67	2.04×10^{-5}
Concentration	0.17	0.843
Coupling	0.52	0.593

Table 18

Manganese ANOVAs at Monitoring T3 (24-52 Weeks Post-ISCO)

Manganese T3 (n=9)		
	F Value	p Value
Site Conditions		
Heterogeneity	12.69	0.001
Permeability	4.33	0.043
Initial ORP	4.34	0.019
Design Approach		
Mass	7.07	0.002
Concentration	16.46	7.69×10^{-6}
Coupling	14.16	1.99×10^{-5}

Table 19

Manganese ANOVAs at Monitoring T4 (52-104 Weeks Post-ISCO)

Manganese T4 (n=3)		
	F Value	p Value
Site Conditions		
Heterogeneity	99.46	1.86×10^{-7}
Permeability	13.67	0.002
Initial ORP	45.90	2.39×10^{-6}
Design Approach		
Mass	45.90	2.39×10^{-6}
Concentration	0.31	0.733
Coupling	0.31	0.733

Table 20

Summary of Manganese ANOVAs Significant Variables for Time

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
T0		X				
T1	X	X	X	X	X	X
T2	X	X	X	X		
T3	X	X	X	X	X	X
T4	X	X	X	X		

Note: Marked box indicates condition is significant to manganese concentration at given time point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

Table 21

Manganese ANOVAs at Distance D0 (Inside Target Treatment Zone)

Manganese D0 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	87.23	2.88×10^{-6}
Permeability	55.21	4.91×10^{-5}
Initial ORP	96.00	2.65×10^{-7}
Design Approach		
Mass	174.22	6.41×10^{-7}
Concentration	12.29	2.86×10^{-3}
Coupling	45.12	1.59×10^{-4}

Table 22

Manganese ANOVAs at Distance D1 (10 feet from Target Treatment Zone)

Manganese D1 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.02	0.871
Permeability	2.41	0.459
Initial ORP	2.86	0.310
Design Approach		
Mass	1.99	0.790
Concentration	0.76	0.903
Coupling	6.52	0.266

Table 23

Manganese ANOVAs at Distance D2 (20 feet from Target Treatment Zone)

Manganese D2 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.55	0.860
Permeability	1.98	0.500
Initial ORP	2.91	0.267
Design Approach		
Mass	1.06	0.610
Concentration	0.77	0.912
Coupling	1.85	0.592

Table 24

Manganese ANOVAs at Distance D3 (30 feet from Target Treatment Zone)

Manganese D3 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.19	0.882
Permeability	1.83	0.519
Initial ORP	3.01	0.298
Design Approach		
Mass	0.97	0.804
Concentration	0.64	0.917
Coupling	1.39	0.608

Table 25

Manganese ANOVAs at Distance D4 (50 feet from Target Treatment Zone)

Manganese D4 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.17	0.891
Permeability	1.71	0.563
Initial ORP	3.29	0.259
Design Approach		
Mass	0.68	0.899
Concentration	0.62	0.926
Coupling	2.67	0.353

Table 26

Manganese ANOVAs at Distance D5 (100 feet from Target Treatment Zone)

Manganese D5 (n=20)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.20	0.876
Permeability	1.75	0.528
Initial ORP	1.06	0.463
Design Approach		
Mass	0.65	0.907
Concentration	0.62	0.926
Coupling	1.87	0.430

Table 27

Summary of Manganese ANOVAs Significant Variables for Distance

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
D0	X	X	X	X	X	X
D1						
D2						
D3						
D4						
D5						

Note: Marked box indicates condition is significant to manganese concentration at given time point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

<u>2 Way ANOVAs.</u> 2 way ANOVAs were run to determine if there were significant ($\alpha = 0.25$) interactions between variables for each parameter. Table 28 shows that mass and heterogeneity significantly interact, as do coupling and heterogeneity, mass and ORP, and coupling and ORP. The other variables do not significantly interact based on a 0.25α.

Table 28

Manganese 2 Way ANOVAs

Variables	Row F Value	Row p Value
Mass and Heterogeneity	4.51	0.003
Mass and Permeability	1.07	0.401
Coupling and Heterogeneity	2.72	0.074
Coupling and Permeability	0.83	0.725
Concentration and Heterogeneity	0.69	0.445
Concentration and Permeability	0.52	0.971
Mass and ORP	12.17	0.008
Coupling and ORP	1.39	0.219

pH

Pearson's Correlation Analyses. Correlation of pH to various other parameters is shown in Table 29. pH levels are strongly positively correlated with ORP and concentration of oxidant delivered. pH is also positively correlated with chromium concentrations, although not as strongly. There also appears to be a slightly positive correlation between pH and manganese (as previously mentioned) and between pH and mass of oxidant delivered.

Table 29
Pearson's Correlation Analyses for pH

Variables	Correlation Coefficient
pH and Initial ORP	0.95
PH and Postoxidation ORP	0.89
pH and Chromium	0.74
pH and Mass Delivered	0.54
pH and Concentration Delivered	0.89

ANOVAs. Table 30 shows results from time and distance ANOVAs ran on pH values. These results correspond with time and distance results found for manganese concentrations, levels begin to approach pre-ISCO levels at monitoring time point T4 (52-104 weeks post-ISCO) and impacts appear to be localized in the target treatment zone. Tables 31-35 show the site and design condition ANOVA results for pH based on monitoring time. Table 36 shows a summary of these results. All parameters affect pH values at one or more time monitoring categories. Mass and concentration affect the values earlier in the monitoring process, whereas heterogeneity and permeability impacts are seen mostly later in the monitoring process. pH impacts were seen in all sites despite site and design conditions. Tables 37-42 show the site and design condition ANOVA results for pH based on distance from target treatment zone. Table 43 shows a summary of these results. Significant results are only seen at distance D0 (inside the target treatment zone), thus supporting the earlier finding that impacts are localized to the target treatment zone.

Table 30

pH Level ANOVAs for Time and Distance

pH (n=25)						
	Average	Average	Range	Range	F Value	p Value
T0 vs. T1	T0= 6.88	T1= 7.11	T0= 3.33- 7.88	T1= 4.90- 8.02	52.94	8.59×10^{-5}
T0 vs. T2	T0= 6.88	T2= 7.09	T0= 3.33- 7.88	T2= 5.21- 9.02	63.97	4.37×10^{-5}
T0 vs. T3	T0= 6.88	T3= 7.25	T0= 3.33- 7.88	T3= 6.25- 9.46	84.36	1.60×10^{-5}
T0 vs. T4	T0= 6.88	T4= 6.79	T0= 3.33- 7.88	T4= 3.81- 7.96	3.49	0.098
D0 vs. D1	D0= 6.98	D1= 7.01	D0= 4.39- 9.51	D1= 4.42- 9.46	76.74	2.48×10^{-5}
D0 vs. D2	D0= 6.98	D2= 7.00	D0= 4.39- 9.51	D2= 4.42- 9.02	63.33	9.17×10^{-4}
D0 vs. D3	D0= 6.98	D3= 6.99	D0= 4.39- 9.51	D3= 4.42- 9.13	73.64	8.04×10^{-4}
D0 vs. D4	D0= 6.98	D4= 7.02	D0= 4.39- 9.51	D4= 4.41- 8.58	108.50	9.54×10^{-5}
D0 vs. D5	D0= 6.98	D5= 7.06	D0= 4.39- 9.51	D5= 4.39- 9.09	285.42	3.97×10^{-6}

Table 31

pH ANOVAs at Monitoring T0 (Pre-ISCO)

pH T0 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.52	0.280
Permeability	1.59	0.299
Initial ORP	2.84	0.062
Design Approach		
Mass	1.51	0.289
Concentration	0.99	0.518
Coupling	3.94	0.022

Table 32

pH ANOVAs at Monitoring T1 (<4 Weeks Post-ISCO)

pH T1 (n=15)		
	F Value	p Value
Site Conditions		
Heterogeneity	2.23	0.139
Permeability	2.93	0.091
Initial ORP	1.97	0.146
Design Approach		
Mass	5.91	0.005
Concentration	4.84	0.011
Coupling	0.41	0.661

Table 33

pH ANOVAs at Monitoring T2 (4-24 Weeks Post-ISCO)

pH T2 (n=13)		
	F Value	p Value
Site Conditions		
Heterogeneity	7.14	0.009
Permeability	0.51	0.479
Initial ORP	12.38	2.98×10^{-5}
Design Approach		
Mass	4.35	0.019
Concentration	9.90	3.00×10^{-4}
Coupling	7.13	0.002

Table 34

pH ANOVAs at Monitoring T3 (24-52 Weeks Post-ISCO)

pH T3 (n=11)		
	F Value	p Value
Site Conditions		
Heterogeneity	0.07	0.787
Permeability	57.64	5.03×10^{-10}
Initial ORP	3.56	0.036
Design Approach		
Mass	0.10	0.903
Concentration	0.78	0.461
Coupling	8.01	0.001

Table 35

pH ANOVAs at Monitoring T4 (52-104 Weeks Post-ISCO)

pH T4 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	5.00	0.032
Permeability	14.92	4.96×10^{-4}
Initial ORP	0.14	0.872
Design Approach		
Mass	1.40	0.264
Concentration	0.26	0.774
Coupling	13.34	6.1×10^{-5}

Table 36

Summary of pH ANOVAs Significant Variables for Time

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
T0			X			X
T1	X	X	X	X	X	
T2	X		X	X	X	X
T3		X	X			X
T4	X	X				X

Note: Marked Box Indicates Condition Significant to pH values at Given Time Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

Table 37

pH ANOVAs at Distance D0 (Inside Target Treatment Zone)

pH D0 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	55.40	1.54×10^{-4}
Permeability	60.21	4.56×10^{-4}
Initial ORP	89.12	3.65×10^{-5}
Design Approach		
Mass	153.88	1.00×10^{-7}
Concentration	23.76	0.008
Coupling	97.82	9.65×10^{-5}

Table 38

pH ANOVAs at Distance D1 (10 feet from Target Treatment Zone)

pH D1 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.32	0.658
Permeability	4.88	0.328
Initial ORP	4.87	0.347
Design Approach		
Mass	3.32	0.444
Concentration	1.08	0.639
Coupling	2.55	0.535

Table 39

pH ANOVAs at Distance D2 (20 feet from Target Treatment Zone)

pH D2 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	2.65	0.430
Permeability	3.60	0.408
Initial ORP	4.00	0.397
Design Approach		
Mass	3.87	0.398
Concentration	0.97	0.871
Coupling	3.01	0.496

Table 40

pH ANOVAs at Distance D3 (30 feet from Target Treatment Zone)

pH D3 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	3.45	0.391
Permeability	3.65	0.376
Initial ORP	3.98	0.312
Design Approach		
Mass	0.45	0.960
Concentration	0.65	0.905
Coupling	4.89	0.288

Table 41

pH ANOVAs at Distance D4 (50 feet from Target Treatment Zone)

pH D4 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.22	0.540
Permeability	1.67	0.598
Initial ORP	1.03	0.497
Design Approach		
Mass	1.20	0.513
Concentration	0.59	0.924
Coupling	1.06	0.499

Table 42

pH ANOVAs at Distance D5 (100 feet from Target Treatment Zone)

pH D5 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.12	0.518
Permeability	1.16	0.502
Initial ORP	0.98	0.695
Design Approach		
Mass	0.98	0.686
Concentration	0.61	0.914
Coupling	0.96	0.769

Table 43

Summary of pH ANOVAs Significant Variables for Distance

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
D0	X	X	X	X	X	X
D1						
D2						
D3						
D4						
D5						

Note: Marked Box Indicates Condition Significant to pH values at Given Time Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

2 Way ANOVAs. Table 44 shows the results of 2 way ANOVAs run on pH values. Mass and ORP and coupling and ORP both significantly ($\alpha = 0.25$) interact to affect pH levels. This finding corresponds to correlation analyses that show that pH is strongly correlated to ORP.

Table 44

pH 2 Way ANOVAs

Variables	Row F Value	Row p Value
Mass and Heterogeneity	0.78	0.766
Mass and Permeability	0.98	0.519
Coupling and Heterogeneity	0.89	0.599
Coupling and Permeability	0.75	0.847
Concentration and Heterogeneity	0.83	0.733
Concentration and Permeability	0.82	0.721
Mass and ORP	1.62	0.136
Coupling and ORP	1.83	0.131

Oxidation Reduction Potential

Pearson's Correlation Analyses. Table 45 shows results from ORP correlation analyses. ORP is strongly positively correlated with pH, chromium, and manganese (as discussed earlier). Levels are slightly positively correlated with mass of oxidant delivered. Finally, there is a very low correlation between ORP and concentration of oxidant delivered.

