ENHANCED MONITORING OF HAZARDOUS WASTE SITE REMEDIATION:
ELECTRICAL CONDUCTIVITY TOMOGRAPHY AND CITIZEN
MONITORING OF REMEDIATION THROUGH THE EPA’S
COMMUNITY ADVISORY GROUP PROGRAM

by

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ABSTRACT

In situ chemical oxidation using permanganate has become a common method for degrading trichloroethene (TCE) in contaminated aquifers. Its effectiveness, however, is dependent upon contact between the oxidant and contaminant. Monitoring permanganate movement after injection is often hampered by aquifer heterogeneity and insufficient well coverage. Time lapse electrical conductivity tomography increases the spatial extent of monitoring beyond well locations. This technique can create two- or three-dimensional images of the electrical conductivity within the aquifer to monitor aquifer chemistry changes caused by permanganate injection and oxidation reactions.

In-phase and quadrature electrical conductivity were measured in homogeneous aqueous and porous media samples to determine the effects of TCE and humate oxidation by permanganate on both measures of conductivity. Further effects of clean sand, 10% kaolinite (v/v), and 10% smectite (v/v) on both types of conductivity were studied as well. Finally, in-phase electrical conductivity was measured over time after injecting permanganate solution into two-dimensional tanks containing artificial groundwater with and without TCE to observe the movement of the permanganate plume and its interaction with TCE and to examine the effectiveness of time-lapse conductivity tomography for monitoring the plume’s movement.

In-phase electrical conductivity after oxidation reactions involving permanganate, TCE, and humate could be accurately modeled in homogeneous batch samples. Use of forward modeling of in-phase conductivity from permanganate concentrations may be useful for improving recovery of conductivity values during survey inversion, but further work combining the chemistry modeling with solute transport models is needed. Small pH-related quadrature
conductivity decreases were observed after TCE oxidation, and large quadrature conductivity increases were observed as a result of sodium ion addition; however, quadrature conductivity could not be related to concentrations of permanganate or reaction products.

Additionally, EPA Superfund sites participating in the Community Advisory Group (CAG) program were examined to determine how communities may have benefitted from the program. While CAG participation was correlated with slower achievement of EPA cleanup milestones, many CAGs successfully achieved five standardized social goals. CAGs that achieved these social goals varied in composition but were similar in their focus on community outreach and ability to extend their influence beyond CAG meetings.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iii

LIST OF FIGURES ............................................................................................................................... x

LIST OF TABLES ................................................................................................................................. xiii

ACKNOWLEDGMENTS ......................................................................................................................... xiv

CHAPTER 1. INTRODUCTION .............................................................................................................. 1

1.1. Background ................................................................................................................................. 1

1.2. Problem Statement ..................................................................................................................... 3

1.3. Theoretical Framework ............................................................................................................... 4

1.3.1. Oxidation of TCE and Natural Organic Matter ................................................................. 4

1.3.2. Charge Formation on Grain Surfaces ............................................................................... 7

1.3.3. Complex Conductivity ....................................................................................................... 8

1.3.4. Potential Effects of ISCO on Complex Conductivity .................................................. 12

1.4. Purpose of the Study .................................................................................................................. 14

1.4.1. Research Questions ........................................................................................................... 14

1.4.2. Hypotheses .......................................................................................................................... 15

1.5. Significance of the Study ........................................................................................................... 16

1.6. Limitations of the Study .......................................................................................................... 17

1.7. Organization of the Study ......................................................................................................... 17

CHAPTER 2. ANALYSIS OF SOURCES OF BULK CONDUCTIVITY CHANGE IN SATURATED SILICA SAND AFTER UNBUFFERED TCE OXIDATION BY PERMANGANATE .......................................................................................................................... 19

2.1. Introduction ............................................................................................................................... 20

2.2. Theoretical Background ........................................................................................................... 22
2.3. Methods ................................................................................................................. 29
  2.3.1. Sand Preparation .............................................................................................. 29
  2.3.2. TCE Oxidation Samples .................................................................................. 30
  2.3.3. Bulk Conductivity Measurements .................................................................. 31
  2.3.4. Formation Factor and Surface Conductivity Calculation ............................. 35
  2.3.5. Adsorption Measurements ............................................................................. 35
  2.3.6. Conductivity Modeling .................................................................................... 36

2.4. Results .................................................................................................................... 37
  2.4.1. Baseline Formation Factor and Surface Charge Calculation ....................... 37
  2.4.2. Manganese Dioxide Precipitation Effects ...................................................... 38
  2.4.3. Conductivity Loss Through Silica Protonation ............................................. 39

2.5. Discussion .............................................................................................................. 42
  2.5.1. Contributions of Processes to Conductivity Change ..................................... 42
  2.5.2. Potential Uses and Limitations ....................................................................... 47

2.6. Conclusion ............................................................................................................. 50

CHAPTER 3. EFFECTS OF CHEMICAL OXIDATION OF TCE USING PERMANGANATE ON IN-PHASE AND QUADRATURE ELECTRICAL CONDUCTIVITY ................................................. 52

3.1. Introduction ........................................................................................................... 53

3.2. Theoretical Background ....................................................................................... 56

3.3. Methods ............................................................................................................... 62
  3.3.1. Materials ......................................................................................................... 62
  3.3.2. Conductivity Measurements ........................................................................... 63
  3.3.3. Permanganate and TCE Concentration Measurements .............................. 65
  3.3.4. Conductivity Modeling .................................................................................... 66
3.3.5. Experimental Setup and Sample Preparation ........................................... 66

3.4. Results ........................................................................................................... 70

3.4.1. Formation Factor and Surface Conductivity ............................................ 70

3.4.2. In-Phase Conductivity Change from TCE Oxidation ............................... 73

3.4.3. In-Phase Conductivity Change from Humate Oxidation ......................... 76

3.4.4. Background Quadrature Conductivity Spectra ........................................ 76

3.4.5. Effects of Ion Injection on Quadrature Conductivity ............................... 78

3.4.6. Effects of pH Change on Quadrature Conductivity ................................. 80

3.4.7. Effects of MnO₂ Production on Quadrature Conductivity ....................... 82

3.5. Discussion ..................................................................................................... 85

3.5.1. In-Phase (Bulk Porous Media and Fluid) Conductivity ......................... 85

3.5.2. Quadrature Conductivity .......................................................................... 88

3.6. Conclusion .................................................................................................... 89

CHAPTER 4. TWO-DIMENSIONAL ANALYSIS OF PERMANGANATE PLUME
MOVEMENT AND INTERACTION WITH TCE THROUGH VISUAL EVIDENCE, WATER
SAMPLING, AND TIME-LAPSE ELECTRICAL CONDUCTIVITY TOMOGRAPHY .......... 91

4.1. Introduction .................................................................................................. 91

4.2. Theoretical Background ............................................................................. 93

4.3. Methods ....................................................................................................... 97

4.3.1. Materials ................................................................................................. 97

4.3.2. Permanganate and TCE Concentration Measurements .......................... 98

4.3.3. Conductivity Estimation from Pore Fluid Composition .......................... 98

4.3.4. Batch Samples ....................................................................................... 99

4.3.5. Adsorption Correction for Batch Samples ............................................. 100

4.3.6. Tank Experiments .................................................................................. 102
CHAPTER 5. EVALUATING THE SUCCESS OF THE SUPERFUND COMMUNITY ADVISORY GROUP PROGRAM THROUGH EFFECTS ON CLEANUP TIME AND ACHIEVEMENT OF SOCIAL GOALS

5.1. Introduction...........................................................................................................119
5.2. Measuring the Success of Community Advisory Groups.................................122
   5.2.1. Measuring Cleanup Progress .......................................................................123
   5.2.2. Evaluating the Public Participation Processes .............................................123
5.3. Milestone Completion at Superfund Sites With and Without CAG Involvement .........................................................................................................................128
5.4. Social Goals Achieved Through CAG Involvement .............................................133
   5.4.1. Eastland Woolen Mill, Corinna, Maine .......................................................133
   5.4.2. Omaha Lead, Omaha, Nebraska ..................................................................136
   5.4.3. Outboard Marine Corporation / Johns-Manville / Yeoman Creek Landfill, Waukegan, Illinois ..............................................................................138
   5.4.4. Pine Street Canal, Burlington, Vermont .......................................................140
   5.4.5. Chemical Commodities, Inc., Olathe, Kansas ..............................................143
   5.4.6. Aerojet General Corporation, Rancho Cordova, California .......................145
   5.4.7. Raymark Industries, Stratford, Connecticut ................................................148
5.5. Discussion..............................................................................................................151
5.6. Conclusion............................................................................................................155

CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS .........................................156
6.1. In-Phase (Bulk and Pore Fluid) Conductivity ......................................................... 156
6.2. Quadrature Conductivity ......................................................................................... 158
6.3. Time Lapse Conductivity Tomography of Permanganate Plume Movement and TCE Oxidation ........................................................................................................ 161
6.4. Application of Results ............................................................................................. 162
6.5. Recommendations for Further Study ..................................................................... 164
REFERENCES CITED ........................................................................................................ 165
APPENDIX A. CALIBRATION DATA .............................................................................. 177
LIST OF FIGURES

Figure 1.1. Oxidation of 8 mM TCE by 20 mM MnO$_4^-$ assuming oxalic acid as an intermediate at pH 8. ................................................................. 5

Figure 1.2. Percentage of unprotonated silanol groups (SiO$^-$) on the surface of silica as function of pH. ................................................................. 8

Figure 1.3. Trigonometric relationship between phase ($\varphi$), absolute conductivity ($| \sigma |$), real conductivity ($\sigma'$), and quadrature conductivity ($\sigma''$). ................................................................. 10

Figure 1.4. Quadrature conductivity spectra for clean sand and 10% smectite saturated with artificial groundwater. ................................................................. 12

Figure 2.1. Bulk conductivity versus frequency for a saturated sand sample containing the reaction products of 7.5 mM KCl, 14 mM KMnO$_4$, and 6 mM TCE. ................................................................. 32

Figure 2.2. Sample holder for saturated sand bulk conductivity measurements. ................................................................. 34

Figure 2.3. Bulk conductivity as a function of pore fluid conductivity in saturated sand at different ionic strengths. ................................................................. 37

Figure 2.4. Bulk conductivity versus pore fluid conductivity for saturated sand samples in which different TCE concentrations were oxidized by KMnO$_4$. ................................................................. 39

Figure 2.5. Measured pore fluid conductivity (diamonds) and pH (triangles) over three hours compared to PHREEQC-modeled conductivity. ................................................................. 41

Figure 2.6. Measured pore fluid conductivity (diamonds) and pH (triangles) over three hours compared to PHREEQC-modeled conductivity for acid-washed sand saturated with a solution containing KCl and KMnO$_4$. ................................................................. 42

Figure 2.7. Effect of MnO$_4^-$ addition, TCE oxidation, and H$^+$ adsorption on observed bulk and pore fluid conductivity. ................................................................. 46

Figure 2.8. Measured versus modeled conductivity in fluid samples (circles) and in saturated sand samples (squares). ................................................................. 47

Figure 3.1. Oxidation of 8 mM TCE by 20 mM MnO$_4^-$ assuming oxalic acid as an intermediate at pH 8. ................................................................. 60

Figure 3.2. Formation factor ($F$) and surface conductivity ($\sigma_s$) calculated in saturated clean sand and in clayey sands containing 10% kaolinite or 10% smectite. ................................................................. 71

Figure 3.3. Bulk conductivity versus pore fluid conductivity for saturated sand samples in which different TCE concentrations were oxidized by KMnO$_4$. ................................................................. 72
Figure 3.4. Oxidized TCE concentration versus formation factor calculated in individual samples assuming no surface conductivity (small dots, dashed regression line) and calculated by sets of samples with the same TCE concentration (large open circles with 95% confidence intervals, solid regression line). ................................................................................................................. 73

Figure 3.5. Measured versus predicted pH in fluid samples in which TCE was oxidized by 10 mM MnO$_4^-$ in artificial groundwater with 2 mM HCO$_3^-$ .......................................................... 74

Figure 3.6. Measured and predicted electrical conductivity in fluid samples in which TCE was oxidized by permanganate. ................................................................................................................. 74

Figure 3.7. Observed pH in porous media samples containing artificial groundwater with 2 mM NaHCO$_3$ in which various TCE concentrations were oxidized by 10 mM KMnO$_4$........................................................................ 75

Figure 3.8. Measured permanganate concentration (triangles) and electrical conductivity (circles) in fluid samples in which 0, 100, 200, or 300 mg/L humic acid was oxidized by 10 mM KMnO$_4$ in artificial groundwater. ................................................................................................................. 77

Figure 3.9. Quadrature conductivity spectra for clean sand, 10% kaolinite, and 10% smectite saturated with artificial groundwater. ................................................................................................................. 78

Figure 3.10. Effect of TCE on quadrature conductivity in sand saturated with artificial groundwater. ................................................................................................................................. 78

Figure 3.11. Quadrature conductivity at (a) 1 Hz and (b) 10 Hz in saturated clean sand samples after adding KCl, NaCl, and KMnO$_4$ to artificial groundwater. ................................................................. 79

Figure 3.12. Comparison between quadrature conductivity change at (a) 1 Hz and (b) 10 Hz in 10% kaolinite and in clean sand after adding KCl to artificial groundwater. ................................................................. 80

Figure 3.13. Quadrature conductivity in saturated 10% smectite after addition of KCl, NaCl, or KMnO$_4$ to artificial groundwater measured at (a) 1 Hz and (b) 10 Hz......................................................... 81

Figure 3.14. Quadrature conductivity at 1 Hz and 10 Hz in saturated (a) sand and 10% kaolinite and (b) 10% smectite containing artificial groundwater in which TCE was oxidized by permanganate................................................................................................................. 82

Figure 3.15. Measured quadrature conductivity (symbols) compared to predicted quadrature conductivity based on pH-induced changes in SiO$_2$ percentage on silica grains (dashed line) in saturated clean sand samples in which TCE was completely oxidized by permanganate. .......................... 83

Figure 3.16. Quadrature conductivity of saturated 10% smectite samples with artificial groundwater pore fluid of varying pH. ................................................................................................................. 84

Figure 3.17. Quadrature conductivity at (a) 1 Hz and (b) 10 Hz versus manganese dioxide concentration in saturated clean sand samples ................................................................. 84
Figure 3.18. Quadrature conductivity change over time in clean sand saturated with artificial groundwater containing 10 mM permanganate and 600 mg/L humic acid (left axis). The right axis shows permanganate loss over the same time period in fluid samples with the same composition................................................................. 85

Figure 4.1. Oxidation of 2 mM TCE by 10 mM MnO$_4^-$ assuming oxalate as an intermediate... 94

Figure 4.2. Change in bulk conductivity at 22.0°C over 44 hours after packing artificial groundwater amended with 10 mM KMnO$_4$ with silica sand at pH 7.68......................... 101

Figure 4.3. Loss of pore fluid conductivity at 22.0°C over the first 1.5 hours after packing duplicate saturated clean sand samples with artificial groundwater amended with 10 mM KMnO$_4$ (a) at pH 7.68 and (b) adjusted for pH 5.75......................................................... 102

Figure 4.4. Tank used for two-dimensional time-lapse experiments................................. 103

Figure 4.5. Change in bulk conductivity at 22.0°C over 8 hours in sand saturated with artificial groundwater mixed with 10 mM KMnO$_4$ and 1.8 mM TCE immediately before packing....... 106

Figure 4.6. Change in bulk conductivity at 22.0°C over 23.3 hours in saturated sand, packed immediately after mixing artificial groundwater, 10 mM KMnO$_4$, and 1.8 mM TCE.......... 107

Figure 4.7. Time lapse photography and electrical conductivity tomography of the permanganate plume as it moved across the tank during the no-TCE iteration. ..................... 109

Figure 4.8. Time lapse photography and electrical conductivity tomography of the permanganate plume as it moved across the tank during the TCE iteration............... 110

Figure 5.1. Percentage of Superfund sites attaining cleanup milestones (full sample set) ..... 130

Figure 5.2. Percentage of Superfund sites listed on the NPL after 1990 attaining cleanup milestones. ........................................................................................................... 130

Figure 5.3. Average number of days elapsed between NPL site listing and attainment of site cleanup milestones (full sample set)......................................................... 131

Figure 5.4. Average number of days elapsed between NPL site listing and attainment of site cleanup milestones for sites listed after 1990.................................................. 131

Figure 5.5. Comparison of average hazard ranking system (HRS) scores between NPL sites that have CAG involvement and sites that do not have CAG involvement........................ 132

Figure A.1. Geometric factor calculation for the porous media sample holders. ............... 177

Figure A.2. Fluid conductivity probe calibration............................................................... 177