Table 45

Pearson's Correlation Analyses for ORP

Variables	Correlation Coefficient
Initial ORP and Chromium	0.91
Postoxidation ORP and Chromium	0.86
ORP and Mass Delivered	0.53
ORP and Concentration Delivered	0.29

ANOVAs. ORP ANOVA results are shown in Tables 46-59. Table 46 shows time and distance results for ORP. As with the other parameters analyzed, ORP begins to approach pre-ISCO levels at time monitoring point T4 (52-104 week post-ISCO) and impacts appear to be localized to the target treatment zone. Tables 47-51 show ANOVA results for site and design condition affects on ORP based on time. Table 52 shows a summary of these results. ORP appears to be most affected by media permeability and mass of oxidant delivered (which corresponds with the correlation results). ORP values were higher in highly permeable homogeneous media. Values were also higher at sites were a large mass of oxidant was injected. Tables 53-58 show site and design affects on ORP based on distance from target treatment zone. Table 59 shows a summary of these results. Distance results support the finding that impacts are localized except for impacts from initial ORP.

Table 46
ORP Level Averages and ANOVAs for Time and Distance

Oxidation Reduction Potential (n=25)						
	Average (mV)	Average (mV)	Range (mV)	Range (mV)	F Value	p Value
T0 vs. T1	T0= 50.55	T1= 190.05	T0= -132.50- 285.24	T1= -186.96- 508.64	107.35	6.51×10^{-6}
T0 vs. T2	T0= 50.55	T2= 160.82	T0= -132.50- 285.24	T2= -124.68- 496.62	1670.25	1.41×10^{-10}
T0 vs. T3	T0= 50.55	T3= 120.41	T0= -132.50- 285.24	T3= -164.89- 528.12	1802.12	1.05×10^{-10}
T0 vs. T4	T0= 50.55	T4= 115.99	T0= -132.50- 285.24	T4= -158.21- 407.89	67.26	0.065
D0 vs. D1	D0= 422.67	D1= 125.33	D0= -23.10- 894.41	D1= -144.25- 407.89	1127.40	4.35×10^{-9}
D0 vs. D2	D0= 422.67	D2= 118.61	D0= -23.10- 894.41	D2= -158.21- 703.51	648.65	1.22×10^{-8}
D0 vs. D3	D0= 422.67	D3= 117.23	D0= -23.10- 894.41	D3= -142.32- 700.73	1568.81	4.41×10^{-10}
D0 vs. D4	D0= 422.67	D4= 113.09	D0= -23.10- 894.41	D4= -132.29- 646.55	940.01	6.45×10^{-9}
D0 vs. D5	D0= 422.67	D5= 110.09	D0= -23.10- 894.41	D5= -186.96- 623.15	550.00	1.01×10^{-5}

Table 47

ORP ANOVAs at Monitoring T0 (Pre-ISCO)

ORP T0 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	1.56	0.214
Permeability	0.51	0.618
Initial ORP		
Design Approach		
Mass	0.49	0.609
Concentration	1.28	0.485
Coupling	3.93	0.022

Table 48

ORP ANOVAs at Monitoring T1 (<4 Weeks Post-ISCO)

ORP T1 (n=15)		
	F Value	p Value
Site Conditions		
Heterogeneity	0.75	0.388
Permeability	19.42	3.00×10^{-5}
Initial ORP	46.98	3.76×10^{-6}
Design Approach		
Mass	1.48	0.237
Concentration	0.49	0.609
Coupling	0.42	0.661

Table 49

ORP ANOVAs at Monitoring T2 (4-24 Weeks Post-ISCO)

ORP T2 (n=12)		
	F Value	p Value
Site Conditions		
Heterogeneity	8.42×10^{-5}	0.993
Permeability	0.37	0.547
Initial ORP	13.22	1.10×10^{-3}
Design Approach		
Mass	10.42	2.57×10^{-4}
Concentration	5.52	0.008
Coupling	7.13	0.002

Table 50

ORP ANOVAs at Monitoring T3 (24-52 Weeks Post-ISCO)

ORP T3 (n=11)		
	F Value	p Value
Site Conditions		
Heterogeneity	12.09	0.001
Permeability	9.71	0.003
Initial ORP	32.29	3.54×10^{-5}
Design Approach		
Mass	0.39	0.679
Concentration	0.42	0.660
Coupling	8.01	9.28×10^{-4}

Table 51

ORP ANOVAs at Monitoring T4 (52-104 Weeks Post-ISCO)

ORP T4 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	0.26	0.615
Permeability	18.15	1.60×10^{-4}
Initial ORP	12.32	1.13×10^{-3}
Design Approach		
Mass	22.67	1.67×10^{-6}
Concentration	0.34	0.712
Coupling	0.17	0.842

Table 52

Summary of ORP ANOVAs Significant Variables for Time

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
T0	X					X
T1		X	X	X		
T2			X	X	X	X
T3	X	X	X			X
T4		X	X	X		

Note: Marked Box Indicates Condition Significant to ORP values at Given Time Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

Table 53

ORP ANOVAs at Distance D0 (Inside Target Treatment Zone)

ORP D0 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	62.29	1.11×10^{-4}
Permeability	69.13	2.31×10^{-4}
Initial ORP		
Design Approach		
Mass	143.72	4.22×10^{-6}
Concentration	39.09	1.76×10^{-3}
Coupling	98.56	2.87×10^{-5}

Table 54

ORP ANOVAs at Distance D1 (10 feet from Target Treatment Zone)

ORP D1 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	3.45	0.278
Permeability	3.11	0.291
Initial ORP	14.89	0.081
Design Approach		
Mass	3.19	0.387
Concentration	1.02	0.455
Coupling	4.45	0.252

Table 55

ORP ANOVAs at Distance D2 (20 feet from Target Treatment Zone)

ORP D2 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	2.97	0.319
Permeability	2.41	0.340
Initial ORP	10.97	0.098
Design Approach		
Mass	3.86	0.276
Concentration	0.96	0.512
Coupling	3.80	0.298

Table 56

ORP ANOVAs at Distance D3 (30 feet from Target Treatment Zone)

ORP D3 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	4.59	0.292
Permeability	5.98	0.288
Initial ORP	11.87	0.090
Design Approach		
Mass	3.95	0.277
Concentration	0.91	0.690
Coupling	2.15	0.301

Table 57

ORP ANOVAs at Distance D4 (50 feet from Target Treatment Zone)

ORP D4 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	3.02	0.410
Permeability	3.98	0.449
Initial ORP	9.61	0.164
Design Approach		
Mass	2.96	0.421
Concentration	0.91	0.694
Coupling	1.19	0.419

Table 58

ORP ANOVAs at Distance D5 (100 feet from Target Treatment Zone)

ORP D5 (n=25)		
	F Value	p Value
Site Conditions		
Heterogeneity	3.17	0.390
Permeability	2.33	0.549
Initial ORP	7.15	0.203
Design Approach		
Mass	1.03	0.614
Concentration	0.64	0.740
Coupling	0.88	0.555

Table 59

Summary of ORP ANOVAs Significant Variables for Distance

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
D0	X	X	X	X	X	X
D1			X			
D2			X			
D3			X			
D4			X			
D5			X			

Note: Marked Box Indicates Condition Significant to ORP values at Given Distance Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO

2 Way ANOVAs. Results for ORP 2 way ANOVAs can be seen in Table 60. Mass and permeability appear too significantly ($\alpha = 0.25$) interact to affect ORP values. This result corresponds with the one-way ANOVA results that show ORP values are more affected by media permeability and mass of oxidant injected than other variables analyzed. Concentration of oxidant injected and media heterogeneity also appear to interact, although not as significantly.

Table 60

ORP 2 Way ANOVAs

Variables	Row F Value	Row p Value
Mass and Heterogeneity	0.97	0.521
Mass and Permeability	1.72	0.011
Coupling and Heterogeneity	1.21	0.297
Coupling and Permeability	0.79	0.335
Concentration and Heterogeneity	1.56	0.059
Concentration and Permeability	0.59	0.998

Chromium

Pearson's Correlation Analyses. Results for chromium correlations are seen in Table 61. As discussed earlier, chromium concentrations are strongly positively correlated with ORP. Concentrations are also positively correlated with pH. As mentioned earlier, there is also a slight positive correlation between manganese and chromium, although it is not significant. There is very low correlation between chromium and mass of oxidant delivered and between chromium and concentration of oxidant delivered. It was expected that chromium would be correlated with mass of oxidant injected; however, the lack of correlation could be due to the limited amount of data available for chromium.

Table 61
Pearson's Correlation Analyses for Chromium

Variables	Correlation Coefficient
Chromium and Mass Delivered	0.05
Chromium and Concentration Delivered	0.27

ANOVAs. Table 62 shows chromium ANOVA results for time and distance. These results show that it takes longer for chromium to be affected by ISCO and that levels return to pre-ISCO levels by time monitoring point T3 (24-52 weeks post-ISCO). The distance results show that impacts are localized to the target treatment zone. Tables 63–66 show time results from ANOVAs run on chromium concentrations based on site and design conditions. Table 67 shows a summary of the site and design condition results for time. Chromium is most impacted by site conditions (higher concentrations are seen in more permeable homogeneous media). However, very little else can be determined by these ANOVAs due to the lack of data available for chromium. Tables 68-73 show distance results for site and design condition impacts on chromium. Table 74 shows a summary of these results. These results correspond with distance ANOVA findings that impacts are localized with the exception of the significant ($\alpha = 0.25$) impact of heterogeneity and permeability at distance D1 (10 feet from the target treatment zone).

Table 62
Chromium Concentration ANOVAs for Time and Distance

Chromium (n=7)						
	Average (μg/L)	Average (μg/L)	Range (μg/L)	Range (μg/L)	F Value	p Value
T0 vs. T1	T0= 8.31	T1= 8.93	T0= 0.001-68.82	T1= 0.011-48.03	0.28	0.614
T0 vs. T2	T0= 8.31	T2= 23.89	T0= 0.001-68.82	T2= 0.019-121.74	40.44	2.18 x 10^{-4}
T0 vs. T3	T0= 8.31	T3= 8.71	T0= 0.001-68.82	T3= 0.0086-33.80	0.13	0.730
T0 vs. T4	T0= 8.31	N/A	N/A	N/A	N/A	N/A
D0 vs. D1	D0= 35.04	D1= 14.04	D0= 0.048-271.03	D1= 0.0086-121.74	161.89	4.00 x 10^{-5}
D0 vs. D2	D0= 35.04	D2= 13.64	D0= 0.048-271.03	D2= 0.0015-117.35	162.98	3.65 x 10^{-5}
D0 vs. D3	D0= 35.04	D3= 12.49	D0= 0.048-271.03	D3= 0.0021-99.09	153.90	1.96 x 10^{-5}
D0 vs. D4	D0= 35.04	D4= 10.95	D0= 0.048-271.03	D4= 0.0026-55.69	149.12	1.02 x 10^{-5}
D0 vs. D5	D0= 35.04	D5= 11.89	D0= 0.048-271.03	D5= 0.0026-68.82	164.45	6.96 x 10^{-5}

Note: N/A = no data available

Table 63
Chromium ANOVAs at Monitoring T0 (Pre-ISCO)

Chromium T0 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	0.99	0.558
Permeability	1.81	0.711
Initial ORP	0.02	0.905
Design Approach		
Mass	2.18	0.530
Concentration	1.52	0.281
Coupling	1.26	0.297

Table 64

Chromium ANOVAs at Monitoring T1 (<4 Weeks Post-ISCO)

Chromium T1 (n=4)		
	F Value	p Value
Site Conditions		
Heterogeneity	17.55	5.51×10^{-4}
Permeability	17.55	5.51×10^{-4}
Initial ORP	N/A	N/A
Design Approach		
Mass	736.28	7.28×10^{-9}
Concentration	736.28	7.28×10^{-9}
Coupling	6.99	0.006

Note: N/A = no data available

Table 65

Chromium ANOVAs at Monitoring T2 (4-24 Weeks Post-ISCO)

Chromium T2 (n=5)		
	F Value	p Value
Site Conditions		
Heterogeneity	3.20	0.086
Permeability	3.20	0.086
Initial ORP	16.49	7.33×10^{-4}
Design Approach		
Mass	0.25	0.786
Concentration	0.15	0.866
Coupling	83.28	5.45×10^{-11}

Table 66

Chromium ANOVAs at Monitoring T3 (24-52 Weeks Post-ISCO)

Chromium T3 (n=3)		
	F Value	p Value
Site Conditions		
Heterogeneity	132.05	3.51×10^{-8}
Permeability	132.05	3.51×10^{-8}
Initial ORP	14.64	0.002
Design Approach		
Mass	72.16	2.13×10^{-5}
Concentration	0.32	0.729
Coupling	6.76	0.011

Table 67

Summary of Chromium ANOVAs Significant Variables for Time

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
T0						
T1	X	X	N/A	X	X	X
T2	X	X	X			X
T3	X	X	X	X		X
T4	N/A	N/A	N/A	N/A	N/A	N/A

Note: Marked Box Indicates Condition Significant to Chromium Concentrations at Given Time Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO. N/A = no data available.

Table 68

Chromium ANOVAs at Distance D0 (Inside Target Treatment Zone)

Chromium D0 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	32.19	0.004
Permeability	45.12	5.05×10^{-3}
Initial ORP	89.44	4.39×10^{-5}
Design Approach		
Mass	163.12	1.29×10^{-7}
Concentration	76.09	2.58×10^{-5}
Coupling	54.18	1.66×10^{-5}

Table 69

Chromium ANOVAs at Distance D1 (10 feet from Target Treatment Zone)

Chromium D1 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	11.12	0.012
Permeability	9.81	0.191
Initial ORP	7.45	0.370
Design Approach		
Mass	9.12	0.260
Concentration	1.03	0.731
Coupling	2.05	0.789

Table 70

Chromium ANOVAs at Distance D2 (20 feet from Target Treatment Zone)

Chromium D2 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	9.01	0.271
Permeability	6.18	0.254
Initial ORP	6.45	0.386
Design Approach		
Mass	8.15	0.398
Concentration	1.26	0.724
Coupling	1.02	0.808

Table 71

Chromium ANOVAs at Distance D3 (30 feet from Target Treatment Zone)

Chromium D3 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	4.90	0.811
Permeability	5.02	0.677
Initial ORP	3.54	0.615
Design Approach		
Mass	6.09	0.527
Concentration	0.88	0.901
Coupling	4.41	0.579

Table 72

Chromium ANOVAs at Distance D4 (50 feet from Target Treatment Zone)

Chromium D4 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	2.12	0.899
Permeability	1.98	0.818
Initial ORP	3.47	0.671
Design Approach		
Mass	2.65	0.799
Concentration	0.91	0.871
Coupling	1.00	0.834

Table 73

Chromium ANOVAs at Distance D5 (100 feet from Target Treatment Zone)

Chromium D5 (n=7)		
	F Value	p Value
Site Conditions		
Heterogeneity	2.45	0.886
Permeability	2.90	0.759
Initial ORP	1.03	0.884
Design Approach		
Mass	2.63	0.768
Concentration	0.76	0.916
Coupling	6.16	0.315

Table 74

Summary of Chromium ANOVAs Significant Variables for Distance

	Heterogeneity	Permeability	Initial ORP	Mass	Concentration	Coupling
D0	X	X	X	X	X	X
D1	X	X				
D2						
D3						
D4						
D5						

Note: Marked Box Indicates Condition Significant to Chromium Concentrations at Given Time Point. T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO. N/A = no data available

CHAPTER 5

DISCUSSION

Discussion Overview

This research consisted of a review of data for 30 contaminated sites in which permanganate (MnO_4^-) ISCO was used to remediate site contaminants. There were three key objectives of this research. The first objective was to determine whether there are long-term impacts on groundwater quality due to the introduction of permanganate into the subsurface (e.g., is manganese remaining in the subsurface too long). The second objective was to determine if manganese concentrations could be predicted by trends in specific pre and postoxidation monitored parameters (i.e., pH and ORP). The final objective was to identify the effects that site and design conditions have on parameter (i.e., manganese, chromium, ORP, and pH) levels postoxidation. Results from statistical analyses of site data over time and distance from delivery first show that manganese and other parameter (i.e., pH and ORP) levels begin to approach pre-ISCO levels by 24 months post-ISCO and that impacts are localized to the TTZ. Second, results show that manganese concentrations can be predicted based on ORP and pH measurements along with media type. Third, site and design conditions have significant impacts on parameters (i.e., manganese, chromium, ORP, and pH).

Long Term Impacts on Groundwater

Time

The results of this research illustrate that there are limited long term groundwater impacts associated with permanganate ISCO. ANOVAs of monitoring time points of manganese, pH, and ORP show that at 24 months post-ISCOparameter levels are beginning to approach pre-ISCO conditions. Results show that, on average, manganese concentrations begin approaching pre-ISCO conditions by 24 months postoxidation. ORP levels also approach pre-ISCO conditions by 12 to 24 months. Chromium levels begin to approach pre-ISCO concentrations at 6 to 12 months postoxidation and are back to pre-ISCO concentrations by 12 to 24 months postoxidation. pH levels are not returned to normal by 24 months post-ISCO but are approaching normal. These pH results could be due to the different contaminants being oxidized. As discussed in Chapter 2, permanganate ISCO can increase or decrease pH depending on the media type and contaminants present. (Case, 1997; Crimi & Siegrist, 2003; Nelson et al., 2001; Siegrist et al., 1999; Siegrist et al., 2000). However, while pH values are significantly ($\alpha = 0.25$) different between time points, the magnitude of these changes are so small (i.e., value changes of 0.2 to 0.4) that it is unlikely to produce adverse impacts.

There are various explanations as to why these parameter levels are beginning to return to “normal” (i.e., pre-ISCO levels). The most important explanation is that it is due to the exhaustion of oxidant. Crother, Shipley, and Vogl (2002) found that significant changes to geochemical parameters occur during permanganate ISCO but are returned to near background levels once the permanganate is depleted. Another explanation is that oxidant depletion allows for the potential sorption of metals to NOM or other media constituents. Under normal circumstances NOM will absorb metals; however, under ISCO conditions NOM can react with the oxidant thus allowing metals to mobilize (Huling & Pivetz, 2006). However, as the oxidized solution moves down gradient it can sorb onto unoxidized NOM. Interactions that can take place in the subsurface once oxidant is exhausted can also aide sites in returning to "normal." This can include changes in cation exchange capacity (CEC) due to the fluctuations in the media pH. At low pH values, metal cations are typically most mobile, while metal anions would tend to sorb to oxide minerals. At higher pH values, cations typically sorb to mineral surfaces, while the anions are mobilized (Evanko & Dzombak, 1997). For example, during the oxidation of PCE and TCE pH levels will drop due to production of H^+ byproducts. Therefore, in this example metal cations are anticipated to be mobilized. Other influences could include up gradient flow, which could provide a dilution and dispersion effect.

Distance

ANOVA results for distances from TTZ show that there is no effect on parameters associated with distance from TTZ. All impacts appear to be localized in the TTZ. It is believed that distance does not impact parameter levels due to the groundwater velocities at each site. At the majority of sites it takes more than 12 months for the groundwater to reach 100 ft (Table 75). Based on the ANOVAs, parameter levels are returning to pre-ISCO conditions before they reach D5 (100 ft). However, ANOVAs run on individual sites at distances from TTZ that corresponded with actual monitoring times show that at certain sites (i.e., those with the highest groundwater velocities) impacts are observed at distances outside the target treatment zone (Appendix D). For example, at site G it takes only 66 days for groundwater to reach 100 ft from the target treatment zone. An ANOVA run on data from this site shows that impacts are not localized, both D2 (20 feet from TTZ) and D3 (30 feet from TTZ) are significantly ($\alpha = 0.25$) impacted. Other sites with reasonably high groundwater velocities (e.g., sites C, U, and δ) show similar results.

Table 75

Groundwater Velocities for Selected Sites Used For This Research

Site	Time to D1 (days)	Time to D2 (days)	Time to D3 (days)	Time to D4 (days)	Time to D5 (days)
A	20	39	58	96	193
C	9	18	27	45	91
F	66	134	200	333	666
G	7	13	20	33	66
I	50	100	150	250	500
J	23	46	68	114	227
L	40	80	120	200	400
M	12	23	35	58	115
U	10	21	31	52	103
V	66	134	200	333	666
Z	100	200	300	500	1000
α	40	80	120	200	400
β	37	74	111	185	370
χ	40	80	120	200	400
δ	8	17	25	41	82

Note: Groundwater velocities were calculated using Darcy's Law. This table only includes 15 of the 30 sites used for this research.

The finding that groundwater impacts are localized in the TTZ (in those sites with relatively medium to low groundwater velocities) is an important finding that can lead to less money being spent on monitoring well implementation and analyses. The sites used for this research appeared to have a "grid" like approach to installing monitoring wells (Figure 9). This involves installing monitoring wells at different locations inside and outside the TTZ. However, because results show that impacts are localized to the TTZ, more focused monitoring well installation can be implemented (Figure 10). This more focused approach can result in thousands of dollars of savings for practitioners.

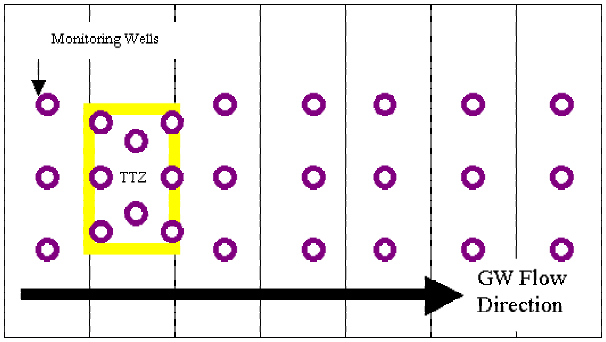

Figure 9 Example of Grid Approach for Installing Monitoring Wells for ISCO.

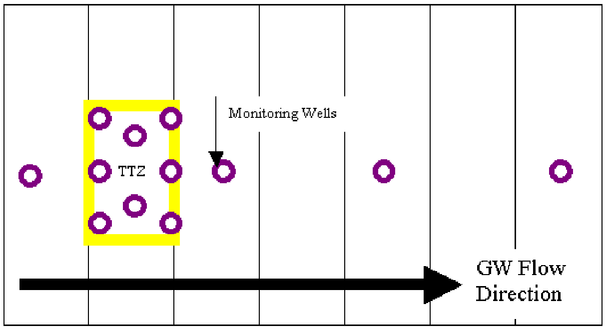

Figure 10 Example of Focused Approach for Installing Monitoring Wells for ISCO.

Predicting Manganese Concentrations

Results from correlation analyses run on parameters correspond with literature by showing that manganese concentrations can be predicted. Manganese is strongly positively correlated with both pre- and post-ISCO ORP as well as the mass of oxidant delivered. Therefore, if high levels of pre-ISCO ORP are observed, it can be predicted that post-ISCO manganese levels will also be high. The same idea goes for post-ISCO ORP and post-ISCO manganese, high post-ISCO ORP can predict high post-ISCO manganese concentrations. These results correspond with literature that state that one of the main subsurface conditions that will influence manganese concentrations is ORP (Duggan, 1993; ITRC, 2005). As ORP increases (>1.4 V), manganese is seen in the form of manganese dioxide solids. As ORP decreases (-1 to 1.4 V), manganese is seen in the form of Mn^{+2} (Duggan, Wildeman, & Updegraff, 1993). These are the common ORP values seen post-ISCO at sites used for this research (as seen in Appendix B). Manganese levels can also be predicted by the mass of oxidant injected, as expected. Manganese is positively correlated with the mass of oxidant injected; therefore, the more oxidant injected the higher manganese concentrations expected. For example, according to findings from this research it takes only 0.031 mg- MnO_4^-/kg -soil injected to cause a manganese concentration of 0.05 mg/L (the secondary drinking water standard set by the US EPA for manganese). Site media also impacts manganese (and other metals) concentrations. Manganese concentrations evaluated qualitatively before analyses were run showed that concentrations are higher in homogeneous permeable media as opposed to heterogeneous impermeable media (Figure 11). This corresponds with literature discussed in Chapter 2 that stated subsurface constituents move easier through homogeneous permeable media (Oberle & Schroder, 2000; Saenton et al., 2002; Soel et al., 2000).

Theoretically, the initial TOC of a site should correspond with manganese concentrations due to the high correlation between TOC and initial ORP. As stated in Chapter 2, TOC is part of the NOD of the media. Literature studies have shown that sites with higher NOD will require more oxidant (Mumford et al., 2004; Weber, McGinley, & Katz, 1992; Zhang & Schwartz, 2000). This increase in oxidant will in turn produce more byproducts (i.e., manganese). However, with the data used for this research it could not be shown that sites with higher initial TOC are injected with a higher mass of oxidant (i.e., extremely low correlation observed (0.158)). Of the nine sites that had data for initial TOC and mass of oxidant injected, the only site that had a high amount of oxidant injected ("high" in this context refers to the injection of oxidant at 500 or greater mg/kg) had an initial low TOC level ("low" in this context refers to an initial TOC measurement of less than 1 mg/L). These findings could be due to TOC not being the only variable analyzed by practitioners to determine NOD and also that not all organic carbon is oxidizable. Studies have found that other constituents including reduced minerals have an impact on the NOD of a site (Haselow, Siegrist, Crimi, & Jarosch, 2003; Honning, Broholm, & Bjerg, 2007; Mumford, Thomson, & Allen-King, 2005). Other studies have found that not all organic carbon at sites is oxidized by permanganate (Ball & Roberts, 1991; Haslow et al., 2003; Mumford et al., 2005; Struse, 1999; Weber et al., 1992).