Figure A.3. Calibration of permanganate (MnO$_4^-$) concentration versus absorbance at 525 nm. .................................................................................................................. 178
LIST OF TABLES

Table 1.1. Predicted conductivity of aqueous solutions of 10 mM KMnO₄ and 5 mM TCE alone and in artificial groundwater containing 2 mM HCO₃⁻. .......................................................... 13

Table 2.1. Diffusion coefficient, $D_i$, and mobility, $\mu_i$, for selected ions at 25°C. .................. 27

Table 2.2. Predicted conductivity resulting from TCE oxidation by MnO₄⁻ in liquid samples calculated at 20°C using Equation 2.3 and PHREEQC, Version 3. TCE and non-aqueous phase components are treated as non-conductive. ....................................................... 28

Table 2.3. Formation factors calculated for different concentrations of TCE oxidized by permanganate. ................................................................................................................ 40

Table 2.4. Fluid conductivity ($\sigma_f$) broken down by individual ionic contribution. ............... 43

Table 3.1. Calculation of conductivity in a simulated groundwater after addition of 10 mM KMnO₄ and after contact of MnO₄⁻ with 0.5 mM and 5 mM TCE. ................................................. 61

Table 3.2. Surface conductivity calculated in TCE oxidation samples. ..................................... 71

Table 3.3. Measured and predicted quadrature conductivity ($\sigma''$) in saturated clean sand with pore fluid in which TCE was oxidized by permanganate in the presence of varying concentrations of NaHCO₃. ........................................................................... 83

Table 4.1. Water samples collected from Sample Tubes 1 and 2. ............................................. 112

Table 4.2. Permanganate recovery at the end of pumping with no TCE in the artificial groundwater. .................................................................................................................... 113

Table 4.3. Permanganate recovery at the end of pumping with TCE in the artificial groundwater. .................................................................................................................... 115

Table 4.4. Estimated average groundwater composition within the plume after injection of artificial groundwater amended with 50 mM KMnO₄ into artificial groundwater containing 1.6 mM TCE. .............................................................. 117

Table 5.1. Major site cleanup milestones as defined by the U.S. EPA. ..................................... 124

Table 5.2. Community Advisory Groups discussed in this study. ........................................ 134

Table 5.3. Attendance at the Aerojet CAG meeting, November 16, 2004................................ 146
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CHAPTER 1. INTRODUCTION

1.1. Background

Soil and groundwater contamination from chlorinated hydrocarbons such as trichloroethene (TCE) and tetrachloroethene (PCE) is a major concern in the United States. TCE has been found in over half of the hazardous waste sites found on the EPA Superfund program’s National Priority List (U.S. EPA, 2013a). Left alone, chlorinated hydrocarbons persist in the subsurface for long periods of time. However, degradation of these chemicals can be accelerated through enhanced in situ remediation methods such as chemical oxidation. During in situ chemical oxidation (ISCO), an oxidant is injected into the subsurface, where it mineralizes the chlorinated hydrocarbon to carbon dioxide, hydrogen ion, and chloride ion (Li and Schwartz, 2004). The most common oxidants used for this purpose are potassium and sodium permanganate, sodium persulfate, and ozone.

Successful employment of ISCO requires physical contact between the injected oxidant and the contaminant. Effective oxidant delivery is hampered, though, by subsurface heterogeneity and insufficient knowledge of where the oxidant has moved. Injected oxidant will often flow preferentially through more permeable aquifer zones, and it is often difficult to predict with certainty where these flowpaths will be (Smith et al., 2008). Traditionally, both oxidant and contaminant concentrations are monitored using wells emplaced throughout the study area. While these wells provide accurate data at the point of the well, extrapolation of that data can be problematic. To reduce installation costs, the number of monitoring wells is often reduced to the minimum number needed to delineate contaminant plume boundaries and protect off-site
receptors. Often, on-site monitoring wells are simply insufficient to adequately track oxidant movement (Halihan et al., 2012).

In cases where permanganate (MnO$_4^-$) is used during ISCO, the addition of time-lapse electrical resistivity tomography (ERT) to traditional monitoring well sampling may provide the necessary data to confidently monitor oxidant delivery and consumption between monitoring wells. The ionic nature of permanganate makes electrical methods potentially useful for monitoring its movement in heterogeneous aquifers. Electrical resistivity has previously been used to monitor saline solution movement during tracer tests, producing much more spatially extensive data than achievable through monitoring well data alone (Cassiani et al., 2006; Singha and Gorelick, 2005). In addition to offering data that are spatially more extensive than wells, electrical surveys are minimally intrusive and have a much faster data turnaround time than processing physical samples in a lab.

Electrical resistivity surveys use electrodes emplaced either in the ground surface or in boreholes to collect resistivity (or conductivity) data along survey lines. The data are then processed (inverted) to provide two- or three-dimensional maps of the resistivity. Time-lapse inversion methods, such as proposed by Karaoulis et al. (2013, 2011), allow the user to account for subsurface heterogeneity and see only the changes in resistivity that may occur over time from oxidant injections or chemical changes within the subsurface.

While time-lapse resistivity tomography has yet to be employed to monitor and adjust ISCO injections at hazardous waste sites, a few sites have used resistivity snapshots on a limited basis to assist in mapping permanganate distribution. Both Halihan et al. (2012) and Harte et al. (2012) used resistivity measurements to document preferential flow of permanganate through more permeable aquifer zones at remediation sites. While both studies were successful in
demonstrating significant conductivity changes after MnO$_4^-\,$ injection, they were largely qualitative in nature, and each study noted difficulties in matching resistivity values with specific MnO$_4^-\,$ concentrations detected through groundwater sampling.

Induced polarization is an extension of traditional direct current resistivity that allows the user to measure the reversible storage of electrical charges in a porous material. These measurements are often expressed as a complex conductivity value. The real (in-phase) conductivity component characterizes the ability of the porous material to carry electrical charges through electromigration. The imaginary or quadrature (out-of-phase) component characterizes the polarization of the porous material.

Time-lapse tomography using the quadrature conductivity component has been less researched than direct current or real conductivity as a means for monitoring remediation performance, especially during ISCO. However, quadrature conductivity anomalies have been reported in the vicinity of various organic contaminant plumes associated with oil (Vanhal, 1997), benzene and ethylene dibromide (Sogade, 2006), and TCE/PCE (Cardarelli and Di Filippo, 2009). The specific mechanisms by which quadrature conductivity anomalies related to such contaminant plumes form, though, have not been well established. Also, changes over time as a result of engineered remediation processes have yet to be characterized.

1.2. Problem Statement

In situ chemical oxidation (ISCO) using permanganate has become well established as a viable option for treating groundwater contamination by organic pollutants (Siegrist et al, 2011). However, successful application of ISCO depends on delivery of the oxidant everywhere there is contaminant. While monitoring wells can provide accurate and detailed point data regarding
oxidant and contaminant concentration, it is difficult to determine if oxidant delivery and therefore remediation has been successful away from monitoring wells. Improved monitoring methods with better spatial resolution are needed to ensure adequate distribution of oxidant to maximize contaminant degradation.

1.3. **Theoretical Framework**

This section presents a basic theoretical overview for analyses and conclusions described in the following chapters of this dissertation.

1.3.1. **Oxidation of TCE and Natural Organic Matter**

TCE oxidation by MnO$_4^-$ can be described as a two-step process with TCE first being oxidized to a carboxylate and then to CO$_2$. The rate of initial TCE oxidation to carboxylate is independent of pH, but the specific carboxylate intermediate formed is dependent on pH. Acidic pH favors formate formation, and neutral to slightly basic pH favoring oxalate formation. Lesser concentrations of glyoxylate and glycolate also form (Yan and Schwartz, 2000). The formate pathway is described in Equations 1.1 and 1.2 in terms of one TCE molecule.

$$\frac{8}{3} \text{H}_2\text{O} + \text{C}_2\text{HCl}_3 + \frac{2}{3}\text{MnO}_4^- \rightarrow 2\text{HCOO}^- + 3\text{Cl}^- + \frac{13}{3}\text{H}^+ + \frac{2}{3}\text{MnO}_2$$  \hspace{1cm} (1.1)

$$2\text{HCOO}^- + \frac{10}{3}\text{H}^+ + \frac{4}{3}\text{MnO}_2 \rightarrow 2\text{CO}_2 + \frac{4}{3}\text{MnO}_2 + \frac{8}{3}\text{H}_2\text{O}$$  \hspace{1cm} (1.2)

Equations 1.3 and 1.4 describe the oxalate pathway.

$$\frac{4}{3}\text{H}_2\text{O} + \text{C}_2\text{HCl}_3 + \frac{4}{3}\text{MnO}_4^- \rightarrow \text{C}_2\text{O}_4 + 3\text{Cl}^- + \frac{11}{3}\text{H}^+ + \frac{4}{3}\text{MnO}_2$$  \hspace{1cm} (1.3)

$$\text{C}_2\text{O}_4^{2-} + \frac{2}{3}\text{MnO}_4^- + \frac{8}{3}\text{H}^+ \rightarrow 2\text{CO}_2 + \frac{2}{3}\text{MnO}_2 + \frac{4}{3}\text{H}_2\text{O}$$  \hspace{1cm} (1.4)

Independent of the pathway, the overall mineralization of TCE can be expressed as

$$\text{C}_2\text{HCl}_3 \text{(TCE)} + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(s) + 2\text{CO}_2(g) + 3\text{Cl}^- + \text{H}^+. \hspace{1cm} (1.5)$$
Both oxidation reactions are first order with respect to each reactant, so the degradation can be generalized by Equations 1.6 and 1.7:

\[
\frac{d[TCE]}{dt} = -k_{2,TCE}[TCE][MnO_4^-] \tag{1.6}
\]

\[
\frac{d[CA]}{dt} = -k_{2,CA}[CA][MnO_4^-] \tag{1.7}
\]

where \(k_{2,TCE}\) and \(k_{2,CA}\) are the second order rate constants for TCE and the carboxylate, respectively, \([TCE]\) is the concentration of TCE, and \([CA]\) is the concentration of the carboxylate. The second-order rate constant for the transformation of TCE to the carboxylate between pH 4 and 8 is in the range of 0.65 to 0.68 M\(^{-1}\)s\(^{-1}\). The rate constants for formate and oxalate oxidation range from 0.075 to 0.35 M\(^{-1}\)s\(^{-1}\) and from 0.073 to 0.11 M\(^{-1}\)s\(^{-1}\), respectively, with rates increasing as pH decreases between pH 4 and 8 (Yan and Schwartz, 2000). Even assuming the slowest second order rate constants, the complete mineralization of TCE occurs quickly in the presence of excess MnO\(_4^-\) as demonstrated in Figure 1.1.

![Figure 1.1](image-url)

**Figure 1.1.** Oxidation of 8 mM TCE by 20 mM MnO\(_4^-\) assuming oxalic acid as an intermediate at pH 8.
Not only do target contaminants exert an oxidant demand on $\text{MnO}_4^-$, but natural organic matter does as well. Humic compounds are commonly occurring natural organics within the soil that exert an oxidant demand on $\text{MnO}_4^-$. While the number of carbons in naturally occurring humic compounds can vary, humate is often modeled as $\text{C}_9\text{H}_8\text{O}_4^{2-}$. When oxidized, many carbohydrates go through a carboxylic acid intermediate, just like TCE. Assuming aquifer pore water with a neutral to slightly basic pH, humate oxidation can be expressed through the following steps with oxalate as the intermediate.

$$\text{C}_9\text{H}_8\text{O}_4^{2-} + 12 \text{MnO}_4^- + 12 \text{H}^+ \rightarrow 9/2 \text{C}_2\text{O}_4^{2-} + 12 \text{MnO}_2 + 10 \text{H}_2\text{O} \quad (1.8)$$

$$9/2 \text{C}_2\text{O}_4^{2-} + 3 \text{MnO}_4^- + 12 \text{H}^+ \rightarrow 9 \text{CO}_2 + 3 \text{MnO}_2 + 6 \text{H}_2\text{O} \quad (1.9)$$

The total reaction then yields:

$$\text{C}_9\text{H}_8\text{O}_4^{2-} + 15 \text{MnO}_4^- + 24 \text{H}^+ \rightarrow 9 \text{CO}_2 + 15 \text{MnO}_2 + 16 \text{H}_2\text{O} \quad (1.10)$$

Manganese oxide solids (depicted as $\text{MnO}_2$ in Equations 1.1-1.5 and 1.8-1.10) form as a result of the reduction of $\text{MnO}_4^-$. In the presence of potassium permanganate, it has been reported that some of the manganese is substituted with potassium, forming $\text{K}_{0.854}\text{Mn}_{1.786}\text{O}_4\cdot1.55\text{H}_2\text{O}$ (Li and Schwartz, 2004). For simplicity, $\text{MnO}_2$ and the term manganese dioxide will be used throughout this dissertation to describe the manganese oxide precipitate formed by $\text{MnO}_4^-$ reduction. $\text{MnO}_2$ solids have the potential to clog aquifer pores, especially if high concentrations of TCE or a high natural oxidant demand are present (Siegrist et al., 2002). Generally, $\text{MnO}_2$ is persistent and insoluble unless organic acids are present to reductively dissolve it to $\text{Mn}^{2+}$. Li and Schwartz (2004) found that after 25 hours, only about 1% of $\text{MnO}_2$ (from an initial concentration of 1.2 mM) had dissolved at pH 2 with an inorganic acid. Within the same amount of time and at the same pH, however, all $\text{MnO}_2$ was dissolved by organic acids.
1.3.2. Charge Formation on Grain Surfaces

Silica and clay minerals such as kaolinites, smectites, and illites all develop negative surface charges when surrounded with water (Duval et al., 2002; Jara et al., 2005; Kraepiel et al., 1999, Ma and Eggleton, 1999). Silica sands contain silanol surface groups (SiOH) that act as acids and gain a proton (pK = -1.0) or lose a proton (pK = 4.0) based on pH (Duval et al., 2002). Figure 1.2 shows the percentage of deprotonated silanol groups (SiO⁻) as a function of pH. While kaolinites and smectites are both types of clay minerals, they are structurally different and have different origins for negative surface charge. The basic smectite structural unit consists of two outer tetrahedral silicate sheets with an inner octahedral aluminum oxide sheet. Smectites may have exposed hydroxyl groups from the silica sheets, but the major source of negative charge formation is from isomorphic substitution of Al³⁺ for Si⁴⁺ in the outer sheets and Mg²⁺ or Fe²⁺ for Al³⁺ in the inner sheets. Approximately 10 times more charge originates from these isomorphic substitutions than from exposed hydroxyls (Kraepiel et al., 1999). Kaolinite (aluminum silicate hydroxide) clays have a two-sheet structure, with a silicate sheet bonded to an aluminum hydroxide sheet. Charge formation in kaolinites is similar to that occurring in silica sands and is caused by exposed hydroxyls (both SiOH and AlOH). Unlike smectites, kaolinites do not exhibit isomorphic substitution to an extent significant enough to influence surface charge (Ma and Eggleton, 1999). The number of negative charges on the mineral surface is often referred to in terms of cation exchange capacity (CEC) because the negatively charged surface groups attract positively charged counterions. A typical CEC for silica ranges from 1.5 to 6.2 × 10⁻⁵ mol/kg (Revil, 2012). For kaolinite, CEC is 2.8 to 10 × 10⁻² mol/kg (Ma and Eggleton, 1999), and CEC for smectite is approximately 9.5 × 10⁻¹ mol/kg (Kraepiel et al., 1999).
MnO$_2$ solids also have the ability to adsorb cations, especially divalent metals (Tonkin et al., 2004). The CEC of MnO$_2$ is low, though, especially when compared to the CEC of silica, kaolinite, or smectite. A CEC of approximately $4 \times 10^{-13}$ mol/kg has been reported at pH 8 for the δ form of MnO$_2$ (Murray, 1974). The zero charge point for MnO$_2$ created during the MnO$_4^-$-TCE reaction has been observed to occur at pH 3.7 (Li and Schwartz, 2004).

1.3.3. Complex Conductivity

A double-layer model can be used to describe the adsorption of counterions to mineral surfaces (Revil, 2012; Revil and Florsch, 2010). Some counterions adsorb directly on the mineral surface in the Stern layer, while others are held more loosely in the diffuse layer. When an electrical current is introduced, the counterions move toward the negative pole of the electrical field. Because grains are touching within the porous material of an aquifer formation, the diffuse layers of multiple grains overlap, allowing charges in the diffuse layer to move from grain to grain. The movement of diffuse layer ions across the mineral surfaces results in surface conductivity. Unlike the counterions of the diffuse layer, the Stern layer counterions remain

![Figure 1.2.](image)

**Figure 1.2.** Percentage of unprotonated silanol groups (SiO$^-$) on the surface of silica as function of pH. Data from Duval et al. (2002).
attached to a single grain. They are, however, able to move to one side of the mineral surface in response to the electric field, creating a dipole moment (Revil and Florsch, 2010). When the electric field is removed, the counterions in the Stern layer relax. The effect of this relaxation can be observed as a delayed return to zero voltage after direct current is turned off or as a phase lag (a delay between injected and measured voltage waveforms) if an alternating current is injected.

When measured using an alternating current, the conductive ability of the pore fluid, the surface conductivity, and the charge storage within the Stern layer can all be described in terms of a complex conductivity $\sigma^*$, such that

$$\sigma^* = \sigma' + i\sigma''$$

(1.11)

where $\sigma'$ is the real or in-phase component of conductivity, $\sigma''$ is the imaginary or out-of-phase component (also called quadrature conductivity), and $i$ is $-1^{1/2}$. The absolute (or bulk) conductivity ($|\sigma|$), phase ($\phi$), $\sigma'$ and $\sigma''$ are related to each other through a trigonometric relationship (Figure 1.3). This relationship yields the following functions:

$$|\sigma| = \sqrt{\sigma'^2 + \sigma''^2},$$

(1.12)

$$\tan \phi = \frac{\sigma''}{\sigma'}.$$  

(1.13)

Because phases observed in natural geologic formations are very small (< 100 mrad), $|\sigma| \approx \sigma'$ and $\phi \approx \sigma'' / \sigma'$.

Assuming insulating grains within an aquifer, the real component of conductivity is a function of the migration of charge carriers through pore fluid and the surface conductivity and can be calculated by

$$\sigma' = \frac{1}{f} \sigma_f + \sigma_s,$$

(1.14)
where $\sigma_f$ (in S m\(^{-1}\)) denotes the conductivity of the pore water, $\sigma_s$ (in S m\(^{-1}\)) the surface conductivity in the electrical double layer, and $F$ the formation factor (dimensionless) (Revil et al., 2013). The formation factor is related to the connected porosity ($\phi$) by Archie’s Law, $F = \phi^m$, where $m$ is called the cementation or porosity exponent (Archie, 1942). The imaginary component of conductivity, on the other hand, is a function of the charge storage in the Stern layer and can be expressed in terms of the CEC by

$$\sigma'' = \frac{2}{3} \rho_g \beta_s^s f \text{ CEC}, \quad (1.15)$$

where $\rho_g$ is the grain density, $\beta_s^s$ is the mobility of the counterions in the Stern layer, and $f$ is the fraction of counterions in the Stern layer (Revil, 2012).

![Figure 1.3. Trigonometric relationship between phase ($\phi$), absolute conductivity ($|\sigma|$), real conductivity ($\sigma'$), and quadrature conductivity ($\sigma''$).](image)

The mobility of the counterions within the Stern layer is impacted by their density (Revil et al., 2013) and by how closely to the mineral surface the ion is held (Revil and Florsch, 2010). For example, a typical $\beta_s^s$ for Na\(^+\) (at 25°C) for silica sand is approximately $5.2 \times 10^{-8}$ m\(^2\) s\(^{-1}\) V\(^{-1}\), and for clay minerals it is approximately $1.5 \times 10^{-10}$ m\(^2\) s\(^{-1}\) V\(^{-1}\) (Revil et al., 2013). Ions that loosely adsorb to the mineral surface, such as sodium, display a higher mobility within the Stern layer than stronger-sorbing ions such as copper, zinc, and lead (Vaudelet et al., 2011a, 2011b).
In addition to the Stern layer polarization described above, two other polarization mechanisms can occur in the frequency range of 1 mHz to 10 kHz: membrane polarization and Maxwell-Wagner polarization. Membrane polarization results from delays in the back-diffusion of ions within the pore fluid when moving through pore throats either when a direct current is shut off or during injection of an alternating current (Titov et al., 2002). In the presence of an electric field, the cations within the pore fluid will migrate in the direction of the electric field while anions migrate in the opposite direction. This causes an excess of charge to build up in either direction of the electric field. Upon release of the electric field, the ions diffuse back into equilibrium; however, diffusion can be delayed by blockages and electrostatic interactions at narrow pore throats. Although Titov et al. (2002) used time-domain (direct current) induced polarization techniques, they found membrane polarization in sands to be highest at time periods equivalent to 10 to 25 mHz if an alternating current were used. Membrane polarization is generally much less than Stern layer polarization except at very high fluid salinities (Revil, 2012).

Maxwell-Wagner polarization occurs as a result of different phases within a medium having greatly differing dielectric permittivities and electrical conductivities, such as occurs between the solids and liquids within an aquifer. In an electric field, charges accumulate at the mineral interfaces (but outside the electric double layer) (Chen and Or, 2006). The relaxation time scales for this phenomenon are much shorter than for Stern layer polarization; it is generally observed between 100 Hz and 100 MHz. Like the other forms of polarization described here, Maxwell-Wagner polarization increases with increasing salinity (Chen and Or, 2006). The magnitude of Maxwell-Wagner polarization, though, is much greater than the magnitudes of the other two polarization mechanisms (Figure 1.4).
Figure 1.4. Quadrature conductivity spectra for clean sand and 10% smectite saturated with artificial groundwater. Maxwell-Wagner polarization for clean sand is evident at frequencies above 100 Hz with Stern layer polarization imperceptible at this scale. The Stern layer and Maxwell-Wagner polarizations overlap between 100 Hz and 1 kHz for the 10% smectite sample.

1.3.4. Potential Effects of ISCO on Complex Conductivity

The most dramatic changes to conductivity caused by ISCO result from changes in the pore fluid conductivity. On its own, injection of a highly saline solution such as concentrated potassium or sodium permanganate would increase the conductivity of the fluid. Additionally, though, redox reactions between permanganate and both target contaminants and natural organic matter cause subsequent changes to the pore fluid conductivity. Equations 1.5 and 1.10 show that ions can be both depleted and formed through oxidation of TCE and humate by permanganate. During both TCE and humate oxidation, MnO$_4^-$ ions are lost from the pore fluid as they are transformed into a solid (MnO$_2$) that falls out of solution. On the other hand, TCE oxidation leads to the formation of Cl$^-$ and H$^+$ ions, which may potentially contribute to increased conductivity. However, protons in the pore fluid may be removed through reaction with carbonate and/or bicarbonate and through protonation of mineral surface groups as described in Section 1.3.2. Also, while not an ion itself, CO$_2$ produced through TCE and humate
oxidation may transform to bicarbonate at neutral to slightly alkaline pH values commonly found in groundwater.

Geochemical modeling software such as PHREEQC (Parkhurst and Appelo, 2013) can be used to predict conductivities based on ions already in the groundwater and those ions produced and removed through the oxidation reactions. A thorough discussion of how fluid conductivity is calculated from ion concentrations is presented in Section 2.2.2. PHREEQC may be especially useful to account for carbonate cycle reactions and calculating post-reaction bicarbonate and H⁺ concentrations. Table 1.1 shows the change in conductivity expected in aqueous samples from 10 mM KMnO₄ reacting with 5 mM TCE both alone and within an artificial groundwater containing 2 mM HCO₃⁻ (a full artificial groundwater description is in Section 3.3.1). In aqueous samples, protonation of aquifer formation minerals would not be an issue, although adsorption onto MnO₂ produced from reduction of MnO₄⁻ may affect fluid conductivity. For porous media samples, PHREEQC has a surface complexation model that may be useful for predicting removal of H⁺ through surface group protonation or ionic adsorption; however, this capability is not explored in this document. Instead, pH measurements are used to adjust modeling to account for actual sample pore fluid proton concentrations.

Table 1.1. Predicted conductivity of aqueous solutions of 10 mM KMnO₄ and 5 mM TCE in pure water and in artificial groundwater containing 2 mM HCO₃⁻.

<table>
<thead>
<tr>
<th></th>
<th>Fluid Conductivity (S/m, 22°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM KMnO₄ alone</td>
<td>0.118</td>
</tr>
<tr>
<td>10 mM KMnO₄ + 5 mM TCE</td>
<td>0.317</td>
</tr>
<tr>
<td>Artificial groundwater before KMnO₄ injection</td>
<td>0.046</td>
</tr>
<tr>
<td>10 mM KMnO₄ in artificial groundwater</td>
<td>0.161</td>
</tr>
<tr>
<td>10 mM KMnO₄ + 5 mM TCE in artificial groundwater</td>
<td>0.290</td>
</tr>
</tbody>
</table>
In addition to changes in pore fluid conductivity, oxidation of TCE or other natural materials in the subsurface could potentially change the total cation exchange capacity of the subsurface formation, impacting both surface conductivity and quadrature conductivity. For example, reduced pH could result in lowered cation exchange capacity of silica sands and kaolinite. Conversely, production of MnO$_2$ solids from MnO$_4^-$ reduction could potentially add to surface conductivity or quadrature conductivity. Also, changing the chemical composition of the aquifer pore fluid could change the density and mobility of ions adsorbed onto mineral surfaces, causing changes in quadrature conductivity.

1.4. Purpose of the Study

In this study, I investigate the utility of both traditional in-phase (real) and quadrature (imaginary) conductivity measurements for monitoring fate and transport of oxidant and for detecting reaction processes that occur during in situ chemical oxidation of TCE when permanganate is the chosen oxidant. I examine if electrical conductivity measurements can be used to monitor the concentration of permanganate at a given location within the aquifer and whether its movement can be ascertained. Furthermore, I determine whether these measurements can be used to detect reaction products or the degradation of TCE. The following research questions (Section 1.4.1) and hypotheses (Section 1.4.2) were used to guide this research.

1.4.1. Research Questions

Through this study, I sought to answer the following research questions.
1. Can changes in pore fluid conductivity be predicted accurately based on known equations describing reactions that occur during oxidation of TCE and natural organic matter (humate) by permanganate?

2. Can modeling of pore fluid conductivity changes during ISCO be scaled up to predict bulk conductivity in porous media samples?

3. Does formation of a precipitation product (MnO$_2$) during ISCO affect either in-phase or quadrature conductivity measurements?

4. Do changes in pore fluid chemistry from permanganate solution injection or from ISCO reactions affect quadrature conductivity measurements?

1.4.2. Hypotheses

To evaluate the research questions listed above, the following hypotheses (labeled H.1 through H.7) were investigated throughout this study. Hypotheses H.1 through H.3 apply to in-phase conductivity, while hypothesis H.4 through H.7 are related to quadrature conductivity.

H.1. Using known oxidation reaction equations, the in-phase conductivity of aqueous samples with or without added oxidant or oxidizable material can be predicted with reasonable accuracy.

H.2a. The presence of sand or clay will cause removal of protons produced during ISCO from the pore fluid, which will have a negative (lowering) effect on fluid conductivity in porous media samples when compared to aqueous samples.

H.2b. The change in pH from mineral protonation can be modeled.

H.2c. Accurate adjustments to predicted fluid conductivity can be made based on pH measurements.
H.3a. Fluid conductivity can be calculated from bulk conductivity based on measured pore fluid conductivity to bulk conductivity relationships.

H.3b. \( \text{MnO}_2 \) precipitation will cause measurable increases in both formation factor and surface conductivity, which will change the relationship of pore fluid conductivity to bulk conductivity for the aquifer formation.

H.4. Presence of TCE at dissolved concentrations will not cause a measurable change in quadrature conductivity.

H.5. \( \text{MnO}_2 \) precipitation can be detected through a measurable increase in quadrature conductivity.

H.6. Reduction in pH will cause a decrease in quadrature conductivity resulting from a reduction in pH-dependent cation exchange capacity.

H.7. Injection of potassium or sodium permanganate will cause higher quadrature conductivity as solution concentration increases.

1.5. **Significance of the Study**

While ISCO is an effective method for removing many organic contaminants from the subsurface, traditional methods for monitoring its progress are inadequate. It is extremely difficult to demonstrate where sufficient permanganate has migrated to achieve remediation goals using technologies that rely on physical sampling of contaminated media. This lack of knowledge of oxidant fate and transport often necessitates the use of excess amounts of permanganate solution and additional permanganate injection events to ensure sufficient oxidation, leading to inefficient use of resources and increases in remediation time. While other studies have demonstrated qualitatively that in-phase electrical conductivity measurements can
show the path of permanganate movement during ISCO, this study is the first to quantitatively model electrical conductivity changes in the subsurface as a result of specific changes in pore fluid chemistry that occur during ISCO. Furthermore, this study expands the scope of electrical conductivity use during ISCO to include quadrature conductivity measurements.

1.6. Limitations of the Study

Because complete oxidation of TCE is a relatively quick reaction in the presence of excess permanganate (reaction time on the order of hours), this study only examines the immediate effects of ISCO reactions on real and imaginary components of electrical conductivity. This study does not account for the long-term fate of such reaction products as MnO₂ or for interactions between mineral surfaces and either TCE or reaction products that occur on the order of multiple days to weeks or longer. Also, while this study looks at multiple porous media compositions, such as clean sand and mixes of clay and sand, by no means will the formation factor or surface conductivity of a particular formation of interest be immediately known. Furthermore, the experiments described here were only performed in homogeneous samples. Therefore, converting a bulk conductivity to pore fluid conductivity for a specific field location will require knowledge derived from site-specific studies and will undoubtedly result in larger errors than those observed in the controlled experiments presented here.

1.7. Organization of the Study

The remainder of this dissertation is organized into the following chapters. Chapter 2 discusses the effects of TCE oxidation by permanganate on bulk and pore fluid conductivity in simplified unbuffered saturated clean sand systems with a focus on the effects of silanol
protonation. The chapter was adapted from an article published in the *Journal of Contaminant Hydrology*. Chapter 3 is adapted from a manuscript that will be submitted to *Water Resources Research*. It discusses both bulk conductivity and quadrature conductivity in samples more representative of actual aquifers with carbonate-buffered artificial groundwater and porous media with sand-clay mixtures. Chapter 4 presents data from an up-scaled two-dimensional tank experiment and demonstrates the use of time-lapse bulk resistivity measurements. Beyond implementation of improved technologies, successful remediation often requires input from communities to fully address their needs. Therefore, Chapter 5 discusses how some communities have benefitted from the EPA’s Community Advisory Group (CAG) Program. This 20-year-old program enables citizens to monitor and have input into the progress of remediation of hazardous waste sites. Chapter 6 presents conclusions and recommendations based on data collected throughout this whole study.

All chapters in this dissertation present data collected, analyses performed, and conclusions developed primarily by myself, except for Chapter 4, which was a joint experiment performed with Dr. Deqiang Mao, a post-doctoral researcher in the Geophysics Department at Colorado School of Mines. In the experiment described in Chapter 4, I was responsible for packing and emptying the tanks, determining the composition of the tank materials, calculating predicted conductivities, and calculating concentrations of permanganate. Dr. Mao was predominantly responsible for collecting bulk resistivity as well as other geophysical data (time domain induced polarization and self-potential, not presented here) and creating the inversion model to recover the conductivity tomograms for each time period. The analysis and conclusions presented in Chapter 4 are predominantly my own.
CHAPTER 2. ANALYSIS OF SOURCES OF BULK CONDUCTIVITY CHANGE IN SATURATED SILICA SAND AFTER UNBUFFERED TCE OXIDATION BY PERMANGANATE

Modified from a paper published in *Journal of Contaminant Hydrology*¹

Ryan D. Hort²,³, André Revil⁴, and Junko Munakata-Marr⁵

**Abstract.** Time lapse resistivity surveys could potentially improve monitoring of permanganate-based in situ chemical oxidation (ISCO) of organic contaminants such as trichloroethene (TCE) by tracking changes in subsurface conductivity that result from injection of permanganate and oxidation of the contaminant. Bulk conductivity and pore fluid conductivity changes during unbuffered TCE oxidation using permanganate are examined through laboratory measurements and conductivity modeling using PHREEQC in fluid samples and porous media samples containing silica sand. In fluid samples, oxidation of one TCE molecule produces three chloride ions and one proton, resulting in an increase in fluid electrical conductivity despite the loss of two permanganate ions in the reaction. However, in saturated sand samples in which up to 8 mM TCE was oxidized, at least 94% of the fluid conductivity associated with the presence of

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protons was removed within three hours of sand contact, most likely through protonation of silanol groups found on the surface of the sand grains. Minor conductivity effects most likely associated with pH-dependent reductive dissolution of manganese dioxide were also observed but not accounted for in pore-fluid conductivity modeling. Unaccounted conductivity effects resulted in an under-calculation of post-reaction pore fluid conductivity of 2.1% to 5.5%. Although small increases in the porous media formation factor resulting from precipitation of manganese dioxide were detected (about 3%), these increases could not be confirmed to be statistically significant. Both injection of permanganate and oxidation of TCE cause increases in bulk conductivity that would be detectable through time-lapse resistivity surveys in field conditions.