The finding that manganese concentrations can be predicted based on certain site and design conditions has an important implication. Together ORP and pH help dictate the species of manganese that will be found post-ISCO (Figure 12). For example, average pH values for sites used in this research were 6-8, while average ORP ranges were –1 to 1.4 Volts. This corresponds to Mn^{+2} species of manganese. This along with the strong correlation between ORP and manganese is an important finding. ORP and pH monitoring is relatively inexpensive and easy to monitor and can be measured real time (i.e., can be measured in the field). It is feasible to measure ORP and pH (and not manganese) until an ORP increase is observed or until the ORP and pH values indicate dissolved manganese is formed. When this is observed, more expensive corroborative manganese monitoring could begin. This could save practitioners both time and money.

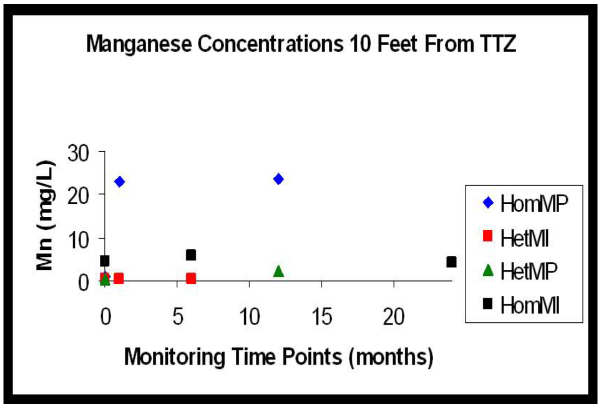

Figure 11 Example Manganese Data.
This figure shows manganese concentrations versus time for one site of each media type. Homogeneous mostly permeable media (HomMP) has the highest manganese concentrations, followed by Homogeneous most impermeable (HomMI), Heterogeneous mostly permeable (HetMP), and lastly heterogeneous mostly impermeable (HetMI), which shows the lowest manganese concentrations.

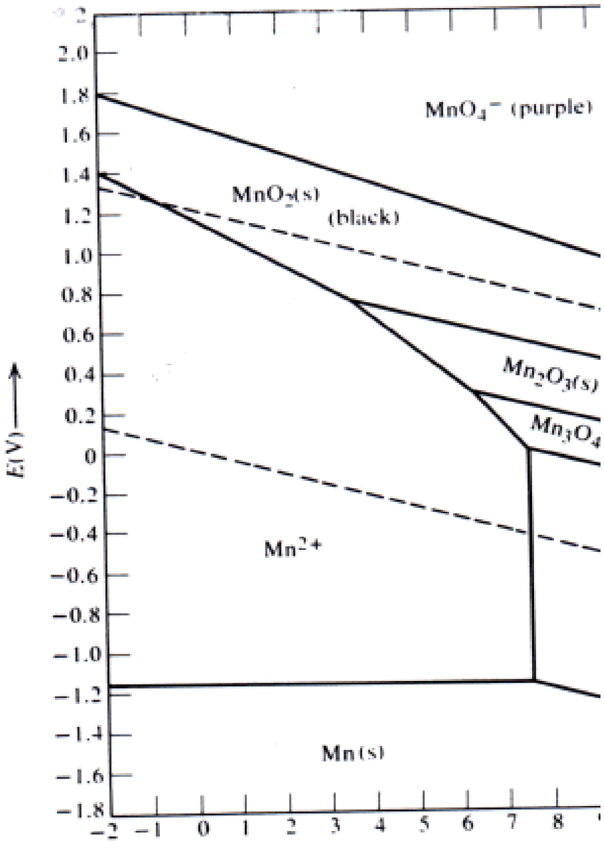

Figure 12 Diagram Eh versus pH (Adapted from Duggan et al., 1993).

Impacts of Site and Design Conditions

Time

Site and design conditions statistically impact parameter values throughout the ISCO monitoring process (i.e., at all monitoring times). Site media type is an important variable to consider when implementing permanganate ISCO (Cadorette, Walker, & Hesbitt, 2005; Nelson et al., 2001; Oberle & Schroder, 2000; Soel et al., 2003). Based on the ANOVA results from this research, soil permeability has more of an effect on parameter levels than does heterogeneity. However, 2 way ANOVA results show that heterogeneity has more significant ($\alpha = 0.25$) interactions with other variables than does permeability. Both permeability and heterogeneity affect the movement of constituents through the subsurface. As discussed earlier, more permeable and homogenous media allow for more movement through the subsurface. Although impacts to groundwater quality are relatively short lived, it was noted that heterogeneity has more of an impact after 6 months postoxidation and the impact of permeability is seen throughout the postoxidation period. As discussed in Chapter 4, higher permeability and homogeneity result in higher manganese and chromium concentrations. The observed permeability results could be due to the impact the permanganate ISCO technology can have on soil permeability. As discussed in Chapter 2, permanganate ISCO can result in reductions in the soil permeability through production of MnO_2 solids or through carbon dioxide gas production from permanganate oxidation (Li & Schwartz, 2003, 2004; Schroth, Oostrom, Wietsma, & Istok, 2001). Therefore, because MnO_2 decreases permeability, manganese and chromium concentrations should also decrease due to MnO_2 sorption (Davies &

Morgan, 1989; Fu, Allen, & Cowan, 1991; Murray, 1975), thus resulting in less manganese and chromium in groundwater.

The discovery that site media impacts parameter levels has an important implication. As discussed, homogeneous permeable media will result in higher manganese and chromium (and other metals) levels in groundwater. Therefore, at sites that have homogeneous permeable media a more strenuous monitoring plan will need to be implemented.

Other site conditions that impact geochemical parameters are initial ORP and initial TOC. Initial ORP significantly ($\alpha = 0.25$) affects manganese and chromium concentrations at each monitoring time (where data were available). High pre-ISCO ORP correlates with high manganese and chromium concentrations. Increases in post-ISCO ORP result in more oxidation, thus more manganese byproducts being produced and more trivalent chromium being oxidized to hexavalent chromium. This corresponds with results from correlation analyses that show that manganese and chromium are strongly positively correlated to pre and post-ISCO ORP. Initial ORP levels also appear to have a significant ($\alpha = 0.25$) association with pH values at monitoring times 6 to 12 months. As ORP increases and constituents are being oxidized, the pH increases or decreases depending on the contaminants being oxidized and the mineral components of the subsurface. Also, permanganate measurements (actual values and visual color analyses) were examined qualitatively to compare with ORP measurements to determine if ORP values drop as soon as permanganate is gone or if it persists. Of the 30 sites used for this research, only 4 of them performed monitoring for permanganate. Three of these analyses were visual color analyses (i.e., dark purple = high permanganate concentration, etc.) and

1 was an actual permanganate measurement. Qualitative results for these 4 sites show that ORP values drop dramatically once the permanganate has been exhausted, as expected. Therefore, any contaminants left will not be oxidized and further remediation will be needed.

Once again, these results have important implications. As discussed earlier in this chapter, ORP can be used as an indicator of manganese and chromium. The qualitative permanganate results show that ORP can also be used as an indicator of permanganate. As stated earlier in this chapter, ORP is a good, relatively inexpensive, “real time” analysis.

Initial TOC also appears to affect manganese, chromium, and ORP levels, although these results are not significant at a 75% confidence interval. TOC is also strongly positively correlated with ORP (correlation coefficient = 0.92). At higher ORP values, organic carbon will be oxidized and result in dissolved TOC (Haselow et al., 2003). Therefore, if oxidant is still present, high TOC will correspond with high ORP. However, if oxidant is not present, dissolved carbon can dramatically decrease ORP (Mumford, Thomson, & Allen-King, 2002; Mumford et al., 2004). As discussed earlier in the chapter, ORP levels are correlated with the mass of oxidant injected. Manganese and chromium concentrations are strongly correlated with ORP levels. Thus, in the presence of oxidant higher initial TOC levels can correspond with higher manganese and chromium concentrations.

Design conditions (including delivery approach, mass and concentration of oxidant delivered, and coupled technologies) also affect geochemical parameters at one or more time monitoring points. Delivery approach ANOVA results show effects on each parameter at one or more monitoring points, although this is not significant at a 75% confidence interval. The delivery approach chosen will dictate the concentration and rate of oxidant injected (Cadorett & Walker, 2005). The delivery approach at a site usually corresponds with the media type. For example, more impermeable media may require a different delivery approach (hydraulic fracturing) than would a permeable media (injection wells). As discussed in Chapter 4, media type has a significant impact on geochemical parameter values. However, due to lack of data very little can be said about the effects delivery approach has on geochemical parameters.

Mass and concentration of oxidant injected are other design conditions that affect parameters. According to ANOVA results, total mass of oxidant injected has a greater impact on geochemical parameters than does concentration of oxidant injected. In most cases these impacts are seen early in the postoxidation monitoring (1 to 6 months). 2 way ANOVA results also showed that mass of oxidant delivered interacted significantly with other variables more than concentration of oxidant delivered. These findings were not expected. It was thought that concentration of oxidant delivered would have a greater impact. The observed results are most likely due to the stronger correlation between mass of oxidant injected and ORP than concentration of oxidant delivered and ORP. Increased mass and concentration result in increases of ORP, manganese, and chromium. It also results in changes in pH depending on the type of contaminant being oxidized.

The finding that increased mass and concentration of oxidant delivered will cause increased impacts has an important implication. As discussed earlier in the chapter, this research showed that a mass of oxidant of just 0.031 mg- MnO_4^-/kg- soil will lead to 0.05 mg/L of manganese. Therefore, the more oxidant injected (both mass and concentration), the greater the amount of manganese (and other metals) produced or mobilized.

Coupled technologies are the final design condition analyzed. As discussed in Chapter 3, coupled technologies were broken down into categories based on pre-ISCO application, no coupling, or post-ISCO application. Pre-ISCO coupling consisted of those technologies that were implemented at sites before permanganate ISCO was administered. The most common pre-ISCO technology observed was soil vapor extraction. Post-ISCO technologies consist of those applications that were implemented at some time point after permanganate was administered. The most common of these was natural attenuation. It can be determined that coupling a technology with ISCO does make a significant difference in geochemical parameter values within the context evaluated for this research. For example, it was found that, in most cases, sites that used pre-ISCO coupling had less contaminant to destroy during ISCO. Less contaminant will result in less oxidant being injected and, therefore, less byproducts being produced (i.e., manganese, H^+, OH^-, etc.). Once analyses were run on geochemical parameters for coupling, it was discovered that it is difficult to determine at what time points post-ISCO technologies were implemented. Therefore, parameter levels were looked at qualitatively at sites where pre-ISCO coupling was performed and compared with sites were no coupling or post-ISCO coupling was performed. It was observed that, in general, sites that used some form of coupling had lower concentrations of COCs (baseline COC concentrations were similar at compared sites) to treat with ISCO. Although these findings are only qualitative, it can be theorized that at sites where geochemical issues may be of concern (i.e., sites with highly homogeneous permeable media, sites where public exposure to groundwater is high, etc), another technology before ISCO may minimize the geochemical issues. Of the six sites that used pre-ISCO coupling, four of them coupled ISCO with SVE. While reading through the site summaries it was discovered that at all four of these SVE sites, SVE was actually the technology chosen to remediate the site and was only "coupled" with permanganate ISCO after it failed to achieve desired goals. However, according to these qualitative findings, SVE appears to work well as a coupling technology for permanganate ISCO because it appears to result in a lower amount of contaminants to destroy. It was also determined that coupling was performed more often in heterogeneous media with medium to large target treatment zones. This could impact the interpretation of the findings.

Distance

Site and design conditions do not appear to impact parameters based on distance from target treatment zone, with several exceptions. Post-ISCO ORP is impacted by pre-ISCO ORP at all distances. Chromium appears to be impacted by both heterogeneity and permeability at D1 (10 feet from TTZ); however, this analysis was run on only 7 sites. This finding supports findings from distance ANOVAs run on all 30 sites combined. Impacts are localized inside the target treatment zone. Therefore, that is where monitoring efforts should be focused.