2.1. Introduction

In situ chemical oxidation (ISCO) using permanganate ion (MnO$_4^-$) has become a common method for degrading organic contaminants such as trichloroethene (TCE) in aquifers (Petri et al., 2011; Schnarr et al., 1998; Thomson et al., 2007). As with any chemical remediation technique, ISCO requires physical contact between the injected media and the contaminant. Aquifer heterogeneity can often influence the subsurface movement of MnO$_4^-$ and other oxidants, making delivery unpredictable and leading to uneven contaminant removal (Smith et al., 2008). Furthermore, monitoring wells on site may be insufficient in number to adequately track oxidant movement (Halihan et al., 2012).

Electrical Resistivity Tomography (ERT) offers a possible non-intrusive solution for monitoring MnO$_4^-$ fate and transport with improved resolution over monitoring wells alone. This method uses an array of electrodes emplaced either at the ground surface or in boreholes to
collect resistivity measurements at multiple locations and depths over a period of time (see for instance Kowalsky et al., 2011; Revil et al., 2013). Most commonly, four electrodes are used at a given time, with two injecting a current and the other two measuring the difference in electrical potential. An inversion algorithm is then used to produce a model of the bulk resistivity (or conductivity) distribution below the electrodes or between the wells in the case of cross-hole resistivity tomography. Reviews of the methodologies used to perform ERT measurements and to invert these measurements can be found in Daily et al. (2004) and Revil et al. (2012).

Time-lapse ERT involves the use of different strategies to measure changes in electrical resistivity over time. One common technique is to repeat resistivity surveys multiple times and separately invert the different snapshots and map the conductivity changes among each snapshot. Alternately, using permanent electrode installations, resistivity can be monitored continuously over time with more measurements. Then, rather than inverting individual snapshots, newer inversion algorithms process the data as a whole, regularizing both over space and time (Karaoulis et al., 2011, 2013). This type of inversion can reduce noise and improve recovery of conductivity changes that are correlated with time. Time-lapse ERT has been used to monitor the movement of salt plumes and also to provide flow and transport information in heterogeneous aquifers (Jardani et al., 2013; Kemna et al., 2002, 2006; Vanderborght et al., 2005). Because permanganate-based ISCO involves injecting ions into the aquifer, time-lapse ERT could potentially be used to track the fate and transport of the injected oxidizing solution.

Although investigators have yet to use improved time-lapse inversion methods to monitor ISCO, a few researchers have used multiple ERT snapshots with independent inversions to locate changes in subsurface resistivity that could be attributed to MnO₄⁻ injection (Halihan et al., 2012; Harte et al., 2012; Nyquist et al., 1999). While each study was successful in demonstrating
changes in aquifer resistivity after MnO$_4^-$ injection, certain anomalies appeared that were not explained by the investigators. For instance, after injecting MnO$_4^-$ to oxidize TCE, Nyquist et al. (1999) were unable to explain why increased conductivity values were observed in certain locations where MnO$_4^-$ could not be detected in groundwater samples. Harte et al. (2012) also observed increased bulk conductivity in areas where MnO$_4^-$ could not be detected through groundwater sampling during tetrachloroethene (PCE) oxidation. Additionally, they noted the opposite response in certain locations where they expected MnO$_4^-$ to be located but where conductivity did not increase.

While these initial studies of ERT use during ISCO with MnO$_4^-$ demonstrated that significant conductivity changes can be observed, additional work is needed before such measurements can be used for more quantitative observations of MnO$_4^-$ and contaminant fate and transport. While increased electrode coverage, improved electrode placement, or newer inversion methods would improve the resolution of these measurements, this paper focuses on improving the understanding of subsurface conductivity changes that occur as a result of ISCO when MnO$_4^-$ is the oxidant. Specifically, this study examines the changes in bulk conductivity that occur in saturated sand from the addition of MnO$_4^-$, the reaction between MnO$_4^-$ and TCE, and protonation of the silica sand surface resulting from post-reaction acidity production.

2.2. **Theoretical Background**

At circumneutral pH values, the reaction between TCE and MnO$_4^-$ can be approximated using Equation 2.1 (Yan and Schwartz, 2000).

\[
C_2HCl_3 \text{ (TCE)} + 2 \text{MnO}_4^- \rightarrow 2 \text{MnO}_2(s) + 2 \text{CO}_2(g) + 3 \text{Cl}^- + \text{H}^+ \quad (2.1)
\]
Initially, one molecule of TCE is oxidized by one MnO$_4^-$ molecule to one of various carboxylic acids through a cyclic hypomanganate ester intermediate. The second order rate constant for the transformation of TCE to carboxylic acid is 0.65 to 0.68 M$^{-1}$s$^{-1}$ (Yan and Schwartz, 2000). The carboxylic acid is then oxidized by an additional MnO$_4^-$ to CO$_2$ with a second order rate constant ranging from 0.073 to 0.37 M$^{-1}$s$^{-1}$, depending on the specific carboxylic acid and pH (Yan and Schwartz, 2000). The rate of initial TCE degradation is independent of pH, while lower pH favors increased degradation rate of the carboxylic acids. Both reactions are first order with respect to each reactant, so the degradation can be generalized by Equations 2.2 and 2.3:

$$\frac{d[TCE]}{dt} = -k_{2,TCE}[TCE][MnO_4^-] \quad (2.2)$$

$$\frac{d[CA]}{dt} = -k_{2,CA}[CA][MnO_4^-] \quad (2.3)$$

where $k_{2,TCE}$ and $k_{2,CA}$ are the second order rate constants for TCE and carboxylic acid, respectively, $[TCE]$ is the concentration of TCE, and $[CA]$ is the concentration of carboxylic acid. Differences in the form of manganese produced by the reaction can result from environmental pH differences and incorporation of ions such as potassium into the precipitate. The manganese oxide formed during TCE oxidation with potassium permanganate has been observed to be K$_{0.854}$Mn$_{1.786}$O$_4$·1.55H$_2$O (Li and Schwartz, 2004). For simplicity, the formula MnO$_2$ and the term manganese dioxide will be used in this paper to describe the manganese oxide precipitate formed by MnO$_4^-$ reduction.

An aquifer formation’s pore fluid composition, porosity, and mineralogy all contribute to the measured bulk electrical conductivity ($\sigma_o$). A saturated aquifer has two sources of electrical conductivity: the pore fluid and mineral surfaces. The contribution of these two conductivity sources can be described in a simplified manner by a linear model in which pore fluid
conductivity, $\sigma_f$, and surface conductivity, $\sigma_s$, act in parallel (Revil and Florsch, 2010). This relationship can be written as

$$\sigma_o = \frac{1}{F} \sigma_f + \sigma_s,$$

(2.4)

where $F$ denotes the formation factor, a power law function of porosity according to Archie (1942). For pore fluids with low salinities ($< 1 \text{ mM}$), a non-linear relationship between bulk conductivity and pore fluid conductivity is observed, and this relationship is better described using a differential effective medium theory that considers a change in the tortuosity factors when the conductivity of the pore water decreases (Revil et al., 1998). However, salinity during ISCO is sufficiently high that the linear model described by Equation 2.4 is adequate to describe the pore fluid / bulk conductivity relationship.

The impact that surfaces have on conductivity depends on the composition of the aquifer materials. Silica sand, aluminosilicates, and clay minerals all develop negative surface charges when saturated with water (Duval et al., 2002; Jara et al., 2005; Kraepiel et al., 1999). Silica contains silanol (SiOH) surface groups that can protonate or deprotonate in the following manner (Duval et al., 2002).

$$\text{SiOH}_2^+ \leftrightarrow \text{SiOH} + \text{H}^+ \quad (\text{pK}_1 = -1.0)$$

(2.5)

$$\text{SiOH} \leftrightarrow \text{SiO}^- + \text{H}^+ \quad (\text{pK}_2 = 4.0)$$

(2.6)

At pH 7, approximately 18% of silanol groups are in the form of SiO$^-$ (Duval et al., 2002). Positively charged counterions adsorb onto the negatively-charged surfaces in a thin layer called the Stern layer and are also attracted less tightly further away from the mineral surface in the diffuse layer (Leroy et al., 2008; Revil, 2012). The surface conductivity is then the product of the apparent mobility ($\beta_s$) and volume ($Q_s$) of the counterions, with the apparent mobility
dependent on the intrinsic mobility of the counterion and the partitioning of counterions between
the Stern and diffuse layers (Revil and Florsch, 2010).

The number of negative charges found on silica sand is very low when compared to the
number of charge carriers found in the pore fluid; therefore silica sand provides very little
surface conductivity within aquifers compared to the conductivity of the pore fluid, especially
during ISCO (this is demonstrated below in Section 4.1). Many types of clay, on the other hand,
contribute a much more significant surface charge resulting from their larger surface area (Brady
et al., 1996). While surface conductivity may be negligible in systems containing only sand,
surface conductivity would need to be considered in aquifer systems with measurable clay
content.

Another potential source of surface conductivity specific to ISCO is the manganese
dioxide precipitate formed from the reduction of permanganate. A surface charge of $10^{-8}$ C/m$^2$
has been reported at pH 8 for the $\delta$ form of MnO$_2$ (Murray, 1974). However, the zero charge
point for MnO$_2$ created during the MnO$_4^-$-TCE reaction has been observed to be pH 3.7 (Li and
Schwartz, 2004). While there is potential for surface charge from MnO$_2$ precipitation, the
possibility should decrease greatly under unbuffered low-pH conditions.

While the contribution of surface conductivity to overall bulk conductivity depends on
mineralogy, fluid conductivity is a significant factor in all saturated porous media. Changes in
fluid conductivity during ISCO occur both as a result of MnO$_4^-$ injection and also from the
reduction and oxidation reactions that occur after injecting the oxidant. While addition of MnO$_4^-$
immediately increases pore fluid conductivity, exhaustion of MnO$_4^-$ does not necessarily cause
the pore fluid conductivity to return to baseline values. As seen in Equation 2.1, the oxidation of
one molecule of TCE leads to the production of four ions (three chloride ions and one proton) compared to the loss of two ions (permanganate).

The conductivity contribution of each ion within the pore fluid involved in the oxidation of TCE can be calculated using a series of relationships. At infinite dilution, the conductivity contribution attributed to a single charge carrier is described through the Nernst-Einstein equation,

\[ \Lambda_i^\circ = \frac{|z_i|^2F^2D_i}{RT} \]  

(2.7)

where \( \Lambda_i^\circ \) is the molar conductivity at infinite dilution in S m\(^2\) mol\(^{-1}\) [(S/m)/(mol/m\(^3\))], \( z_i \) is the valence of the charge carrier, \( F \) is the Faraday number, \( D_i \) is the diffusion coefficient for the ion, \( R \) is the gas constant, and \( T \) is the absolute temperature. \( D_i \) is related to the ionic mobility \( \mu_i \) through the Einstein relationship:

\[ D_i = \frac{\mu_iRT}{|z_i|F} \]  

(2.8)

Substituting Equation 2.8 for \( D_i \) in Equation 2.7 yields the following relationship.

\[ \Lambda_i^\circ = |z_i|F\mu_i \]  

(2.9)

Table 2.1 lists both the diffusion coefficient and mobility for selected common ions within water at 25°C. Mobility can be corrected for the temperature-dependent change in viscosity using the equation

\[ \mu'_i = \mu_i^{25^\circ} \frac{\eta_{25^\circ}}{\eta_T} \]  

(2.10)

where \( \mu'_i \) is the mobility at environmental temperature in °C, \( \mu_i^{25^\circ} \) is the mobility at 25°C, \( \eta_{25^\circ} \) is the dynamic viscosity of water at 25°C, and \( \eta_T \) is the viscosity at the environmental temperature in °C (Atkins and de Paula, 2002; Parkhurst and Appelo, 2013).
Table 2.1. Diffusion coefficient, $D_i$, and mobility, $\mu_i$, within water for selected ions at 25°C. Values for $D_i$ from Vanýsek (2012). $\mu_i$ calculated using $\mu_i = D_i|z|F / RT$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>$D_i \times 10^{-10}$ m$^2$s$^{-1}$</th>
<th>$\mu_i \times 10^{-6}$ m$^2$V$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2 Ca$^{2+}$</td>
<td>7.92</td>
<td>6.17</td>
</tr>
<tr>
<td>1/2 Mg$^{2+}$</td>
<td>7.06</td>
<td>5.50</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>13.3</td>
<td>5.19</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>19.6</td>
<td>7.62</td>
</tr>
<tr>
<td>K$^+$</td>
<td>19.6</td>
<td>7.62</td>
</tr>
<tr>
<td>H$^+$</td>
<td>93.1</td>
<td>36.2</td>
</tr>
<tr>
<td>1/2 CO$_3$$^{2-}$</td>
<td>9.23</td>
<td>7.18</td>
</tr>
<tr>
<td>1/2 SO$_4$$^{2-}$</td>
<td>9.59</td>
<td>7.47</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>20.3</td>
<td>8.63</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>11.9</td>
<td>5.03</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>19.0</td>
<td>8.08</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>52.7</td>
<td>22.4</td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>16.3</td>
<td>6.93</td>
</tr>
</tbody>
</table>

To determine the actual conductivity contribution from each ion ($\sigma_i$), the molar conductivity is multiplied by the molal concentration of the ion ($m$), corrected by an electrochemical activity coefficient ($\gamma_{EC}$).

$$\sigma_i = |z|F\mu_i \cdot m\gamma_{EC} \quad (2.11)$$

The electrochemical activity coefficient can be calculated using geochemical modeling software such as PHREEQC, Version 3, which uses a combination of Kohlrausch’s Law and the Debye-Hückel equation to determine $\gamma_{EC}$ (Parkhurst and Appelo, 2013). The Debye-Hückel activity coefficient, $\gamma$, is related to $\gamma_{EC}$ by the relationship $\log \gamma_{EC} = CF \cdot \log \gamma$, where CF is a correction factor approximately equal to $0.6/|z|^{0.5}$ for ionic strength, $I < 0.36|z|$ and $I^{0.5}/|z|$ for $I > 0.36|z|$ (Parkhurst and Appelo, 2013). The derivations for CF and $\gamma_{EC}$ are explained in more depth in http://www.hydrochemistry.eu/exmpls/sc.html (accessed January 21, 2014). The total
conductivity of the system is then the sum of the conductivity contributions from each ion. By applying these relationships to the oxidation of TCE by MnO$_4^-$, one can calculate the increase in fluid conductivity that should occur as a result of the redox reaction between MnO$_4^-$ and TCE (Table 2.2).

Table 2.2. Predicted conductivity resulting from TCE oxidation by MnO$_4^-$ in liquid samples calculated at 20°C using Equation 2.3 and PHREEQC, Version 3. TCE and non-aqueous phase components are treated as non-conductive.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Reactant Conductivity (µS/cm)</th>
<th>Product Conductivity (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 mM KMnO$_4$ + 2 mM TCE</td>
<td>4 mM K$^+$ + 6 mM Cl$^-$ + 2 mM H$^+$ + 4 mM CO$_2$(g) + 4 mM MnO$_2$(s)</td>
<td>457</td>
<td>1230</td>
</tr>
<tr>
<td>8 mM KMnO$_4$ + 4 mM TCE</td>
<td>8 mM K$^+$ + 12 mM Cl$^-$ + 4 mM H$^+$ + 8 mM CO$_2$(g) + 8 mM MnO$_2$(s)</td>
<td>899</td>
<td>2420</td>
</tr>
<tr>
<td>12 mM KMnO$_4$ + 6 mM TCE</td>
<td>12 mM K$^+$ + 18 mM Cl$^-$ + 6 mM H$^+$ + 12 mM CO$_2$(g) + 12 mM MnO$_2$(s)</td>
<td>1330</td>
<td>3590</td>
</tr>
<tr>
<td>16 mM KMnO$_4$ + 8 mM TCE</td>
<td>16 mM K$^+$ + 24 mM Cl$^-$ + 8 mM H$^+$ + 16 mM CO$_2$(g) + 16 mM MnO$_2$(s)</td>
<td>1760</td>
<td>4750</td>
</tr>
</tbody>
</table>

Manganese dioxide solids would not contribute to fluid conductivity; however, dissolved manganese could potentially add to fluid conductivity. The oxidation state of the manganese product can be affected by oxidation potential and pH. Elevated pH and oxidation potential energetically favor MnO$_2$, while reducing conditions and low pH favor reductive dissolution to Mn$^{2+}$. However, while reductive dissolution of MnO$_2$ to Mn$^{2+}$ may be energetically favorable at low pH, Li and Schwartz (2004) found that organic acids were needed to catalyze significant reductive MnO$_2$ dissolution. After 25 hours, all MnO$_2$ was dissolved at pH 2 with organic acids, but only about 1% of the MnO$_2$ had dissolved at pH 2 with a non-organic acid. Therefore, Mn$^{2+}$
production should not be a major contributor to conductivity within the timeframe of the experiments presented here.