Implications

This research began with the objective of creating a protocol of parameters to monitor when administering permanganate ISCO at a site. However, due to the lack of data available for most parameters, this objective was partially abandoned. Instead of a protocol, trends in geochemical impacts seen at various site and design conditions are discussed. The first trend observed is that manganese and chromium concentrations are both higher in homogeneous permeable media. Therefore, when administering permanganate ISCO at a homogeneous permeable site, it is highly important to monitor for these metals. Due to this observation it is also important to monitor for other redox sensitive metals including nickel and selenium at these sites. The second trend observed is that impacts are localized to the TTZ; therefore, more effort should be placed on monitoring closer to the TTZ than at other distances. The next trend observed is that in most cases the design conditions (except coupling) affect geochemical parameters during the earlier monitoring times (1 to 6 months), whereas the site conditions usually affect parameters during the later time monitoring categories (6 months to 2 years). This means later (>6 months) post-ISCO monitoring should focus on site condition effects. Another trend is the finding that “surrogate” parameter monitoring can be a cheap, efficient, “real time” way to monitor for manganese, chromium, and permanganate, until cooperative monitoring is needed. Finally, pre-ISCO coupling has an impact on geochemical parameters and should be considered at sites where geochemical issues could pose a concern.

CHAPTER 6

CONCLUSIONS

This research had three main objectives, (1) to determine if manganese remained in the subsurface too long, (2) to determine if manganese concentrations can be predicted by trends in other parameters, and (3) to determine if site and design conditions had an impact on geochemical parameters. The results provide answers to each of these objectives. Also, the implications of this research can result in cost savings for practitioners.

This research has provided support for the assumption that geochemical parameters will return to pre-ISCO levels. The results of this research show that manganese and ORP begin to return to pre-ISCO levels by 2 years. Chromium returns to pre-ISCO concentrations by 6 months to 1 year. It also gives evidence that impacts are localized at the TTZ, thus monitoring efforts can be focused close to the TTZ. At most sites, it will take the groundwater > 1 year to reach 100 ft. By this time and distance, the parameter levels have begun to return to pre-ISCO levels.

This research also determined that manganese concentrations can be predicted based on other parameters and site and design conditions. These predictive variables include pre- and post-ISCO ORP, TOC, total mass of oxidant injected, and site media type. High ORP values correspond to high manganese concentrations, high-injected mass corresponds to higher manganese concentrations, and site media type can determine the concentration of manganese.

This researcher has concluded that site and design conditions play significant roles in parameter values. It can be expected that manganese and chromium levels will be higher in more homogeneous, more permeable media. Results show that design conditions play a bigger role initially following injection (1-6 months) and site conditions play a role at 6 months to 2 years.

More work is needed to support these findings. More sites need to be collected that contain a wider variety of variables (i.e., more delivery methods, more parameters monitored, etc.). These findings should also be compared to that of other oxidants (i.e., CHP reactions, ozone, persulfate).

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APPENDICES

APPENDIX A

Descriptive Information on Data Sets Used for This Research

Site A

- Location- Florida
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Homogenous Mostly Permeable
- Delivery Approach- Recirculation Well
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- 507.14 mg/kg
- Concentration- 2.5%

Site B

- Location- Florida
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Drycleaner
- Media type- Homogenous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Surfactant)
- Oxidant- Potassium permanganate
- Mass- 1853.98 mg/kg
- Concentration- 0.3%

Site C

- Location- North Carolina
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Hydraulic Fracturing
- Coupled Technology- Postcoupling (Other Oxidant)
- Oxidant- Potassium permanganate
- Mass- 2085.73 mg/kg
- Concentration- 5%

Site D

- Location- Wisconsin
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Manufacture Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site E

- Location- New York
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Manufacture Site
- Media type- Homogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Soil Vapor Extraction)
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- 20%

Site F

- Location- Colorado
- COCs- PAHs, creosote
- Site Type- Manufacture Site
- Media type- Homogeneous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Postcoupling (Other Oxidant)
- Oxidant- Potassium permanganate
- Mass- 17.79 mg/kg
- Concentration- N/A

Site G

- Location- California
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Manufacture Site
- Media type- Homogeneous Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- 114.21 mg/kg
- Concentration- 2.5%

Site H

- Location- Wisconsin
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Manufacturing site
- Media type- Homogenous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site I

- Location- New York
- COCs- VOCs (PCE, TCE, DCE, VC) and CFCs
- Site Type- Manufacturing site
- Media type- Homogenous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site J

- Location- Nebraska
- COCs- VOCs (PCE, TCE, DCE, VC) and BTEX
- Site Type- Manufacturing site
- Media type- Homogenous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Sodium permanganate
- Mass- 3436 mg/kg
- Concentration- 20%

Site K

- Location- Georgia
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Other (Landfill)
- Media type- N/A
- Delivery Approach- N/A
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site L

- Location- Pennsylvania
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium Permanganate
- Mass- 531.12 mg/kg
- Concentration- 5%

Site M

- Location- Minnesota
- COCs- VOCs (PCE, TCE, DCE, VC) and BTEX
- Site Type- Former Drycleaner
- Media type- Homogeneous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Postcoupling (Other Oxidant)
- Oxidant- Sodium Permanganate
- Mass- 247.55 mg/kg
- Concentration- 10%

Site N

- Location- Oregon
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Drycleaner
- Media type- Homogenous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Soil Vapor Extraction)
- Oxidant- Potassium permanganate
- Mass- 16.33 mg/kg
- Concentration- 4%

Site O

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Former Drycleaner
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Sodium Permanganate
- Mass- 247.55 mg/kg
- Concentration- 10%

Site P

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Former Drycleaner
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium Permanganate
- Mass- 14.55 mg/kg
- Concentration- 2%

Site Q

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Former Drycleaner
- Media type- Heterogeneous Mostly Impermeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Sodium Permanganate
- Mass- 15.84 mg/kg
- Concentration- 10%

Site R

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Former Drycleaner
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Natural Attenuation)
- Oxidant- Sodium Permanganate
- Mass- 33.00 mg/kg
- Concentration- 10%

Site S

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Drycleaner
- Media type- N/A
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site T

- Location- Tennessee
- COCs- VOCs (PCE, TCE, DCE, VC) and BTEX
- Site Type- Drycleaner
- Media type- N/A
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Soil Vapor Extraction)
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site U

- Location- Florida
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Heterogeneous Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site V

- Location- Florida
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Former Drycleaner
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium Permanganate
- Mass- 123.37 mg/kg
- Concentration- 0.5%

Site W

- Location- Maine
- COCs- VOCs (PCE, TCE, DCE, VC), BTEX, Dioxins, Metals, Asbestos
- Site Type- Manufacturing Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Precoupling (Soil Vapor Extraction)
- Oxidant- Sodium permanganate
- Mass- 22.63 mg/kg
- Concentration- 10%

Site X

- Location- California
- COCs- VOCs (PCE, TCE, DCE, VC), PAHs, Pesticides, PCBs, Metals
- Site Type- Government Site
- Media type- Homogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium permanganate
- Mass- 12.15 mg/kg
- Concentration- 5%

Site Y

- Location- Ohio
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government
- Media type- Homogeneous Mostly Permeable
- Delivery Approach- Recirculation Well
- Coupled Technology- None
- Oxidant- Potassium Permanganate
- Mass- 651. 41 mg/kg
- Concentration- 2%

Site Z

- Location- Colorado
- COCs- VOCs (PCE, TCE, DCE, VC) and BTEX
- Site Type- Military
- Media type- Homogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- None
- Oxidant- Potassium Permanganate
- Mass- 471.32 mg/kg
- Concentration- 2%

Site α

- Location- Wyoming
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Postcoupling (Natural Attenuation)
- Oxidant- Potassium Permanganate
- Mass- 5.84 mg/kg
- Concentration- 1.5%

Site β

- Location- Wyoming
- COCs- VOCs (PCE, TCE, DCE, VC), SVOCs, PCBs, Dioxins, Furans
- Site Type- Government Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Hydraulic Fracturing
- Coupled Technology- Postcoupling (Natural Attenuation)
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site χ

- Location- Wyoming
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Government Site
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Postcoupling (Natural Attenuation)
- Oxidant- Potassium permanganate
- Mass- N/A
- Concentration- N/A

Site δ

- Location- Wisconsin
- COCs- VOCs (PCE, TCE, DCE, VC)
- Site Type- Drycleaner
- Media type- Heterogeneous Mostly Permeable
- Delivery Approach- Multipoint Injection Wells
- Coupled Technology- Postcoupling (Natural Attenuation)
- Oxidant- Potassium permanganate
- Mass- 115.73 mg/kg
- Concentration- N/A

APPENDIX B

Interpolated Values

Table 76

Interpolated Manganese Values for T0 and T1

Site	Mn_{T0D1}	Mn_{T0D2}	Mn_{T0D3}	Mn_{T0D4}	Mn_{T0D5}	Mn_{T1D1}	Mn_{T1D2}	Mn_{T1D3}	Mn_{T1D4}	Mn_{T1D5}
A	0.07	0.08	0.08	0.09	0.10					
B	4.44	4.11	3.73	3.17	2.78					
C	0.03	0.03	0.06	0.01	0.07	4.67	2.44	2.27	1.54	0.39
D	0.01	0.01	0.01	0.01	0.01	1.13	1.24	1.24	0.99	0.35
E	0.23	0.24	0.23	0.20	0.20	0.98	0.77	0.73	0.74	0.75
F	3.06	5.41	7.22	5.27	6.62	13.80	10.21	8.35	6.80	7.86
G	0.93	0.98	1.05	1.22	3.38	23.08	24.78	25.90	25.16	15.58
I	0.51	0.55	0.58	0.59	0.54	5.29	5.71	6.19	8.15	22.54
J	7.46	9.02	6.67	5.77	6.77	9.53	9.27	6.58	5.62	6.08
L	0.22	0.21	0.24	0.48	0.84					
N	0.16	0.16	0.16	0.16	0.17	0.12	0.12	0.116	0.109	0.10
O	0.16	0.25	0.29	0.32	0.56	1.38	1.58	1.65	1.55	1.20
P	0.25	0.12	0.09	0.37	1.99	0.39	0.21	0.16	0.49	1.68
Q	0.86	0.87	0.87	0.88	0.89					
U	0.08	0.05	0.07	0.11	0.14	79.79	43.07	55.09	65.04	66.80
W	0.06	0.06	0.05	0.06	0.07	14.94	13.48	12.76	12.73	13.60
X	0.81	0.82	0.82	0.81	0.72					
Z	0.19	0.14	0.11	0.13	0.05					
α	0.01	0.01	0.01	0.01	0.01	3.19	3.08	2.96	2.72	2.06
δ	0.64	0.48	0.40	0.37	0.48					

Note: T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. Manganese concentrations are reported in mg/L.

Table 77

Interpolated Manganese Values for T2, T3, and T4

Site	Mn_{T2D1}	Mn_{T2D2}	Mn_{T2D3}	Mn_{T2D4}	Mn_{T2D5}	Mn_{T3D1}	Mn_{T3D2}	Mn_{T3D3}	Mn_{T3D4}	Mn_{T3D5}	Mn_{T4D1}	Mn_{T4D2}	Mn_{T4D3}	Mn_{T4D4}	Mn_{T4D5}
A						1.68	1.53	1.41	1.42	1.83					
B	5.69	5.41	4.99	4.22	3.84						4.09	3.92	3.63	3.11	3.10
C	1.80	0.94	0.89	0.63	0.18										
D	2.16	2.92	3.53	3.56	2.53										
E	0.53	0.28	0.28	0.52	0.71										
F	10.60	10.72	10.80	9.82	11.20										
G						23.60	25.30	26.50	25.97	20.10					
I	0.94	1.04	1.12	1.17	1.15										
J	1.91	2.30	2.70	3.47	5.34	1.32	1.11	1.73	2.21	2.71	20.95	9.74	7.11	7.38	9.20
L						2.28	2.20	2.44	4.03	7.22					
N						0.17	0.18	0.19	0.23	0.26					
O															
P	0.34	0.18	0.15	0.39	1.52										
Q						0.08	0.14	0.25	0.55	0.63	0.25	0.26	0.28	0.29	0.51
U															
W															
X						18.60	18.74	18.80	18.87	17.90					
Z	9.02	8.17	7.59	7.08	3.82										
α	0.16	0.16	0.15	0.04	0.11	0.06	0.06	0.05	0.05	0.04					
δ	125.00	86.91	69.70	60.00	61.60	1.91	1.23	0.95	0.83	0.92					

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. Manganese concentrations are reported in mg/L.