In addition to the reduction and oxidation reactions that impact the pore fluid conductivity, acid dissociation/association reactions involving sand grains can potentially influence pore fluid conductivity, as well. As shown in Equation 2.1, oxidation of TCE has the potential to produce substantial acidity. ISCO involving TCE has resulted in groundwater pH as low as 3 (Stewart, 2002). While silica sand may provide negligible surface conductivity compared to pore fluid conductivity, SiO$^-$ surface groups provide a sink for protons produced during TCE oxidation. At a pH of 8 (a common pH for aquifers), approximately 20% of silanol groups are in the form of SiO$^-$, while at pH 3, this percentage drops to about 10% (Duval et al., 2002). Removal of protons from the pore fluid through association with silanol groups would cause a loss of conductivity that otherwise would result from proton production related to TCE oxidation.

2.3. Methods

This section details the materials and experimental methods used in the investigations described in this chapter.

2.3.1. Sand Preparation

Although most aquifers consist of mixes of sands and clays (in addition to silt and gravel), well-sorted clean sand was chosen as the solid material for porous media samples to investigate the effects of one major aquifer component. Unimin industrial quartz with a nominal #70 mesh size was sieved with a Tyler #80 sieve (0.175 mm openings). The sand was then
heated to a temperature of 550°C for three hours in order to remove organic matter and subsequently rinsed in a 2-liter glass bottle with deionized water until the rinsate was clear and had a conductivity of less than 3 µS/cm (8 to 10 rinses). The muffled and rinsed sand was heated to 105°C until completely dry (about 20 to 30 hours). After drying, the sand was sieved again with the same sieve (Tyler #80) to ensure consistent removal of fine-grained material among different batches of sand, rinsed an additional three times with deionized water, and redried at 105°C until completely dry. Sand preparation resulted in sand that was very well sorted with a $d_{10}$ grain size of approximately 0.175 mm, and a $d_{50}$ grain size of approximately 0.21 mm (#70 mesh size). The sand grains were predominantly angular. When packed, the sand had an estimated effective porosity of 0.42, measured by observing the displacement of water by a known volume of sand within a graduated cylinder. Multiple batches of prepared sand were placed in a large storage container and mixed in order to improve consistency between porous media samples.

### 2.3.2. TCE Oxidation Samples

$\text{KMnO}_4$ was mixed with unamended deionized water and deionized water saturated with TCE in polytetrafluoroethylene (PTFE) jars with screw-on PTFE lids to create aqueous ISCO samples. The samples were then allowed to react for two days (at least 40 hours) before any measurements occurred. TCE was added in concentrations of approximately 2 mM, 4 mM, 6 mM, and 8 mM. $\text{KMnO}_4$ was added in concentrations that would result in 2 mM $\text{MnO}_4^-$ remaining after reaction (6 mM, 10 mM, 14 mM, and 18 mM).

For safety reasons, TCE was added to the samples within a fume hood, and samples were maintained in the fume hood throughout the two days during which the reaction was allowed to
occur. Physical TCE losses (other than reaction with permanganate) were somewhat unpredictable because some TCE could potentially volatilize within the fume hood during addition to the sample, and some loss of TCE can also occur to the headspace within the sample container. Therefore, the difference between the residual and initial permanganate concentrations was used to calculate the concentration of TCE that had been present within the fluid, according to the stoichiometry presented in Equation 2.1. This calculation assumes that after two days of reaction, all TCE and carboxylic acids had been oxidized by permanganate. Residual permanganate concentration after reaction was measured by removing 5 ml of sample, centrifuging for five minutes at a force of 3000 times gravity to remove precipitate, and measuring absorbance of the aqueous fraction at 525 nm (similar to Standard Method 4,500-KMnO₄ (Eaton et al., 2005)).

Assuming second order rate constants of 0.65 M⁻¹s⁻¹ for TCE degradation to carboxylic acids and 0.2 M⁻¹s⁻¹ for degradation of carboxylic acids to CO₂, all TCE should be removed within three hours in samples that had 8 mM TCE added. Less than 0.05 mM carboxylic acid should remain after twenty-five hours in such samples. Both rate constants are in accordance with Yan and Schwartz (2000), with the carboxylic acid degradation rate constant being conservative given the low pH measured in the samples.

2.3.3. Bulk Conductivity Measurements

Bulk resistance of the porous media samples was measured at room temperature with an impedance spectrometer constructed by Forschungzentrum Jülich (Zimmermann et al., 2008) using a four-electrode approach separating the two current electrodes from the two voltage electrodes in order to avoid electrode polarization. A constant voltage of one volt was applied
across the samples at frequencies from 10 mHz to 45 kHz, moving from low frequency to high frequency. The bulk conductivity was determined by taking the reciprocal of the bulk resistance (bulk conductance) and dividing by the geometric factor, which is influenced by the sample holder geometry and electrode arrangement. An example plot of conductivity versus frequency shows that frequency dependence is negligible (Figure 2.1). The bulk conductivities observed at 1 Hz are reported in this study, as this frequency is representative of field measurements.

![Graph showing bulk conductivity versus frequency](image)

**Figure 2.1.** Bulk conductivity versus frequency for a saturated sand sample containing the reaction products of 7.5 mM KCl, 14 mM KMnO₄, and 6 mM TCE. Conductivity was measured three hours after creating the saturated sand sample. Error bars (the lines within the circles) represent the standard deviation of 3,000 measurements at each frequency.

Two porous media sample holders were used, consisting of 30-cm long glass columns (not counting valve threading) with an inner diameter of 3 cm (Figure 2.2). The columns had four in-line threaded glass ports for fittings capable of holding 6-mm or 0.25-inch diameter electrodes. The ports were 8 cm apart from the center-line of the ports to accommodate a Wenner electrode array (AMNB with A and B the current electrodes and M and N the voltage electrodes with the same spacing between the electrodes). Current was injected through the outer electrodes, and potential was measured between the inner two electrodes. Copper rods
were selected for the current injection (A and B) electrodes because they could extend across the entire diameter of the column, ensuring a straight electric field pathway. Furthermore, they are minimally reactive with permanganate (Cole-Parmer, 2013). Because an active current is maintained between the injection electrodes during measurement, non-polarizing electrodes (such as silver-silver chloride) are not necessary for current injection. The potential measurement electrodes (M and N) consisted of non-polarizing silver-silver chloride electrodes encased in glass containing 3 M NaCl with a porous Vicor frit. Non-polarizing electrodes were selected for potential measurement so that induced polarization data could also be collected at the same time as traditional resistivity data. As expected based on the theoretical discussion presented in Section 2, minimal induced polarization effect was observed from the sand, and no additional effect was observed from manganese dioxide production, so induced polarization data will not be presented in this paper. The potential electrodes did not extend into the main column zone; they were in contact with the sample but not directly in line with the injected electric field to further minimize electrode polarization. The sample holders had geometric factors of 7.13 mm and 7.49 mm respectively, determined through calibration using KCl solutions of varying conductivity.

Saturated sand samples for bulk conductivity measurements were created by wet-packing, such that fluid was added first and then sand added to the fluid. The fluid in the saturated sand samples consisted of the fluids described in Section 3.2 in which TCE had been allowed to oxidize for two days or control fluids with no TCE added. While adding the sand to the liquid, the sample holder was periodically vibrated with a vortex mixer to encourage compaction of sand grains and maintain mixing of the fluid during packing. As the sand was already well sorted (essentially one size), sorting of sand by grain size due to vibration was not
an issue. All saturated sand samples were static samples (no flow) kept in an upright position to maintain packing.

Figure 2.2. Sample holder for saturated sand bulk conductivity measurements. Current electrodes A and B are copper rods, while potential measurement electrodes M and N (shown in the inset) are non-polarizing silver-silver chloride electrodes.

To account for slight differences in sample temperature between the initial fluid sample conductivity measurement and the saturated sand bulk conductivity measurement, fluid sample conductivity was measured at three different temperatures prior to packing to develop a conductivity-temperature curve so that bulk conductivity and fluid conductivity could be compared at the same temperature. Immediately before measuring bulk conductivity with the impedance spectrometer, temperature was measured within the porous media sample by inserting a temperature probe through a valve at the end of the sample holder. All bulk conductivity measurements were taken at room temperature (21 ± 1°C).

Unless otherwise stated, bulk conductivity measurements were collected three hours after packing was completed. The results shown in Section 4.3 show that although pore fluid conductivity did not reach complete equilibrium within three hours in some samples, pore fluid conductivity changed 0.5% or less in the time period between two and three hours after combining fluid samples with sand.
2.3.4. Formation Factor and Surface Conductivity Calculation

Fluid samples described in Section 3.2 were split into six 100-ml subsamples. Varying concentrations of KCl from 0 to 1,000 mg/L were then added to the subsamples to achieve different fluid electrical conductivities. Saturated sand samples were created with each fluid subsample and measured for bulk electrical conductivity as described above in Section 3.3. Bulk conductivity measurements were then plotted on the y-axis against pore fluid conductivity on the x-axis. A linear curve fit was then plotted. Based on Equation 2.4, the inverse of the slope of the fitted curve is equal to the formation factor of the saturated sand sample, and the y-intercept is equal to the surface conductivity. Additional plots were also created with individual saturated sand samples with pore fluids of varying ionic strength achieved by addition of KCl, KMnO$_4$, and NaHCO$_3$. These additional samples did not have TCE added and were used as a control to determine how manganese dioxide formation affected formation factor and surface conductivity.

The standard deviations for the formation factors were determined by reversing the x and y axes (plotting bulk conductivity on the x-axis and pore fluid on the y-axis) and calculating the standard error of the slope. 95% confidence intervals were then calculated by multiplying the standard error by a factor determined using a standard t-table and the number of degrees of freedom (number of samples plotted minus one).

2.3.5. Adsorption Measurements

To measure adsorption effects over time, duplicate 500 ml liquid TCE oxidation samples were split into five 100-ml aliquots, which were added individually to PTFE jars. Sand was then added to each jar to the top of the liquid; the jar was tapped as sand was added to compact the sand as much as possible. Once sand was added, each sample was allowed to sit for 10 minutes,
30 minutes, 60 minutes, 120 minutes, or 180 minutes before the liquid was extracted from the sand with a vacuum pump. Pore fluid conductivity and pH were measured at 21°C.

In order to evaluate adsorption of non-H⁺ ions at a low pH, a similar time-series test was also conducted with sand samples saturated with fluid containing only KCl and KMnO₄. To provide a similar pH to the TCE oxidation samples without excess H⁺ coming from the pore fluid solution itself, the sand was rinsed with 0.1 M HCl for three hours and then rinsed 12 to 15 times with deionized water until the rinsate had a conductivity less than 5 μS/cm. The sand was then dried at 550°C prior to making saturated sand samples. Duplicate saturated sand samples containing 7.5 mM KCl + 10 mM KMnO₄ and 7.5 mM KCl + 20 mM KMnO₄ were allowed to sit for 3 minutes, 15 minutes, 45 minutes, 90 minutes, or 180 minutes. The electrical conductivity and pH of the vacuum-extracted pore fluid was then measured at 22°C.

2.3.6. Conductivity Modeling

PHREEQC Version 3.0.6 from the U.S. Geological Survey (Parkhurst and Appelo, 2013) was used as the basis for all non-measurement conductivity calculations. The phreeqc database provided with the program package was modified such that log_k (log of the equilibrium constant for the reduction of MnO₄⁻ to Mn²⁺), delta_h (standard enthalpy), and gamma coefficients (coefficients a° and b for determining ion-specific activity from the Debye-Hückel equation) for MnO₄⁻ were added from the WATEQ database (also provided with the program); and diffusion coefficient (D_w) for MnO₄⁻ was added using the value from Vanýsek (2012).

While this version of PHREEQC produces overall solution conductivity values, in order to break conductivity down into the individual ionic contributions, a spreadsheet was created reproducing the PHREEQC calculation for each ion. Dynamic viscosity values for diffusion coefficient
temperature corrections were calculated according to the equation given by Kestin et al. (1978). Total solution conductivity values calculated in the spreadsheet were within 0.05% of the values produced by the PHREEQC program itself.

2.4. Results

Results of the investigations described in Section 2.3 are presented in this section.

2.4.1. Baseline Formation Factor and Surface Charge Calculation

Figure 2.3 shows formation factor and surface charge calculations for saturated sand samples in which no TCE was added or oxidized. The pH for these samples was between 7.6 and 8.1, a typical range for groundwater. Based on the y-intercept of the fit curve, the surface conductivity was only approximately $6 \times 10^{-4}$ S/m. This shows that the surface conductivity of the sand is negligible. The formation factor was calculated to be $3.88 \pm 0.02$ (the margin of error represents the 95% confidence interval).

![Figure 2.3. Bulk conductivity as a function of pore fluid conductivity in saturated sand at different ionic strengths. Formation factor is reported plus or minus the 95% confidence interval.](image-url)
2.4.2. Manganese Dioxide Precipitation Effects

To determine if either formation factor or surface conductivity were affected by MnO₂ precipitation, bulk versus pore fluid conductivity curves were produced for saturated sand samples containing fluid in which KMnO₄ had oxidized TCE (Figure 2.4). Under the unbuffered test conditions, there was no indication that MnO₂ production added measureable surface conductivity. The regression line y-intercepts were essentially zero for both the 2 mM and 4 mM TCE plots (0.0000 S/m and 0.0001 S/m, respectively), indicating no detectable surface conductivity. The y-intercepts for the 6 mM and 8 mM TCE samples were both negative (-0.0019 S/m and -0.0048 S/m respectively). However, determining a surface conductivity from the y-intercept for these two (6 mM and 8 mM TCE) sample sets is problematic because the measurement points are too far from the graph’s origin compared to their distance from each other, magnifying errors in y-intercept calculation. Because negative surface conductivity cannot be physically explained, and because the y-intercepts for the 2 mM and 4 mM TCE concentration plots were essentially zero, the y-intercepts were set at zero for all four graphs when calculating formation factor.

The formation factors for each sample set are shown in Table 2.3. Slightly higher formation factors were observed in samples in which at least 8 mM MnO₄⁻ was reduced to MnO₂ (at least 4 mM TCE was oxidized). The measured increase in formation factor was 2.3% for the 4 mM and 8 mM TCE sample sets and 3.4% for the 6 mM TCE sample set. However, the formation factor was unchanged in the sample set in which only 4 mM MnO₄⁻ was reduced (2 mM TCE was oxidized). Based on standard deviations, the 4 mM and 6 mM TCE samples may have a significantly higher formation factor than the no-TCE samples, although they are not
significantly different from each other (Table 2.3). However, if 95% confidence intervals are used, then none of the sample sets are statistically different from each other.

![Graphs showing bulk conductivity versus pore fluid conductivity for different TCE concentrations oxidized by KMnO₄.](image)

**Figure 2.4.** Bulk conductivity versus pore fluid conductivity for saturated sand samples in which different TCE concentrations were oxidized by KMnO₄. Different pore fluid conductivities were produced by adding varying concentrations of KCl. Formation factor is reported plus or minus the 95% confidence interval.

### 2.4.3. Conductivity Loss Through Silica Protonation

While manganese dioxide precipitation could slightly change the bulk conductivity to pore fluid conductivity relationship, protonation of silanol groups would potentially change the conductivity of the pore fluid itself. Figure 2.5 shows the extent of pore fluid proton loss (in the
Table 2.3. Formation factors calculated for different concentrations of TCE oxidized by permanganate.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Formation Factor</th>
<th>Standard Deviation</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>No TCE, pH 7.6 - 8.1</td>
<td>3.88</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>6 mM KMnO$_4$ + 2 mM TCE</td>
<td>3.88</td>
<td>0.04</td>
<td>0.09</td>
</tr>
<tr>
<td>10 mM KMnO$_4$ + 4 mM TCE</td>
<td>3.97</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>14 mM KMnO$_4$ + 6 mM TCE</td>
<td>4.01</td>
<td>0.09</td>
<td>0.21</td>
</tr>
<tr>
<td>18 mM KMnO$_4$ + 8 mM TCE</td>
<td>3.97</td>
<td>0.12</td>
<td>0.30</td>
</tr>
</tbody>
</table>

form of pH increase) and conductivity decrease over three hours in saturated sand samples containing the reaction products of 2 mM to 8 mM TCE oxidized by MnO$_4^-$ . Within 10 minutes of contact with the sand, the pore fluid conductivity dropped dramatically, while at the same time the pH increased. Conductivity and pH remained relatively stable after about one hour in 2 mM and 4 mM TCE samples. In the more concentrated TCE samples (6 mM and 8 mM), some change continued to occur through three hours; however, the decrease in conductivity between 2-hour and 3-hour measurement points was only 0.4% to 0.5%, which accounted for 0.7% to 0.8% of the overall 3-hour conductivity decrease for these samples. In 2 mM TCE samples, 98.8% of the 3-hour change occurred in the first 10 minutes, while in 8 mM TCE samples, 93.1% of the 3-hour change occurred during the first 10 minutes. The observed conductivity loss corresponds well with the modeled loss of conductivity predicted using PHREEQC based on the pH increase, although PHREEQC appears to slightly under-predict the conductivity (Figure 2.5).

Although the initial pH of the acid-washed sand is unknown, the average pore fluid pH values in the two KCl + KMnO$_4$ samples were 3.48 and 3.64 respectively after three minutes of contact with the sand despite the fluid being circumneutral prior to adding the fluid to the sand (Figure 2.6). After three minutes, some re-protonation of the sand grain surface apparently
Figure 2.5. Measured pore fluid conductivity (diamonds) and pH (triangles) over three hours compared to PHREEQC-modeled conductivity. The pH trendline is a logarithmic fit of the non-time-zero pH data. The conductivity trendline reflects the conductivity modeled in PHREEQC based on the fitted pH. Error bars represent the standard deviation of two samples.

occurred as the fluid pH increased slightly over three hours (by 0.17 to 0.19). The measured conductivity tracks very well with the conductivity change predicted using PHREEQC based on the pH change, which suggests that no measurable adsorption of non-H\(^+\) ions from the pore fluid onto the sand occurred.

Table 2.4 estimates the conductivities associated with the presence of each of the ions within the TCE oxidation samples depicted in Figure 2.5 using electrochemical activities derived from PHREEQC. The reaction products used in the calculations were based on Equation 2.1, except for H\(^+\), which was determined from actual pH measurements. Nearly all of the
42

Figure 2.6. Measured pore fluid conductivity (diamonds) and pH (triangles) over three hours compared to PHREEQC-modeled conductivity for acid-washed sand saturated with a solution containing KCl and KMnO$_4$. The pH trendline is a logarithmic fit of the non-time-zero pH data. The conductivity trendline reflects the conductivity modeled in PHREEQC based on the fitted pH. Error bars represent the standard deviation of two samples.

Conductivity attributed to the production of H$^+$ from TCE oxidation was removed within three hours of sand contact. The average loss of H$^+$-associated conductivity was 98.7% in the 2 mM TCE samples, 97.1% in the 4 mM TCE samples, 94.7% in the 6 mM TCE samples, and 94.3% in 8 mM TCE samples.

2.5. Discussion

This section explains the significance of the results described in Section 2.4.

2.5.1. Contributions of Processes to Conductivity Change

The overall effects of MnO$_4^-$ addition, reaction with TCE, and loss of fluid H$^+$ to silanol protonation are summarized in Figure 2.7. The addition of MnO$_4^-$ causes a measurable increase in both pore fluid and bulk conductivity with the pore fluid to bulk conductivity ratio being the same as the background ratio. The reaction between MnO$_4^-$ and TCE releases additional ions
**Table 2.4.** Fluid conductivity ($\sigma_f$) broken down by individual ionic contribution. Each set is an average of two samples.

### 6 mM KMnO$_4$ + 1.97 mM TCE + 7.5 mM KCl

#### Before Contact With Sand:

<table>
<thead>
<tr>
<th>Ion</th>
<th>mol/L</th>
<th>$Y_{EC}$</th>
<th>°C</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.0134</td>
<td>0.927</td>
<td>21.0</td>
<td>0.0864</td>
<td></td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.0135</td>
<td>0.927</td>
<td>21.0</td>
<td>0.0837</td>
<td></td>
</tr>
<tr>
<td>MnO$_4^-$</td>
<td>0.0021</td>
<td>0.925</td>
<td>21.0</td>
<td>0.0106</td>
<td></td>
</tr>
<tr>
<td>H$^+$</td>
<td><strong>0.0024</strong></td>
<td>0.938</td>
<td>21.0</td>
<td><strong>0.0710</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>0.2517</strong></td>
<td><strong>0.2600</strong></td>
</tr>
</tbody>
</table>

Modeled Conductivity Loss from pH Change: 0.0697 S/m  
Measured Conductivity Loss from pH Change: 0.0747 S/m

### 3 Hours After Contact With Sand:

<table>
<thead>
<tr>
<th>Ion</th>
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<th>$Y_{EC}$</th>
<th>°C</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.0134</td>
<td>0.931</td>
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<td>0.0866</td>
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<tr>
<td>K$^+$</td>
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<tr>
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<td><strong>Total:</strong></td>
<td></td>
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<td></td>
<td><strong>0.1820</strong></td>
<td><strong>0.1853</strong></td>
</tr>
</tbody>
</table>

### 10 mM KMnO$_4$ + 4.09 mM TCE + 7.5 mM KCl

#### Before Contact With Sand:

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<td>K$^+$</td>
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<td><strong>Total:</strong></td>
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<td></td>
<td></td>
<td><strong>0.3753</strong></td>
<td><strong>0.3932</strong></td>
</tr>
</tbody>
</table>

Modeled Conductivity Loss from pH Change: 0.1283 S/m  
Measured Conductivity Loss from pH Change: 0.1368 S/m

### 3 Hours After Contact With Sand:

<table>
<thead>
<tr>
<th>Ion</th>
<th>mol/L</th>
<th>$Y_{EC}$</th>
<th>°C</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
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<tbody>
<tr>
<td>Cl$^-$</td>
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<tr>
<td>K$^+$</td>
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<td></td>
<td></td>
<td><strong>0.2471</strong></td>
<td><strong>0.2564</strong></td>
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</table>

Modeled Conductivity Loss from pH Change: 0.1283 S/m  
Measured Conductivity Loss from pH Change: 0.1368 S/m
Table 2.4 (cont). Fluid conductivity ($\sigma_f$) broken down by individual ionic contribution for the samples depicted in Figure 2.5.

### 14 mM KMnO$_4$ + 6 mM TCE + 7.5 mM KCl

**Before Contact With Sand:**

<table>
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<th>$\ ^\circ C$</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
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<td>0.908</td>
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<td>H$^+$</td>
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<td>0.925</td>
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<td>Total:</td>
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<td></td>
<td><strong>0.4740</strong></td>
<td><strong>0.5329</strong></td>
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Modeled Conductivity Loss from pH Change: 0.1615 S/m  
Measured Conductivity Loss from pH Change: 0.2033 S/m

### 3 Hours After Contact With Sand:

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<th>Ion</th>
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<th>$Y_{EC}$</th>
<th>$\ ^\circ C$</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
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<td>0.911</td>
<td>21.0</td>
<td>0.1628</td>
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<tr>
<td>K$^+$</td>
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<td><strong>0.3296</strong></td>
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</table>

### 18 mM KMnO$_4$ + 8.02 mM TCE + 7.5 mM KCl

**Before Contact With Sand:**

<table>
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<th>Ion</th>
<th>mol/L</th>
<th>$Y_{EC}$</th>
<th>$\ ^\circ C$</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
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<tbody>
<tr>
<td>Cl$^-$</td>
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<td>K$^+$</td>
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<td>H$^+$</td>
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<td><strong>0.5758</strong></td>
<td><strong>0.6235</strong></td>
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</table>

Modeled Conductivity Loss from pH Change: 0.2007 S/m  
Measured Conductivity Loss from pH Change: 0.2390 S/m

### 3 Hours After Contact With Sand:

<table>
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<tr>
<th>Ion</th>
<th>mol/L</th>
<th>$Y_{EC}$</th>
<th>$\ ^\circ C$</th>
<th>Modeled $\sigma_f$ (S/m)</th>
<th>Measured $\sigma_f$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>0.0316</td>
<td>0.9054</td>
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<tr>
<td>K$^+$</td>
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<td></td>
<td><strong>0.3752</strong></td>
<td><strong>0.3845</strong></td>
</tr>
</tbody>
</table>

Modeled Conductivity Loss from pH Change: 0.00207 S/m  
Measured Conductivity Loss from pH Change: 0.002390 S/m
that increase the pore fluid conductivity despite loss of MnO$_4^-$; however protonation of silanol removes protons produced by TCE oxidation from the pore fluid. The precipitation of MnO$_2$, the product of MnO$_4^-$ reduction, may slightly increase the formation factor due to a small decrease in porosity. It is difficult to determine the significance of the formation factor differences among the sample sets, though, based on overlapping standard deviations and/or 95% confidence intervals. The observed increases in formation factor are illustrated in Figure 2.7 by the post-TCE reaction conductivity points being slightly below the line representing the non-TCE oxidation pore fluid to bulk conductivity curve for the porous media. For these sample sets, using the no-TCE curve to estimate the post reaction bulk conductivities would result in an over-prediction of 1.5% for the 2 mM TCE samples, 2.7% in the 4 mM TCE samples, 3.3% in the 6 mM TCE samples, and 4.6% in the 8 mM TCE samples.

In each of the samples, the measured conductivity was slightly higher than predicted in the modeling (Figure 2.8). A possible source of this error is reductive dissolution of MnO$_2$ to Mn$^{2+}$ caused by the low pH. Dissolved Mn$^{2+}$ would increase the conductivity of the fluid. Although Li and Schwartz (2004) reported that reductive dissolution of MnO$_2$ at pH 2 is limited without organic acids present (Li and Schwartz, 2004), that study examined MnO$_2$ concentrations of approximately 1.2 mM, while the approximate concentrations produced from the reduction of MnO$_4^-$ in the samples in this study are 4 mM, 8 mM, 12 mM, and 16 mM for TCE oxidation concentrations of 2 mM, 4 mM, 6 mM, and 8 mM, respectively. The difference between predicted and actual conductivity increased as the concentration of oxidized TCE increased, which is consistent with a greater mass of MnO$_2$ dissolved at lower pH and/or greater MnO$_2$ concentration. Also, within sample sets of equal TCE concentration, the difference between predicted and measured conductivity was greater before adsorption when the pH was
lower than it was after adsorption. Additionally, simplification of the MnO$_4^-$ / TCE reaction products assumed in the modeling may be a source of error. Despite not accounting for dissolution and the overall generalization of the reaction, the measured post-adsorption fluid conductivities are still within 2.1% to 5.5% of the modeled fluid conductivities in the saturated sand samples.

**Figure 2.7.** Effect of MnO$_4^-$ addition, TCE oxidation, and H$^+$ adsorption on observed bulk and pore fluid conductivity. Bulk and pore fluid conductivity was measured in saturated sand samples with pore fluid containing 7.5 mM KCl (circles), 7.5 mM KCl + KMnO$_4$ (triangles), and 7.5 mM KCl + KMnO$_4$ + TCE (diamonds). Specific concentrations of KMnO$_4$ and TCE are stated above each graph. Squares depict what the bulk conductivity would be without silica protonation based on the actual fluid conductivity measured before adding sand to the samples. Error bars represent the standard deviation of two samples for KCl and KCl + KMnO$_4$ samples and three samples for TCE oxidation samples.
**Figure 2.8.** Measured versus modeled conductivity in fluid samples (circles) and in saturated sand samples (squares). The line represents a 1:1 relationship.

### 2.5.2. Potential Uses and Limitations

While this study provides a simplified model for predicting bulk conductivity as a function of TCE and MnO$_4^-$ concentration, in a field situation inverse modeling would be necessary to calculate the concentration of MnO$_4^-$ present and the amount of TCE that was oxidized from measured bulk conductivities. Of course, the inverse problem will not yield a unique solution if solely relying upon bulk conductivity measurements under the conditions presented in this study because MnO$_4^-$ and TCE oxidation products both contribute to the conductivity of the aquifer.

Under conditions in which the contaminant plume contains less TCE than presented here, however, it may be possible to use resistivity measurements to monitor the movement and breakdown of MnO$_4^-$ by natural oxidant demand. Site-specific study may be necessary to determine if the dominant contributors to oxidant demand produce ions as a result of degradation. The TCE concentrations used in this study (2 mM to 8 mM or 263 mg/L to 1,050 mg/L) represent the high end of dissolved TCE concentrations. These concentrations are most likely to be found in the vicinity of source zones, while much lower concentrations are often
found in older plumes or sections of plumes farther away from the source. Degradation of TCE concentrations of 0.1 mM (13 mg/L) or less would not likely contribute to electrical conductivity in a measureable manner, as addition of 0.3 mM Cl\textsuperscript{-} would result in no more than a 0.002 S/m (20 µS/cm) increase in fluid conductivity.

Even in locations with high TCE concentrations, time-lapse electrical conductivity measurements may be helpful for delineating zones of TCE degradation, especially if used in conjunction with other types of data such as traditional monitoring well data, MnO\textsubscript{4}\textsuperscript{-} injection concentrations, and/or oxidation-reduction potential or self-potential measurements to monitor the oxidation potential front. Increases in conductivity beyond what is expected from the presence of MnO\textsubscript{4}\textsuperscript{-} ion alone could indicate areas where substantial TCE degradation is occurring, while consistency between MnO\textsubscript{4}\textsuperscript{-} concentrations and conductivity measurements may indicate locations where only low concentrations of TCE or no TCE is present.

Although only degradation of TCE was presented in this study, the modeling can be extended to other contaminants of concern if the degradation products are known. For example, PCE oxidation would not produce protons, but it would produce four chloride ions instead of the three produced by TCE oxidation. By plugging the products into a table similar to Table 2.4, the change in pore fluid conductivity could be predicted. Additional measurements using site samples could be used to estimate the proton exchange capacity of the site materials in order to improve predictions of electrical conductivity loss through protonation.

Because of the relatively close agreement of the measured post-adsorption conductivities with the modeled conductivity values, it is inconclusive whether reductive dissolution of MnO\textsubscript{2} to Mn\textsuperscript{2+} would be a relevant contributor to conductivity change during ISCO at the field scale. Pre-adsorption conductivities would not be detected in a field situation because of the rapid rate
at which silanol protonation occurs. The pH values found in the unbuffered samples presented in this study represent the lowest possible pH that would be expected to occur when dissolved TCE is encountered. Higher pH values could reduce the likelihood of significant MnO$_2$ dissolution in the short term. It is possible, though, that more MnO$_2$ could dissolve given periods of time longer than the two days that fluid samples were allowed to incubate in this study. Further study of long-term MnO$_2$ dissolution behavior may be warranted.

This study used a simplified porous media setup that simulated the sand and pore water found in an aquifer. Additional study is needed to determine how conductivity would change during ISCO in the presence of clays. One potential impact of clays is that they would change the slope and y-intercept of the pore fluid versus bulk conductivity curve due to the inherent porosity differences and surface conductivity of clays. The pore fluid versus bulk conductivity curve may be estimated for specific aquifer locations, though, by taking representative aquifer formation samples and obtaining preliminary bulk conductivity measurements. Secondly, the higher cation exchange capacity could also increase the rate and magnitude of proton loss from the pore fluid. However, even with just sand, the degree of protonation observed in the samples in this study was enough to remove at least 94% of the conductivity attributed to the presence of H$^+$ within three hours when the concentration of TCE being oxidized was below the solubility limit. The presence of clays would likely increase removal to nearly 100%. Testing of site-specific samples could be used to improve predictions of proton exchange capacity. Other less predictable changes may occur in the presence of clays, though, such as dissolution of clay minerals and alteration of adsorption characteristics at low pH.

Pure-phase (NAPL) TCE source zones may also cause conductivity behavior that is less predictable than what has been presented here. Reaction with pure-phase TCE may produce
enough MnO₂ precipitate to significantly change the aquifer’s porosity and formation factor. On the other hand, the extremely low pH in source zones could cause significant dissolution of MnO₂, affecting both formation factor and Mn²⁺ concentration. Because TCE is non-conductive, a NAPL TCE layer could also cause a zone of resistivity different from the surrounding aquifer.

Finally, other environmental factors may also impact conductivity measurements in different ways. Aquifer buffering from carbonates would both act as a further sink for produced H⁺ and also be an additional source of conductivity loss as the valence of the carbonate would reduce as it accepted protons. Oxidation of reduced metals may remove conductivity from the pore fluid; however, decreases in pH could increase dissolution and have the opposite effect on conductivity. Additional study is also needed to determine how oxidation of naturally occurring organic materials would influence electrical conductivity measurements.

2.6. Conclusion

Multiple processes can influence bulk conductivity measurements during in situ chemical oxidation of TCE using MnO₄⁻. This research examines how ion addition through MnO₄⁻ injection, ion production through TCE oxidation, porosity change from precipitate production, and loss of produced H⁺ through protonation of silanol all cause changes in conductivity. By accounting for these processes, it was possible to predict within a reasonable margin of error the bulk conductivity measurement that corresponded with a specific concentration of MnO₄⁻ and oxidized TCE in clean sand samples.