Table 78

Interpolated pH Values for T0, T1, and T2

Site	pH_{T0D1}	pH_{T0D2}	pH_{T0D3}	pH_{T0D4}	pH_{T0D5}	pH_{T1D1}	pH_{T1D2}	pH_{T1D3}	pH_{T1D4}	pH_{T1D5}	pH_{T2D1}	pH_{T2D2}	pH_{T2D3}	pH_{T2D4}	pH_{T2D5}
A	4.42	4.423	4.42	4.42	4.39										
B	6.48	6.421	6.38	6.34	6.28						6.77	6.72	6.69	6.68	6.58
C	6.35	6.41	6.39	6.36	6.38	7.13	7.06	7.05	7	6.72	8.75	9.02	8.57	7.7	7.09
D	6.88	6.85	6.83	6.83	6.83	7.18	7.17	7.16	7.1	6.94	7.5	7.52	7.53	7.49	7.34
E	7.74	7.09	7	7.05	7.09	6.38	6.22	6.27	6.54	6.61	5.98	5.9	5.92	6.11	6.27
F	3.33	5.19	6.28	6.81	6.36	7.31	7.1	6.98	7.06	7	6.75	6.79	6.67	6.9	6.69
G	7.14	7.14	7.14	7.14	7.11	7.65	7.66	7.67	7.64	7.4					
H	7.87	7.87	7.88	7.86	7.85						7.78	7.8	7.84	7.84	7.81
I	6.93	6.91	6.92	7.15	9.22	7.35	7.35	7.38	7.58	9.37	7.13	7.11	7.11	7.29	9.09
J	6.75	6.89	6.88	6.85	6.82	6.61	6.42	6.52	6.6	6.65	6.53	6.36	6.51	6.62	6.66
L	7.41	7.41	7.4	7.35	7.27										
M	7.41	7.36	7.31	7.25	7.26										
N	6.89	6.9	6.91	6.91	6.92	7.58	7.53	7.45	7.32	7.18					
O	7.45	7.43	7.4	7.28	5.63	7.84	7.74	7.69	7.67	7.58					
P	6.18	6.06	6.03	6.34	6.47	5.28	4.98	4.9	5.66	5.93	5.43	5.26	5.21	5.67	5.9
Q	7.69	7.71	7.72	7.76	7.7										
R	7.95	7.84	7.68	7.32	6.91										
U	7.46	7.51	7.45	7.43	7.42	8.02	7.76	7.65	7.56	7.46					
V	5.99	6.15	6.25	6.45	6.84	7.22	7.27	7.3	7.27	7.18	8.09	8.11	8.14	8.09	7.87
W	7.77	7.8	7.82	7.75	7.64	7.63	7.68	7.71	7.65	7.5					
X	6.78	6.78	6.79	6.79	6.77										
Y	7.19	7.19	7.2	7.16	6.91	7.12	7.22	7.27	7.28	7.35					
Z	6.48	6.51	6.52	6.54	6.73						6.51	6.41	6.34	6.46	6.69
α	7.07	7.07	7.07	7.07	7.08	6.75	6.77	6.79	6.84	6.96	7.43	7.41	7.4	7.37	7.29
δ	6.93	6.92	6.93	6.89	6.85						7.6	7.64	7.66	7.68	7.67

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ.

Table 79

Interpolated pH Values for T3 and T4

Site	pH_{T3D1}	pH_{T3D2}	pH_{T3D3}	pH_{T3D4}	pH_{T3D5}	pH_{T4D1}	pH_{T4D2}	pH_{T4D3}	pH_{T4D4}	pH_{T4D5}
A	7.76	7.517	7.33	7.23	7.09					
B						6.33	6.31	6.32	6.35	6.34
C										
D										
E										
F										
G	7.38	7.4	7.42	7.43	7.41					
H	7.53	7.54	7.55	7.55	7.55	7.98	7.97	7.95	7.95	7.96
I										
J	6.86	6.84	6.78	6.76	6.74	6.78	6.73	6.79	6.81	6.78
L	7.29	7.28	7.28	7.31	7.32					
M						7.54	7.48	7.43	7.38	7.41
N	7.25	7.23	7.21	7.15	7.1					
O										
P										
Q	9.46	9.34	9.13	8.58	8.06	8.04	7.91	7.74	7.39	6.39
R	6.77	6.44	6.25	6.33	6.99	3.81	3.99	4.34	5.53	7.35
U										
V						6.68	6.62	6.57	6.52	6.41
W										
X	7.02	7.03	7.03	7.03	6.99					
Y										
Z										
α	6.57	6.58	6.59	6.62	6.69					
δ	7.01	7	6.98	6.96	6.96					

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ.

Table 80

Interpolated ORP Values for T0 and T1

Site	ORP$_{T0D1}$	ORP$_{T0D2}$	ORP$_{T0D3}$	ORP$_{T0D4}$	ORP$_{T0D5}$	ORP$_{T1D1}$	ORP$_{T1D2}$	ORP$_{T1D3}$	ORP$_{T1D4}$	ORP$_{T1D5}$
A	36.86	32.62	29.43	24.80	19.58					
B	66.89	66.67	65.76	63.93	65.42					
C	-52.11	-71.30	-59.47	-31.65	-7.37	250.05	183.04	155.45	91.35	107.84
D	94.60	88.62	84.52	83.02	85.13	153.26	154.49	153.06	145.09	114.23
E	88.83	57.88	65.94	118.52	145.91	639.87	703.51	700.73	646.55	623.15
F	-65.02	-50.73	-34.44	-17.88	-64.12	-37.51	-13.75	-4.73	25.98	35.66
G	22.69	20.17	18.08	19.07	52.41	311.24	310.88	310.94	310.13	276.00
H	179.02	182.79	181.98	174.47	168.32					
I	-32.19	-35.77	-37.93	-35.22	-1.51	-76.18	-85.29	-92.88	-107.30	-187.00
J	0.30	-20.70	-6.97	1.08	0.79	-37.96	-56.99	-53.80	-45.39	-31.60
L	45.78	45.03	47.77	66.45	96.53					
M	35.63	37.45	38.97	41.47	48.63					
N	77.89	79.58	81.83	86.56	91.60	184.23	183.31	181.99	179.08	176.86
O	115.52	123.14	128.14	132.48	116.86	535.83	466.99	405.08	314.23	294.08
P	67.59	66.6	66.41	61.46	55.11	324.65	342.88	347.57	311.95	253.48
Q	279.38	280.22	281.08	282.75	285.24					
R	221.73	202.90	177.09	115.14	42.31					
U	-131.70	-127.30	-118.30	-125.30	-132.50	159.40	98.86	93.42	75.33	50.92
V	-3.92	16.06	15.79	10.69	-8.91	-78.46	-48.55	-32.56	-37.60	-22.22
W	-5.01	-5.03	-5.27	3.99	22.67	127.45	121.82	119.41	106.50	81.13
X	-47.83	-47.81	-48.32	-51.39	-74.68					
Y	-46.27	-27.84	-10.97	14.49	0.01	508.64	324.08	232.44	126.69	97.47
Z	207.19	205.77	204.05	202.96	191.85					
α	-71.15	-73.55	-76.15	-81.93	-99.20	430.16	425.92	421.46	411.92	385.51
δ	168.22	167.35	167.73	167.57	169.04					

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. ORP values expressed in mV.

Table 81

Interpolated ORP Values for T2 and T3

Site	ORP_{T2D1}	ORP_{T2D2}	ORP_{T2D3}	ORP_{T2D4}	ORP_{T2D5}	ORP_{T3D1}	ORP_{T3D2}	ORP_{T3D3}	ORP_{T3D4}	ORP_{T3D5}
A						-96.48	-127.50	-156.30	-164.90	-150.30
B										
C	-124.70	-123.50	-101.40	-43.46	90.50					
D	530.50	531.82	531.02	522.50	519.00					
E	139.64	226.93	230.04	169.91	129.23					
F	496.62	188.79	137.67	193.86	228.78					
G						47.38	45.74	44.65	46.77	84.82
H	389.19	399.06	392.60	349.59	323.88	400.65	383.25	343.46	298.61	302.95
I	-60.14	-65.88	-69.59	-66.89	-13.23					
J	-68.24	-76.76	-68.23	-62.57	-61.10	-104.20	-111.20	-99.42	-94.04	-96.04
L						490.93	490.98	492.68	503.01	528.12
M										
N						116.92	118.99	121.25	124.54	126.92
O										
P	140.60	120.93	115.56	176.44	136.37					
Q						203.11	203.45	204.20	206.92	201.04
R						284.10	275.58	265.04	244.14	227.79
U										
V	-108.50	-99.67	-95.29	-91.40	-79.90					
W										
X						7.84	7.87	7.60	5.89	-6.07
Y										
Z	282.89	376.69	452.83	349.64	104.83					
α	151.39	150.24	148.97	146.03	136.73	-2.34	-0.21	2.01	6.74	19.64
δ	235.83	266.40	291.68	312.54	312.15	13.18	66.38	85.51	93.30	87.60

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. ORP values expressed in mV.

Table 82

Interpolated ORP Values for T4

Site	ORP_{T4D1}	ORP_{T4D2}	ORP_{T4D3}	ORP_{T4D4}	ORP_{T4D5}
A					
B	13.22	8.63	6.59	16.69	172.89
C					
D					
E					
F					
G					
H	407.89	386.38	342.37	292.95	299.59
I					
J	-128.30	-158.20	-142.30	-130.30	-124.20
L					
M	121.60	138.27	152.94	173.55	183.35
N					
O					
P					
Q	297.75	294.69	298.15	337.03	311.91
R	191.38	197.90	209.89	250.46	315.68
U					
V	-144.30	-137.30	-132.70	-132.70	-131.60
W					
X					
Y					
Z					
α					
δ					

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. ORP values expressed in mV.

Table 83

Interpolated Chromium Values for T0 and T1

Site	Cr_{T0D1}	Cr_{T0D2}	Cr_{T0D3}	Cr_{T0D4}	Cr_{T0D5}	Cr_{T1D1}	Cr_{T1D2}	Cr_{T1D3}	Cr_{T1D4}	Cr_{T1D5}
B	0.03	0.03	0.03	0.03	0.03					
C	0.79	0.78	0.90	1.07	0.77	2.30	1.65	1.75	1.86	3.03
H	1.04	1.04	1.02	0.96	0.94					
I	50.43	52.27	53.72	55.69	68.82	29.90	27.70	26.30	27.00	48.00
L	0.03	0.02	0.03	0.06	0.11					
U	0.01	0.001	0.002	0.002	0.002	3.42	1.06	1.39	1.58	1.47
α	0.01	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. Chromium concentrations are expressed as µg/L.

Table 84

Interpolated Chromium Values for T2, T3, and T4

Site	Cr_{T2D1}	Cr_{T2D2}	Cr_{T2D3}	Cr_{T2D4}	Cr_{T2D5}	Cr_{T3D1}	Cr_{T3D2}	Cr_{T3D3}	Cr_{T3D4}	Cr_{T3D5}	Cr_{T4D1}	Cr_{T4D2}	Cr_{T4D3}	Cr_{T4D4}	Cr_{T4D5}
B	0.04	0.03	0.02	0.02	0.02										
C	1.14	1.14	1.89	1.40	3.02										
H	121.70	117.35	99.09	74.61	72.01	33.80	32.00	25.90	19.20	19.20	21.10	20.00	16.10	11.80	11.80
I	21.88	23.84	25.09	24.27	8.17										
L						0.07	0.07	0.07	0.11	0.18					
U															
α	0.11	0.11	0.10	0.09	0.07	0.01	0.01	0.01	0.01	0.01					

T0=pre-ISCO, T1=<4weeks postoxidation, T2=4-24weeks postoxidation, T3=24-52weeks post-ISCO, T4= 52-104weeks post-ISCO, D1=10 ft from TTZ, D2= 20 ft from TTZ, D3= 30 ft from TTZ, D4= 50 ft from TTZ, and D5= 100 ft from TTZ. Chromium concentrations are expressed in μg/L.

APPENDIX C

2D Interpolated ArcMap Maps for Selected Sites

This appendix contains ArcMap 9.2 2D interpolation maps for selected parameters and sites. These interpolation maps are based on the assigned X and Y coordinates at each site. The parameters values are shown at the chosen distances (10 ft, 20 ft, 30 ft, 50 ft, and 100 ft). At several sites the TTZ area is so small that not all distances were interpolated. The maps also show locations of site monitoring wells represented by small blue dots. The color palate goes from “hot” colors (darker colors) to “cool” colors (lighter colors). The parameter values follow this palate. The darker colors represent a higher parameter level, whereas lighter colors represent lower parameter values.