More study is needed to show how TCE oxidation by MnO₄⁻ would affect bulk conductivity under a wider range of conditions than demonstrated in this study, such as in the presence of clays, metals, and natural organic matter. However, this study demonstrates the
potential utility of time-lapse ERT for assisting in the monitoring of permanganate injections and TCE degradation during permanganate-based ISCO.

Acknowledgements

We thank the NSF IGERT Program for partial funding of this research through a fellowship to R.D. Hort from the Colorado School of Mines SmartGeo Program (Project IGERT: Intelligent Geosystems; DGE-0801692).
CHAPTER 3. EFFECTS OF CHEMICAL OXIDATION OF TCE USING PERMANGANATE ON IN-PHASE AND QUADRATURE ELECTRICAL CONDUCTIVITY

A paper to be submitted to Water Resources Research

Ryan D. Hort\textsuperscript{1,2}, André Revil\textsuperscript{3}, and Junko Munakata-Marr\textsuperscript{4}

Abstract. Because permanganate ($\text{MnO}_4^-$) is an ion, electrical resistivity measurements can be used to remotely monitor in situ chemical oxidation of contaminants such as trichloroethene (TCE). We have investigated the change of both in-phase and quadrature electrical conductivity as a result of trichloroethene (TCE) and humate oxidation by $\text{MnO}_4^-$ in artificial groundwater. These investigations were performed in aqueous solutions and in saturated porous media with clean sand, sand with 10\% kaolinite (v/v), and sand with 10\% smectite (v/v). In-phase conductivity was modeled in aqueous samples in which TCE or humate was oxidized by $\text{MnO}_4^-$ using PHREEQC and reaction stoichiometry and then compared to experimental results. Experimental in-phase conductivity values were within 4.0\% of predicted values for TCE oxidation samples and within 3.6\% of predicted values for humate oxidation samples. Buffering capacity of the porous media had a significant impact on pH, which in turn affects porous media

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\textsuperscript{2}Primary researcher and author, corresponding author
\textsuperscript{3}Associate Professor, Department of Geophysics, Colorado School of Mines; ISTerre, Université de Savoie
\textsuperscript{4}Associate Professor, Department of Civil \& Environmental Engineering, Colorado School of Mines
conductivity. Quadrature conductivity was unaffected by production of MnO₂. Changes in pH from TCE oxidation influenced quadrature conductivity in clean sand and 10% kaolinite but not in 10% smectite samples. Quadrature conductivity change as a result of addition of Na⁺ or K⁺ was dependent on cation for all porous media types. Therefore, the choice of NaMnO₄ or KMnO₄ as the oxidant would influence quadrature conductivity. Changes to in-phase conductivity could be modeled with sufficient accuracy to be useful for monitoring permanganate movement and reduction during in situ chemical oxidation (ISCO) of TCE. The utility of quadrature conductivity measurements may be limited, though, because of a lack of changes specific to TCE oxidation or MnO₄⁻ reduction under a wide variety of conditions.

3.1. Introduction

In situ chemical oxidation (ISCO) using permanganate has been demonstrated as an effective means of mineralizing many organic contaminants such as trichloroethene (TCE). During ISCO, the oxidant is injected as a solution into the groundwater where it oxidizes the contaminant, leaving harmless reaction products. However, the efficacy of the process is dependent on contact between the oxidant and contaminant. It follows that the efficient use of chemicals during ISCO requires monitoring of the oxidant to ensure it is delivered where needed.

Traditional monitoring of contaminant and oxidant concentrations using monitoring wells can provide accurate concentration data, but only at the point of well installation. Monitoring wells are often costly and cannot be installed with sufficient density to fully characterize oxidant movement, especially in heterogeneous aquifer formations. Uncharacterized preferential flow paths and density effects can lead to oxidants and contaminants bypassing monitoring wells.
Furthermore, monitoring wells are invasive and may themselves influence oxidant or contaminant flow.

The ionic nature of permanganate makes time-lapse electrical resistivity tomography a potentially useful method for monitoring its movement in heterogeneous aquifers. Electrical resistivity has previously been used to monitor saline solution movement during tracer tests, producing much more spatially extensive data than achievable through monitoring well data alone (Cassiani et al., 2006; Singha and Gorelick, 2005). Furthermore, the combination of multiple-channel field resistivity equipment, parallel processing, and more efficient data inversion algorithms now allow resistivity data to be collected and processed at a rate that is sufficiently fast for near-real-time data collection and processing.

While true time-lapse resistivity tomography has yet to be employed to monitor and adjust ISCO injections at hazardous waste sites, a few sites have used resistivity snapshots on a limited basis to assist in mapping permanganate distribution. At a remediation site for the contaminant RDX (cyclotrimethylenetrinitramine), Halihan et al. (2012) used resistivity measurements to evaluate the uniformity of a permanganate curtain emplaced between injection and extraction wells. They noted changes in electrical resistivity post-injection in more permeable sections of the aquifer but not in the less permeable zones, indicating preferential flow. Harte et al. (2012) also used resistivity measurements to document movement of permanganate through more permeable zones and lack of penetration through lower permeability zones after injection. Both studies were largely qualitative in nature, though, as the investigators did not report permanganate concentrations calculated from resistivity (or conductivity) values.

Quantification of permanganate concentrations from electrical resistivity change is confounded by the production of ions from the oxidation of both target and non-target materials.
However, reduction-oxidation reactions involving permanganate and various organic compounds have been well characterized throughout the literature (Damm et al., 2002; Huang et al., 2002; Rodríguez et al., 2007; Yan and Schwartz, 2000). Electrical conductivity can be calculated for solutions containing most ions found in significant quantities in groundwater using readily available geochemical modeling software such as PHREEQC (Parkhurst and Appelo, 2013).

Induced polarization is an extension of traditional direct current resistivity that allows measurement of the reversible storage of electrical charges in a porous material. Low-frequency (< 1 Khz) polarization phenomena are related to the polarization of the electrical double layer coating the surface of the mineral grains (e.g., Revil, 2012, 2013). These measurements are often expressed as a complex conductivity value. The real (in-phase) component characterizes the ability of the porous material to carry electrical charges through electromigration. The imaginary or quadrature (out-of-phase) component characterizes the polarization of the porous material. Time-lapse tomography using the quadrature conductivity component has been less researched than direct current or real conductivity as a means for monitoring remediation performance, especially during ISCO. Quadrature conductivity anomalies have been reported in the vicinity of various organic contaminant plumes associated with oil (Vanhala, 1997), benzene and ethylene dibromide (Sogade, 2006), and TCE/PCE (Cardarelli and Di Filippo, 2009). The specific mechanisms by which these anomalies formed, however, have not been well established. Also, changes over time as a result of engineered remediation processes have yet to be characterized.

In our previous work (Hort et al., 2014), we successfully modeled bulk electrical conductivity changes in simple saturated sand systems containing unbuffered pore fluid in which TCE was oxidized by permanganate. In the present paper, we advance our modeling to include
changes in bulk conductivity in porous media containing buffered artificial groundwater, kaolinite and smectite clays, and a natural organic material (humate). We also investigate the potential of quadrature conductivity for monitoring permanganate-based ISCO.

3.2. Theoretical Background

By applying an alternating current to a porous medium and measuring the voltage using a second set of electrodes, one can observe both the difference in magnitude between the injected current and measured voltage (the resistance) and the phase lag between the injected and measured waveforms. The two measurements can be expressed in terms of a complex conductivity value with a real, in-phase component ($\sigma'$) and an imaginary or quadrature, out-of-phase component ($\sigma''$). The absolute (or bulk) conductivity ($|\sigma|$), phase ($\phi$), $\sigma'$ and $\sigma''$ are related trigonometrically as follows:

\[
|\sigma| = \sqrt{\sigma'^2 + \sigma''^2},
\]

\[
tan \phi = \frac{\sigma''}{\sigma'}.
\]

Because phases observed in natural geologic formations are very small ($< 100 \text{ mrad}$ in the absence of metallic conductors or semi-conductors), $|\sigma| \approx \sigma'$ and $\phi \approx \frac{\sigma''}{\sigma'}$.

In a porous material with insulating grains, the conduction of electrical current occurs both in the pore water phase and in the electrical double layer (Stern and diffuse layer) covering the surface of the grains. The in-phase conductivity can be obtained by (Revil et al., 2013)

\[
\sigma' = \frac{1}{F} \sigma_f + \sigma_s,
\]

where $\sigma_f$ (in S m$^{-1}$) denotes the conductivity of the pore water, $\sigma_s$ (in S m$^{-1}$) the surface conductivity in the electrical double layer, and $F$ the formation factor (dimensionless). The formation factor is related to the connected porosity ($\phi$) by Archie’s Law, $F = \phi^m$, where $m$ is
called the cementation or porosity exponent (Archie, 1942). In general, at moderate pore fluid salinities, the contribution of surface conductivity to the overall bulk conductivity of a saturated porous medium is small when compared to the contribution of the pore fluid. However, because surface conductivity is controlled by the cation exchange capacity of the clay minerals, significant surface conductivity has been measured in some smectite clay-rich soils (Friedman, 2005).

Both surface conductivity and quadrature conductivity are the result of charges that form on the surfaces of silica (Revil et al., 2014) and clay minerals such as kaolinite, illite, or smectite (Leroy and Revil, 2009). The negative surface charges of silica sands and kaolinite clays form in a similar manner through exposed hydroxyl surface groups (SiOH in silica, SiOH and AlOH in kaolinite). Both silanol (SiOH) and aluminol (AlOH) groups deprotonate with relatively low pK values, 4.0 for SiOH ↔ SiO\textsuperscript{-} + H\textsuperscript{+} (Duval et al., 2002) and 4.73 for AlOH ↔ AlO\textsuperscript{-} + H\textsuperscript{+} (Kaufhold et al., 2011). Based on data from Duval et al. (2002), the percentage of negatively-charged silanol groups (SiO\textsuperscript{-}) can be approximated for a given pH by \% SiO\textsuperscript{-} = 6.4033 \times e^{0.1352 pH}. Kaolinite clays have a larger density of negatively charged surface groups per pore volume than silica sands mainly because of their small size and tighter packing (Ma and Eggleton, 1999). Smectite clays also have pH-dependent negative charges from silanol groups on their mineral edges, but the negative charge of smectites is dominated by non-pH-dependent negative charges formed through permanent isomorphic substitution of Al\textsuperscript{3+} for Si\textsuperscript{4+} and Mg\textsuperscript{2+} or Fe\textsuperscript{2+} for Al\textsuperscript{3+} (Kraepiel et al., 1999). Unlike smectites, kaolinites do not derive any significant surface charge from isomorphic substitutions.

The fixed, negative charges on the mineral surface are counterbalanced by sorbed cations adjacent to the mineral surface in the Stern layer and more loosely attracted cations farther from
the surface in the diffuse layer. The number of positive charges that a mineral can store in the
Stern and diffuse layers is often referred to as the cation exchange capacity (CEC). CEC is on
the order of $9.5 \times 10^{-1}$ mol/kg for smectite (Kraepiel et al., 1999), $2.8 \times 10^{-2}$ mol/kg for
kaolinite (Ma and Eggleton, 1999), and $1.5 \times 6.2 \times 10^{-3}$ mol/kg for silica sand (Revil, 2012).

Because grains are touching in a consolidated porous material, the diffuse layers of
multiple grains overlap, allowing charges in the diffuse layer to move from grain to grain when
an electric field is introduced. For this reason, in-phase surface conductivity is associated with
counterions in the diffuse layer. However, the Stern layers of individual grains remain separate,
so counterions within the Stern layer move to one side of the grain when an electric field is
introduced, creating a dipole moment (Revil and Florsch, 2010). The delay in movement of this
dipole during an alternating electric field causes a phase lag or quadrature conductivity response.
The quadrature conductivity can be expressed as a function of the CEC by

$$\sigma'' = \frac{2}{3} \rho_g \beta_{(+)}^S f \text{CEC}, \quad (3.4)$$

where $\rho_g$ is the grain density (approximately 2650 kg/m$^3$), $\beta_{(+)}^S$ is the mobility of the counterions
in the Stern layer, and $f$ is the fraction of counterions in the Stern layer (Revil, 2012).

The mobility of a counterion within the Stern layer can be similar to or significantly less
than its mobility in the bulk fluid depending on the ion and also the adsorbing mineral. For
example, the mobility of sodium in the bulk fluid is approximately $5.2 \times 10^{-8}$ m$^2$s$^{-1}$V$^{-1}$. In the
Stern layer of silica sand the mobility is the same, whereas in the Stern layer of smectites, which
have a much higher density of surface charges, the mobility is approximately $1.5 \times 10^{-10}$ m$^2$s$^{-1}$V$^{-1}$
(Revil, 2013). Ions with higher charge density such as copper, zinc, and lead, which adsorb
more strongly to mineral surfaces, also display significantly reduced mobility within the Stern
layer (Vaudelet et al., 2011a, 2011b). Solvation of the counterion may also impact how strongly
it binds to the mineral surface. For example, kosmotropes such as sodium are strongly hydrated (Kiriukhin and Collins, 2002) and maintain their hydrated state when bound to mineral surfaces such as silica (Persello, 2000). This may explain why sodium has the same mobility in the bulk water as in the Stern layer of silica grains. However, weakly hydrated chaotropes such as potassium are more likely to shed their water molecules (Kiriukhin and Collins, 2002) and form stronger polar bonds with mineral surfaces (Persello, 2000). It follows then that a chaotrope such as potassium may have a lower mobility in the Stern layer than in the bulk fluid in contrast to kosmotropes such as sodium.

Anything that changes the pore fluid conductivity or the mineral surface properties could potentially change the complex conductivity within the subsurface. During ISCO, the most dramatic change would be to the conductivity of the pore fluid. Injection of highly saline potassium or sodium permanganate solution increases the pore fluid conductivity. Subsequent redox reactions between the permanganate and target substances (chemical contaminants), as well as non-target substances like natural organic matter, further impact the pore fluid conductivity through depletion of permanganate and production of other ions.

The oxidation of TCE by MnO$_4^-$ can be described as a two-step process with TCE first being oxidized to a carboxylic acid and then to CO$_2$. The carboxylic acid intermediate formed is dependent on pH, with acidic pH favoring formic acid and neutral to slightly basic pH favoring oxalic acid (Yan and Schwartz, 2000). The specific carboxylic acid intermediate has no effect on the stoichiometry of the overall mineralization reaction, which can be expressed as

$$C_2HCl_3 \text{ (TCE)} + 2 \text{ MnO}_4^- \rightarrow 2 \text{ MnO}_{2(s)} + 2 \text{ CO}_2(\text{g}) + 3 \text{ Cl}^- + \text{ H}^+. \quad (3.5)$$

TCE oxidation occurs quickly. The second-order rate constant for the transformation of TCE to carboxylic acid is 0.65 to 0.68 M$^{-1}$s$^{-1}$ and is consistent over a wide pH range; the rate
constant for carboxylic acid to CO$_2$ ranges from 0.073 to 0.37 M$^{-1}$s$^{-1}$ and is dependent on pH and the specific carboxylic acid (Yan and Schwartz, 2000). Given these rate constants, a degradation curve can be calculated for 8 mM TCE being oxidized by 20 mM KMnO$_4$ (Figure 3.1). In this example, the lowest rate constants for each step were assumed. Even with this conservative assumption, TCE at a concentration near the solubility limit is oxidized to the carboxylic acid within 15 minutes and mineralized to CO$_2$ within 4 hours in the presence of excess MnO$_4^{-}$.

![Figure 3.1. Oxidation of 8 mM TCE by 20 mM MnO$_4^-$ assuming oxalic acid as an intermediate at pH 8.](image)

From Equation 3.5, while TCE oxidation will lead to loss of conductivity from the consumption of MnO$_4^{-}$ ion, Cl$^-$ and H$^+$ ions are produced. Both ions would potentially contribute to increased conductivity. Conductivity increases from addition of H$^+$ are limited, though, by protonation of mineral surface groups (Hort et al., 2014) and by carbonate buffering. Additionally, loss of HCO$_3^-$ from reacting with H$^+$ will potentially reduce conductivity. Each of these impacts, though, can be accounted for by modeling the conductivity in PHREEQC. Table 3.1 shows the change in conductivity expected from addition of 10 mM KMnO$_4$ into an artificial
groundwater with 2 mM HCO$_3^-$ (full composition described in Section 3.3.1) and from contact of the MnO$_4^-$ with TCE. The simulation in Table 3.1 does not account for protonation of subsurface minerals, which can have a significant impact on conductivity, especially when high TCE concentrations are oxidized (Hort et al., 2014). Accounting for the protonation can be accomplished through pH measurements.

**Table 3.1.** Calculation of conductivity in a simulated groundwater after addition of 10 mM KMnO$_4$ and after contact of MnO$_4^-$ with 0.5 mM and 5 mM TCE.