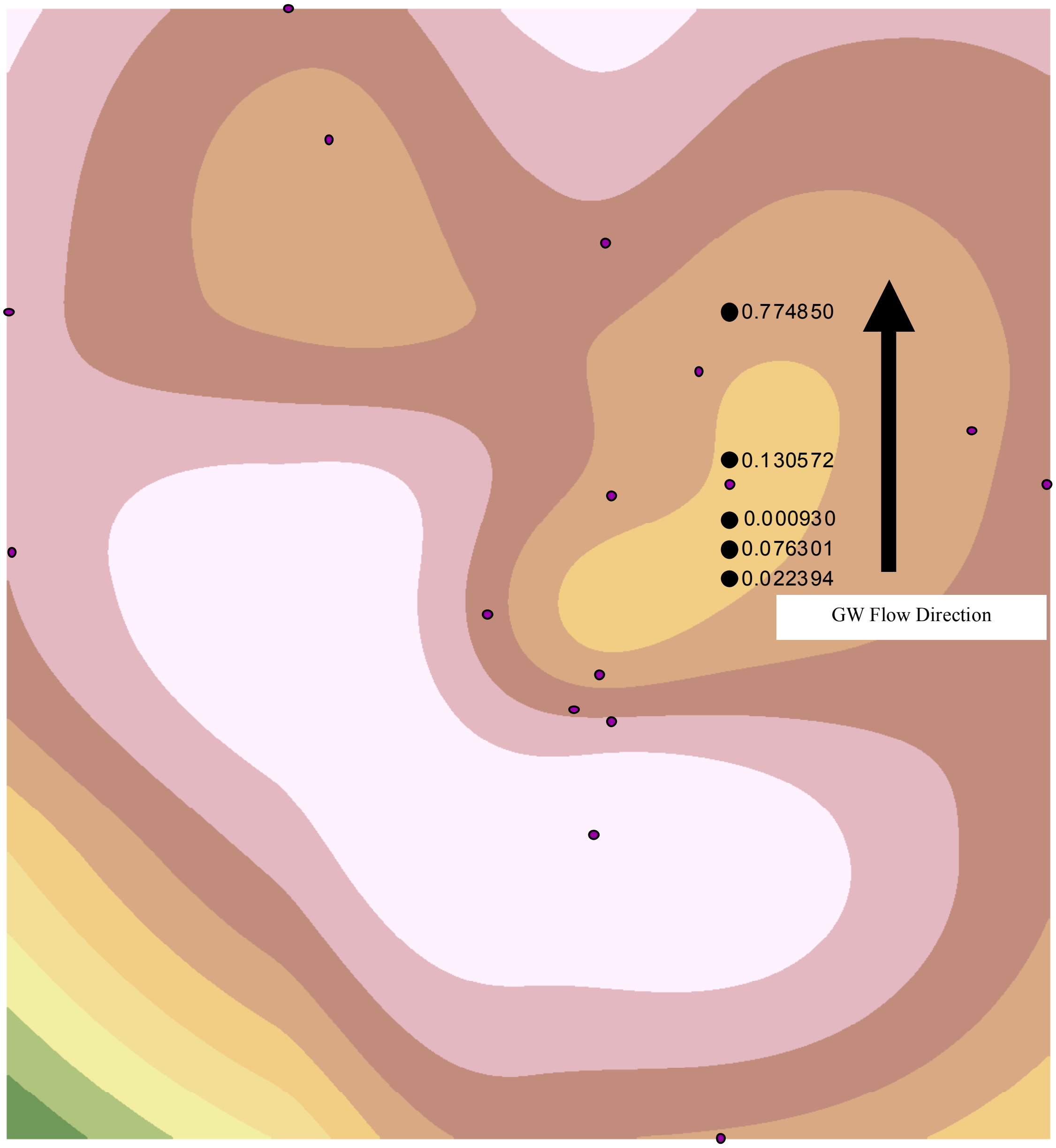

Figure 13 Interpolated 2D Map of Manganese Concentrations at Site A at T0 (Pre-ISCO)

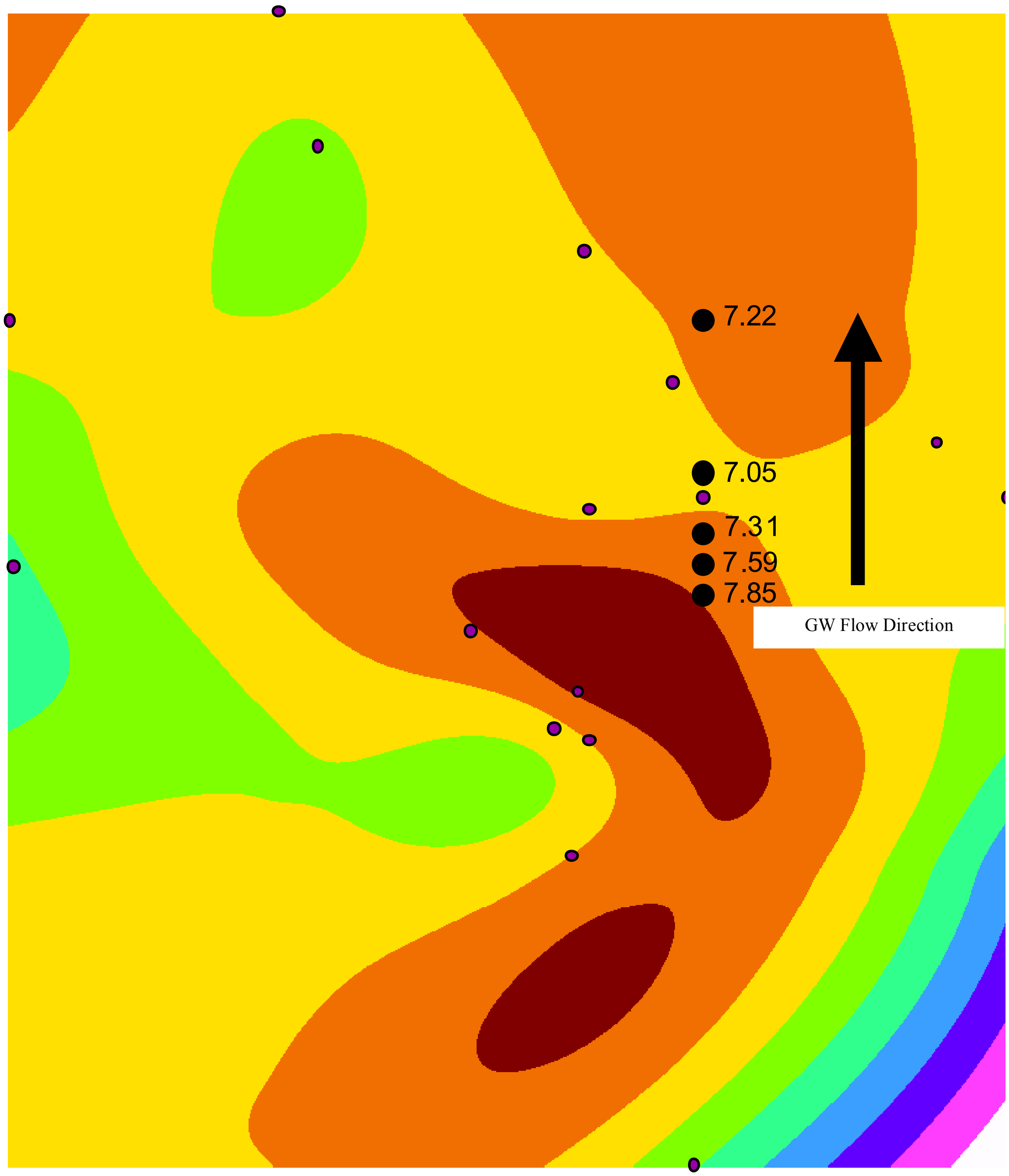

Figure 14 Interpolated 2D Map of pH Values at Site A at T3 (24-52 Weeks Post-ISCO)

Figure 15 Interpolated 2D Map of Manganese Concentrations at Site N at T1 (<4 Weeks Post-ISCO)

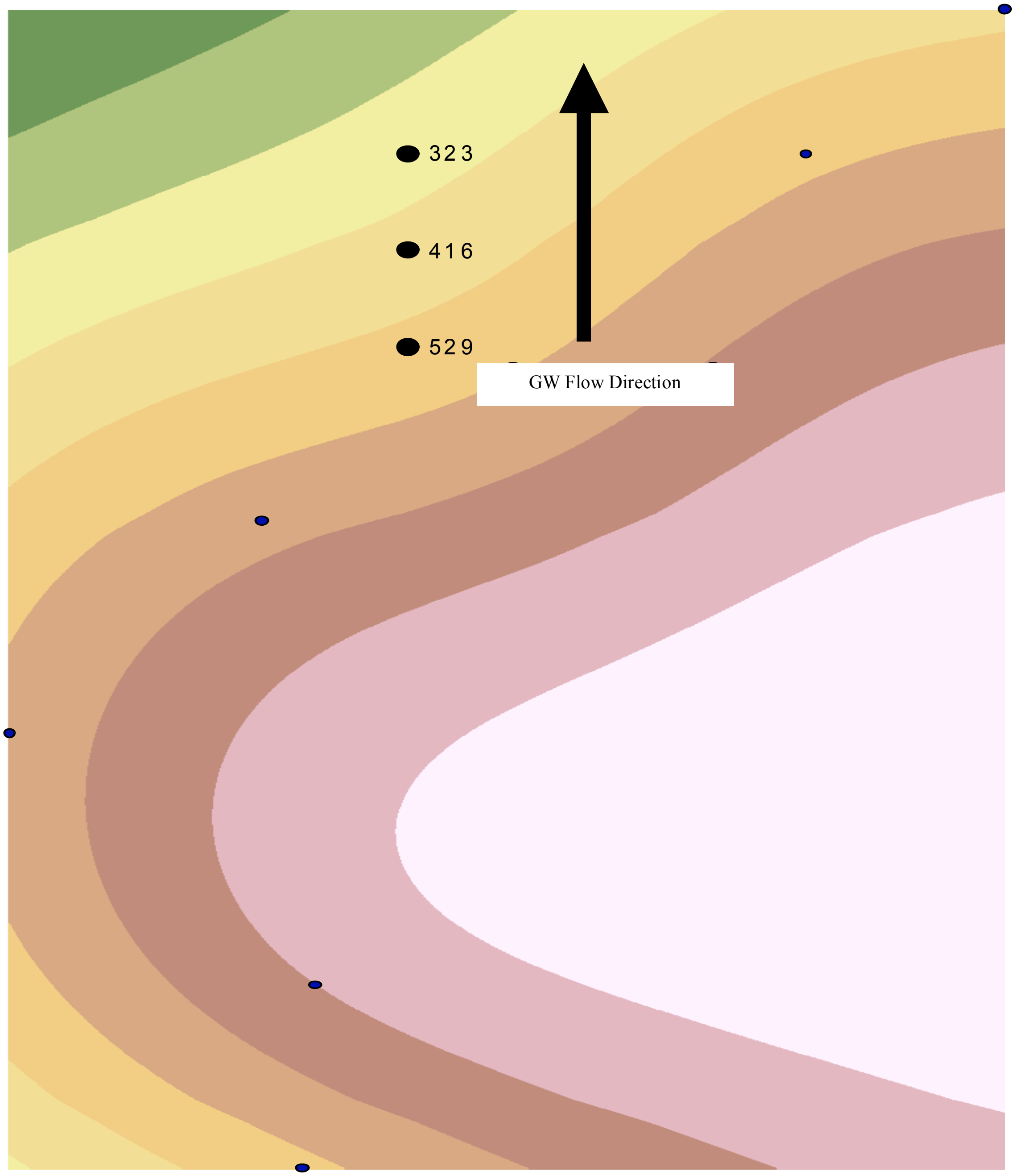

Figure 16 Interpolated 2D Map of ORP Values at Site N at T1 (<4 Weeks Post-ISCO)

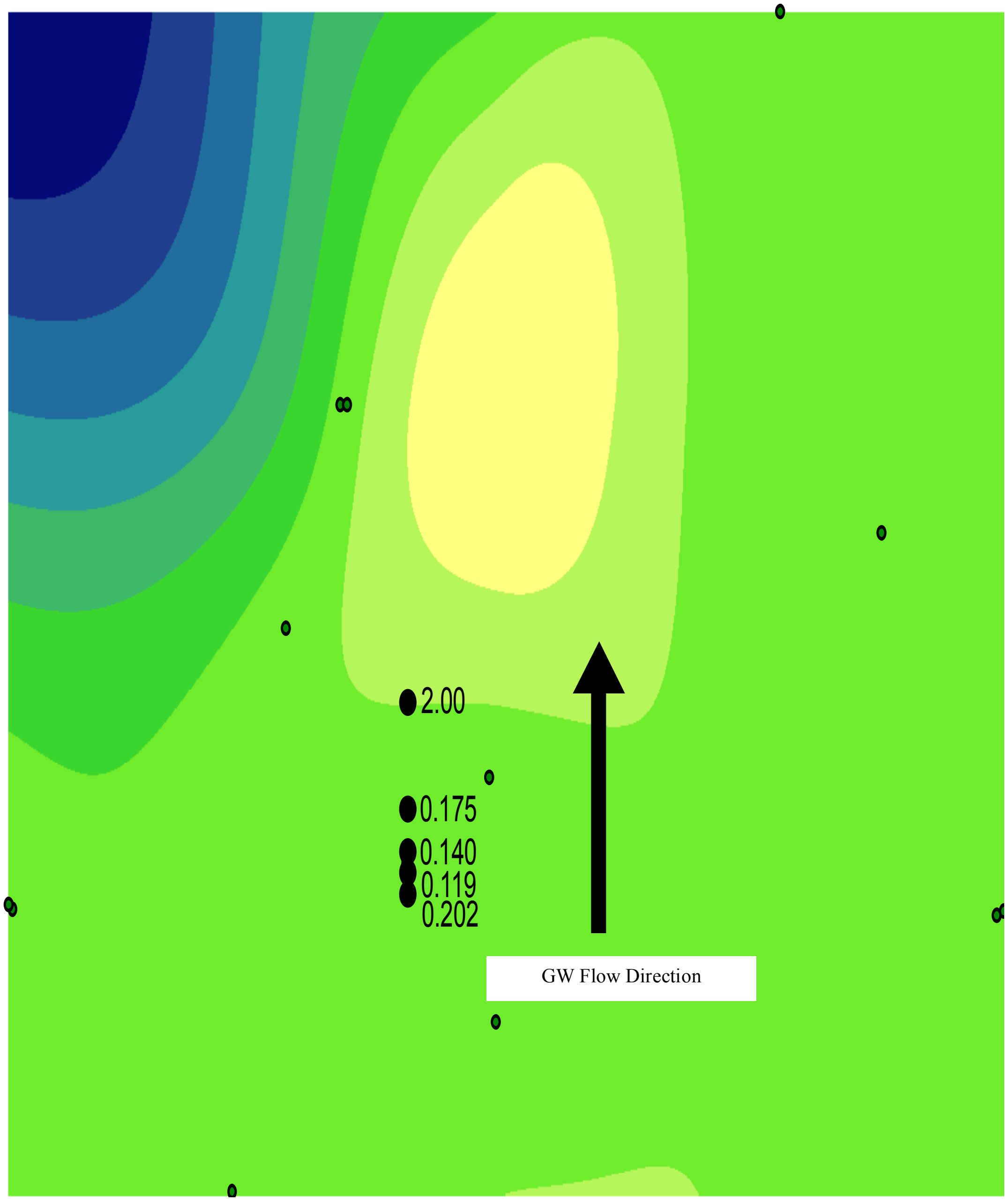

Figure 17 Interpolated 2D Map of Manganese Concentrations at Site Z at T0 (Pre-ISCO)

APPENDIX D

Individual Site ANOVAs Based on GW Velocities

Table 85

Individual Site ANOVAs for Manganese Concentrations Based on GW Velocities

Manganese										
	D0 vs. D1		D1 vs. D2		D2 vs. D3		D3 vs. D4		D4 vs. D5	
	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value
A	24.22	1.22 x 10^{-3}	2.15	0.344	2.98	0.288	N/A	N/A	N/A	N/A
B	52.14	2.65 x 10^{-4}	N/A	N/A	1.05	0.618	N/A	N/A	N/A	N/A
C	14.79	4.87 x 10^{-3}	8.03	0.007	N/A	N/A	N/A	N/A	N/A	N/A
D	23.51	2.76 x 10^{-4}	3.48	0.261	N/A	N/A	N/A	N/A	N/A	N/A
E	11.85	4.40 x 10^{-3}	3.71	0.258	N/A	N/A	N/A	N/A	N/A	N/A
F	N/A	N/A	N/A	N/A	0.45	0.738	N/A	N/A	0.36	0.884
G	10.22	1.65 x 10^{-3}	8.01	0.002	6.15	0.012	N/A	N/A	N/A	N/A
I	N/A	N/A	N/A	N/A	N/A	N/A	0.51	0.741	0.49	0.768
J	32.56	3.41 x 10^{-3}	3.50	0.288	N/A	N/A	N/A	N/A	1.87	0.511
L	N/A	N/A	N/A	N/A	N/A	N/A	0.47	0.663	0.34	0.790
N	67.60	5.27 x 10^{-5}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
O	39.15	3.76 x 10^{-4}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
P	12.18	0.004	5.23	0.257	N/A	N/A	N/A	N/A	N/A	N/A
Q	N/A	N/A	N/A	N/A	N/A	N/A	12.04	0.001	N/A	N/A
U	69.43	8.49 x 10^{-5}	N/A	N/A	11.12	0.005	N/A	N/A	N/A	N/A
W	36.86	1.84 x 10^{-3}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
X	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Z	N/A	N/A	0.24	0.891	N/A	N/A	0.13	0.951	N/A	N/A
α	N/A	N/A	N/A	N/A	N/A	N/A	0.52	0.538	0.48	0.699
δ	17.12	5.89 x 10^{-3}	N/A	N/A	N/A	N/A	7.43	0.012	N/A	N/A

Note: Highlighted sites are those that show a distance impact other than at D0 (inside target treatment zone). N/A = no data available.

Table 86

Individual Site ANOVAs for pH Values Based on GW Velocities

	pH									
	D0 vs. D1		D1 vs. D2		D2 vs. D3		D3 vs. D4		D4 vs. D5	
	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value
A	19.42	1.42×10^{-3}	5.16	0.410	5.71	0.381	N/A	N/A	N/A	N/A
B	25.08	4.00×10^{-4}	N/A	N/A	1.51	0.815	N/A	N/A	N/A	N/A
C	51.77	4.21×10^{-4}	26.27	1.53×10^{-3}	N/A	N/A	N/A	N/A	N/A	N/A
D	2.51	0.023	0.91	0.991	N/A	N/A	N/A	N/A	N/A	N/A
E	11.02	1.31×10^{-3}	6.12	0.618	N/A	N/A	N/A	N/A	N/A	N/A
F	N/A	N/A	N/A	N/A	0.79	0.711	N/A	N/A	0.61	0.796
G	63.63	2.90×10^{-4}	44.01	9.00×10^{-3}	41.75	3.28×10^{-3}	N/A	N/A	N/A	N/A
H	NA	NA	NA	NA	NA	NA	1.80	0.599	1.56	0.611
I	N/A	N/A	N/A	N/A	N/A	N/A	1.42	0.612	1.33	0.682
J	16.42	1.46×10^{-3}	3.41	0.261	N/A	N/A	N/A	N/A	3.29	0.375
L	N/A	N/A	N/A	N/A	N/A	N/A	0.63	0.541	0.21	0.860
M	49.72	3.59×10^{-4}	19.18	6.04×10^{-3}	NA	NA	NA	NA	NA	NA
N	9.01	1.11×10^{-3}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
O	13.39	4.91×10^{-3}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
P	29.60	3.65×10^{-4}	7.53	0.374	N/A	N/A	N/A	N/A	N/A	N/A
Q	N/A	N/A	N/A	N/A	N/A	N/A	11.32	0.084	N/A	N/A
R	23.11	2.28×10^{-3}	NA	NA	NA	NA	NA	NA	NA	NA
U	7.75	1.00×10^{-3}	N/A	N/A	6.32	0.090	N/A	N/A	N/A	N/A
V	NA	NA	3.55	0.690	NA	NA	NA	NA	NA	NA
W	18.52	1.42×10^{-3}	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
X	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Y	15.83	1.17×10^{-3}	NA	NA	7.12	0.350	NA	NA	NA	NA
Z	N/A	N/A	0.34	0.884	N/A	N/A	0.21	0.916	N/A	N/A
α	N/A	N/A	N/A	N/A	N/A	N/A	0.79	0.410	0.77	0.426
δ	70.03	2.78×10^{-5}	N/A	N/A	N/A	N/A	12.75	0.030	N/A	N/A

Note: Highlighted sites are those that show a distance impact other than at D0 (inside target treatment zone). N/A = no data available.

Table 87

Individual Site ANOVAs for ORP Values Based on GW Velocities

Oxidation Reduction Potential										
	D0 vs. D1		D1 vs. D2		D2 vs. D3		D3 vs. D4		D4 vs. D5	
	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value
A	27.25	7.62 x 10^{-4}	11.06	0.011	4.10	0.804	NA	NA	NA	NA
B	31.88	1.47 x 10^{-4}	NA	NA	9.31	0.590	NA	NA	NA	NA
C	56.00	4.27 x 10^{-5}	28.41	2.37 x 10^{-4}	NA	NA	NA	NA	NA	NA
D	17.06	5.87 x 10^{-3}	3.02	0.610	NA	NA	NA	NA	NA	NA
E	7.62	0.058	3.12	0.661	NA	NA	NA	NA	NA	NA
F	NA	NA	NA	NA	1.32	0.714	NA	NA	3.82	0.691
G	29.93	2.83 x 10^{-4}	15.62	8.03 x 10^{-3}	13.41	0.019	NA	NA	NA	NA
H	NA	NA	NA	NA	NA	NA	0.61	0.871	0.61	0.821
I	NA	NA	NA	NA	NA	NA	5.59	0.650	6.14	0.720
J	17.50	3.52 x 10^{-3}	7.02	0.375	NA	NA	NA	NA	2.61	0.681
L	NA	NA	NA	NA	NA	NA	3.61	0.792	5.75	0.699
M	51.75	3.61 x 10^{-5}	31.44	8.01 x 10^{-4}	NA	NA	NA	NA	NA	NA
N	41.04	3.88 x 10^{-3}	NA	NA	NA	NA	NA	NA	NA	NA
O	11.42	0.019	NA	NA	NA	NA	NA	NA	NA	NA
P	15.06	4.92 x 10^{-4}	4.73	0.580	NA	NA	NA	NA	NA	NA
Q	NA	NA	NA	NA	NA	NA	24.44	0.012	NA	NA
R	18.46	3.11 x 10^{-3}	NA	NA	NA	NA	NA	NA	NA	NA
U	42.61	5.21 x 10^{-3}	NA	NA	25.65	1.08 x 10^{-3}	NA	NA	NA	NA
V	NA	NA	1.11	0.748	NA	NA	NA	NA	NA	NA
W	8.44	0.225	NA	NA	NA	NA	NA	NA	NA	NA
X	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Y	23.30	6.82 x 10^{-3}	NA	NA	16.41	0.299	NA	NA	NA	NA
Z	NA	NA	10.05	0.387	NA	NA	7.42	0.563	NA	NA
α	NA	NA	NA	NA	NA	NA	3.61	0.859	4.07	0.631
δ	81.02	4.00 x 10^{-5}	NA	NA	NA	NA	31.77	3.80 x 10^{-3}	NA	NA

Note: Highlighted sites are those that show a distance impact other than at D0 (inside target treatment zone). N/A = no data available.

Table 88

Individual Site ANOVAs for Chromium Concentrations Based on GW Velocities

Chromium										
	D0 vs. D1		D1 vs. D2		D2 vs. D3		D3 vs. D4		D4 vs. D5	
	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value	F Value	p Value
B	42.12	2.55 x 10^{-4}	NA	NA	2.80	0.318	NA	NA	NA	NA
C	25.65	2.11 x 10^{-3}	17.41	4.11 x 10^{-2}	NA	NA	NA	NA	NA	NA
H	NA	NA	NA	NA	NA	NA	1.14	0.673	2.94	0.694
I	NA	NA	NA	NA	NA	NA	3.20	0.817	3.56	0.781
L	NA	NA	NA	NA	NA	NA	1.15	0.932	1.48	0.899
U	31.44	1.73 x 10^{-5}	NA	NA	25.34	7.02 x 10^{-4}	NA	NA	NA	NA
α	NA	NA	NA	NA	NA	NA	12.15	0.351	6.41	0.779

Note: Highlighted sites are those that show a distance impact other than at D0 (inside target treatment zone). N/A = no data available.

VITA

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Moore, K., Crimi, M.L., & Huling, S. (2007). *Long-term post geochemical effects of manganese when using permanganate for ISCO.* AEHS Conference, San Diego, CA.

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