<table>
<thead>
<tr>
<th></th>
<th>Fluid Conductivity (S/m, 22°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater Before KMnO$_4$ injection</td>
<td>0.046</td>
</tr>
<tr>
<td>After 10 mM KMnO$_4$ injection</td>
<td>0.161</td>
</tr>
<tr>
<td>After Contact Between MnO$_4^-$ and 0.5 mM TCE</td>
<td>0.164</td>
</tr>
<tr>
<td>After Contact Between MnO$_4^-$ and 5 mM TCE</td>
<td>0.290</td>
</tr>
</tbody>
</table>

The effects of natural organic matter oxidation on electrical conductivity can be modeled in a similar manner to TCE oxidation. Humate is commonly found in soils and can be used as a model natural organic substance in the subsurface. While the number of carbons in naturally occurring humic compounds can vary, humate is often modeled as C$_9$H$_8$O$_4^{2-}$. Because it is a carbohydrate, we can propose a two-step oxidation process to CO$_2$ with carboxylic acid as an intermediate (similar to TCE oxidation). For the purposes of modeling, we assume here a neutral to slightly basic pore water and that the carboxylic acid is oxalate (C$_2$O$_4^{2-}$). The two steps of humate oxidation can be modeled in terms of one humate molecule as follows:

$$C_9H_8O_4^{2-} + 12 MnO_4^- + 12 H^+ \rightarrow 9/2 C_2O_4^{2-} + 12 MnO_2 + 10 H_2O,$$  
$$9/2 C_2O_4^{2-} + 3 MnO_4^- + 12 H^+ \rightarrow 9 CO_2 + 3 MnO_2 + 6 H_2O. $$

The total reaction then yields:

$$C_9H_8O_4^{2-} + 15 MnO_4^- + 24 H^+ \rightarrow 9 CO_2 + 15 MnO_2 + 16 H_2O.$$
We show in Section 3.4.3 with experimental data that this modeling combined with the use of PHREEQC is sufficient for predicting conductivity change from humate oxidation.

In addition to changes in pore fluid conductivity, oxidation of TCE or other natural materials in the subsurface could potentially change the combined cation exchange capacity of the subsurface formation and therefore impact surface conductivity and quadrature conductivity. Because H\(^+\) is a product of TCE oxidation, resulting lowered pH could lower the cation exchange capacity of silica sands and kaolinite. Conversely, production of MnO\(_2\) solids from MnO\(_4^-\) reduction could potentially add to surface conductivity or quadrature conductivity. In a previous study under non-buffered conditions, MnO\(_2\) solids formed during TCE oxidation did not measurably contribute to surface conductivity in saturated sand samples; however, pH in those samples ranged from 3.4 to 4.6 (Hort et al., 2014).

3.3. Methods

This section details the materials and experimental methods used in the investigations described in this chapter.

3.3.1. Materials

Porous media samples were created with either clean sand or clean sand mixed with 10% smectite clay (bentonite, sodium form, Alfa Aesar) or 10% kaolinite clay (aluminum silicate, Alfa Aesar) by volume. The sand used in all experiments was Unimin #70 mesh size (nominal) industrial quartz. Sand was sieved with a Tyler #80 sieve (0.175 mm openings), muffled three hours at 550°C, and rinsed with deionized water as described by Hort et al. (2014). Smectite and kaolinite were also heated at 550°C in a muffle furnace for three hours to remove organic
materials, but were not sieved or rinsed. Batches of 10% smectite and 10% kaolinite were created by mixing prepared sand (sieved, muffled, and rinsed) with muffled smectite or kaolinite. Multiple batches of clay/sand mixture were combined in a large container to ensure consistent porous media content between samples.

In this chapter, the term artificial groundwater is used to describe a solution of deionized water containing 4 mM Na$^+$, 0.2 mM Ca$^{2+}$, 0.1 mM Mg$^{2+}$, 2.4 mM Cl$^-$, 2 mM HCO$_3^-$, and 0.1 mM SO$_4^{2-}$. Humate was added to samples in the form of humic acid sodium salt (Alfa Aesar). The manufacturer’s assay listed the contents of the humic acid sodium salt as 50% humic acid, 13% water, and 15.3% water-insoluble matter. No significant dissolution of sodium into solution was evident after adding the product to artificial groundwater. The conductivity of the artificial groundwater only increased by 1 to 2 x 10$^{-4}$ S/m after adding 600 mg/L humic acid sodium salt. For conductivity modeling purposes, 600 mg/L humic acid sodium salt was treated as 300 mg/L humate, and possible added sodium was ignored.

3.3.2. Conductivity Measurements

Bulk resistance and phase were measured in porous media samples using the SIP-Lab-2 impedance spectrometer from Radic Research. Electrode polarization was minimized by using four electrodes in a Wenner array with two outer current electrodes and two inner potential-measurement electrodes. Silver-silver chloride electrodes were used for the potential electrodes and positioned outside the current path to further minimize polarization. The electrodes and sample holder geometry are further described in Hort et al. (2014). A 3-volt alternating current was applied across the outer electrodes at frequencies from 10 mHz to 10 kHz, moving from high frequency to low frequency. Because bulk resistance and phase measurements took 17
minutes to complete, they were measured at room temperature rather than attempting to adjust the sample’s temperature prior to measurement. Change in sample temperature during measurement could increase phase errors by changing the resistance during sampling, especially at lower frequencies. Porous media sample temperature was measured to the nearest 0.1 °C prior to complex resistivity measurement by inserting a Thermoworks RT600C-N temperature probe through the upper valve of the sample holder (when vertically oriented).

Bulk conductivity was calculated by dividing the conductance (the reciprocal of the bulk resistance) by the geometric factor for the sample holder, which was calculated from a calibration curve using various KCl solutions of known conductivity. The quadrature conductivity was calculated at each frequency according to Equations 3.1 and 3.2. Quadrature conductivities at 1 Hz and 10 Hz are reported in this study, as these frequencies are representative of feasible time-scales for field induced polarization measurements. Bulk conductivity (at 1 Hz) is reported rather than real conductivity because they are essentially the same value (due to the small phase).

Conductivity was measured in fluid samples using a conductivity probe that had been calibrated against 23 KCl solutions ranging in conductivity from 0.0377 S/m to 0.6893 S/m determined using PHREEQC. The 95% confidence interval for the fluid conductivity measurements was ± 0.85%. Fluid from porous media samples was extracted using a vacuum pump after complex resistivity was measured. The conductivity of the extracted fluid was then measured at the same temperature as the complex resistivity measurement. Fluid-only samples were measured at 22°C. For time-lapse porous media measurements, it was not feasible to measure at 22°C. To account for temperature-related conductivity changes, a conductivity at 22°C was calculated from the measured conductivity using a temperature correction similar to
the one employed in PHREEQC: \( \sigma_T = \sigma_{22^\circ} \frac{\eta_{22^\circ}}{\eta_T} \), where \( \sigma_T \) is the conductivity at temperature \( T \), \( \sigma_{22^\circ} \) is the conductivity at 22°C, \( \eta_T \) is the viscosity of water at the \( T \), and \( \eta_{22^\circ} \) is the viscosity of water at 22°C.

### 3.3.3. Permanganate and TCE Concentration Measurements

Permanganate (MnO₄⁻) concentration was measured in TCE oxidation samples by removing 2 ml of sample, centrifuging for 8 minutes at a force of 3000 times gravity to remove precipitate, and measuring absorbance of the aqueous fraction at 525 nm, similar to Standard Method 4500-KMnO₄ (Eaton et al., 2005). The aqueous fraction was diluted with an appropriate volume of deionized water prior to measurement to achieve an absorbance between 0.2 and 1.0 (1/20 to 1/100 dilution). In aqueous humate oxidation samples, 0.4 or 0.2 ml of sample were removed and 1/50 or 1/100 dilutions were created.

The solubility limit of TCE at room temperature has been reported at concentrations ranging from 1,300 mg/L (Heron et al., 1998) to 1,420 mg/L (Knauss et al., 2000). For samples with a TCE concentration of less than 1 mM, the TCE concentration was determined by assuming a concentration of 1,360 mg/L for the saturated dissolved TCE added to the samples. TCE concentration in samples with 1 mM or greater TCE was calculated by measuring the residual permanganate concentration (as described in the paragraph above) after reaction completion and dividing the concentration of permanganate used in the reaction by two to determine the oxidized TCE concentration.
3.3.4. Conductivity Modeling

Conductivity predictions were calculated using PHREEQC, 3.0.6 from the U.S. Geological Survey (Parkhurst and Appelo, 2013), using the PHREEQC database provided with the software with slight modification as described below. Diffusion coefficients for permanganate and oxalate were added to the phreeqc database as listed in the CRC Handbook of Chemistry and Physics, 93rd Edition (Vanýsek, 2012). Coefficients \(a^*\) and \(b\) for determining ionic activity, \(\gamma\), by the equation \(\log \gamma = \left[(-Az_e^2\sqrt{\mu})/(1 + Ba_0\sqrt{\mu})\right] + b\mu\) (where \(A\) and \(B\) are constants at a given temperature and pressure, \(z_e\) is the number of equivalents of exchanger in the exchange species, and \(\mu\) is the ionic mobility) for MnO\(_4^-\) were transferred from the WATEQ database (also provided with the PHREEQC program). For oxalate, values of 4.5 and 0 were selected for \(a^*\) and \(b\), respectively.

3.3.5. Experimental Setup and Sample Preparation

All saturated porous media samples were wet-packed in column-shaped glass sample holders designed for complex resistivity measurement with valves on both ends (sample holders described in Hort et al., 2014). Aqueous samples (described in the following paragraphs) were added to the sample holder first and then clean sand, 10% smectite, or 10% kaolinite prepared as described in Section 3.3.1 was scooped into the sample holder. The sample holder was vibrated after each scoop to remove bubbles and assist compaction. The samples were created such that they were completely saturated, but with minimal standing water on top of the porous media. The saturated porous media samples were maintained and measured with the column oriented vertically. All samples were static samples except as described in Section 3.3.5.1.
3.3.5.1 Formation Factor and Surface Conductivity

Formation factor and surface conductivity were initially calculated for clean sand, 10% kaolinite, and 10% smectite. Individual saturated porous media samples were packed as described in the previous paragraph with artificial groundwater amended with various concentrations of sodium chloride, potassium chloride, or potassium permanganate to achieve different pore fluid conductivities. Samples were allowed to sit for two hours before measuring complex conductivity to allow ionic adsorption to cease. Conductivity change essentially ended 1.5 hours after packing in saturated clean sand samples with a pore fluid consisting of artificial groundwater with 10 mM KMnO₄ (data not shown). Because the smectite used in samples had a high concentration of ions (resulting in a fluid conductivity nearly 10 times as high as the background artificial groundwater conductivity in 10% smectite samples), the 10% smectite samples were flushed with the intended pore fluid at a rate of 1 ml/min for 15 minutes, 1.5 ml/min for an additional 15 minutes, and 2 ml/min for the remaining time until approximately 3 pore volumes (270 ml) had flowed through the sample. The fluid was pumped from the bottom of the sample holder, which was vertically oriented.

Saturated clean sand samples were also created using artificial groundwater in which TCE was oxidized by permanganate. Two days prior to creating saturated sand samples, two 410-ml aqueous artificial groundwater samples with TCE and excess KMnO₄ (approximately twice the TCE concentration plus 2 mM) were mixed in 420-ml polytetrafluorethylene (PTFE) jars with screw-on PTFE lids. Prior to packing the saturated sand samples, the two aqueous samples were combined, MnO₄⁻ concentration was measured spectrophotometrically, and the oxidized TCE concentration was calculated as described in Section 3.3. The combined aqueous sample was then split into eight 100-ml aliquots, and KCl was added to each in concentrations
ranging from 0 mg/L to 2,400 mg/L. A saturated sand sample was then created with each aliquot and measured for complex conductivity at room temperature after sitting 2 hours. After complex conductivity was measured, the pore fluid was vacuum-extracted and measured for conductivity and pH at the same temperature as the complex conductivity measurement. This process was completed for TCE concentrations of 2.1 mM, 4.0 mM, 5.8 mM, and 7.5 mM. Two sets of 5.8 mM TCE samples were collected for a total of 16 complex conductivity measurements at that concentration. All other TCE concentrations had 8 complex conductivity measurements.

For each data set (clean sand, 10% kaolinite, 10% smectite, and the 4 different oxidized TCE concentrations in clean sand), the bulk conductivity measurements were plotted against pore fluid conductivity. Based on Equation 3.3, the formation factor of the saturated sand sample and the surface conductivity were determined through a linear regression. The formation factor for clean sand and 10% smectite were calculated both with the combined NaCl and KCl data and also with just NaCl and just KCl added to see if the difference in cation affected the bulk conductivity to pore fluid conductivity relationship.

3.3.5.2 Complex Conductivity Change from Permanganate Injection and TCE Oxidation

Quadrature conductivity was examined in the individual non-TCE oxidation samples described in Section 3.5.1 to observe the effects of Na\(^+\), K\(^+\), and MnO\(_4\)\(^-\) addition and determine if injection of NaMnO\(_4\) or KMnO\(_4\) would impact quadrature conductivity differently. Additionally, aqueous and saturated porous media TCE oxidation samples containing simulated groundwater, 10 mM KMnO\(_4\), and TCE ranging in concentration from 1 µM to 3.2 mM were prepared to analyze the effects of increasing concentrations of TCE oxidized in artificial groundwater on fluid conductivity, bulk conductivity, and porous media pH. Individual samples were mixed in
100 ml volumetric flasks with glass stoppers in order to minimize the surface area in contact with air and therefore minimize volatilization of TCE. Samples with less than 1 mM TCE sat for one day prior to measurement, while samples with 1 mM or greater TCE sat for two days. Fluid conductivity and pH were measured prior to packing in the porous media sample holder with clean sand, 10% kaolinite, or 10% smectite. Saturated porous media samples were then allowed to sit for two hours before measuring complex conductivity. Saturated clean sand samples were produced in triplicate except for 3.1 mM TCE samples (duplicate).

Saturated kaolinite and smectite samples were produced in duplicate except for 100 µM and 1 mM TCE samples (triplicate). Unlike the 10% smectite formation factor samples, no additional fluid was pumped through these smectite samples because the effects of the porous media on MnO$_2$ precipitate transport are unpredictable and could artificially impact the complex resistivity measurements. After complex conductivity measurement, the pore fluid was vacuum-extracted and measured for conductivity and pH.

3.3.5.3 Complex Conductivity Change From Humate Oxidation

Aqueous humate oxidation samples were created with simulated groundwater containing 10 mM KMnO$_4$ and 0, 100 mg/L, 200 mg/L, or 300 mg/L humate (added as 200 mg/L, 400 mg/L, or 600 mg/L humic acid sodium salt) to simulate natural organic matter. Adding 600 mg/L humic acid sodium salt to artificial groundwater with no KMnO$_4$ did not result in a significant change in the fluid conductivity ($\sim 1 \text{ to } 2 \times 10^{-4} \text{ S/m}$). The conductivity, pH, and MnO$_4^-$ concentration of the aqueous humate oxidation samples were then monitored for 48 hours in quadruplicate samples. Duplicate saturated sand samples with artificial groundwater, 10 mM KMnO$_4$, and 300 mg humate/L were also created by packing two aqueous samples with clean...
sand in the porous media sample holder immediately after mixing the aqueous sample. Complex conductivity was monitored in these samples for 48 hours.

3.4. Results

Results of the investigations described in Section 3.3 are presented in this section.

3.4.1. Formation Factor and Surface Conductivity

Formation factor was calculated in clean sand and mixtures of 90% sand / 10% kaolinite and 90% sand / 10% smectite (Figure 3.2). The clean sand had a formation factor of 3.83 ± 0.03. The 10% kaolinite and 10% smectite sets had statistically identical formation factors of 4.41 ± 0.08 (kaolinite) and 4.42 ± 0.11 (smectite). No surface conductivity could be detected in the clean sand samples. The kaolinite samples had a surface conductivity of 0.0016 ± 0.0010 S/m, while the smectite samples had a surface conductivity of 0.0041 ± 0.0019 S/m. Addition of NaCl, KCl, or KMnO₄ did not result in any changes to the bulk conductivity to pore fluid conductivity relationship.

Production of MnO₂ from the oxidation of 2.1 to 7.5 mM TCE by permanganate in the presence of 8 mM bicarbonate did not cause significant surface conductivity. The y-intercepts for TCE oxidation sample sets ranged from -0.0003 to 0.0009 S/m (Table 3.2). However, the y-intercepts were all within one standard deviation of the origin. Also, no trend was discernable in surface conductivity (y-intercept) change. For these reasons and because a negative surface conductivity is not physically possible, the regression curve for each of the TCE oxidation sample sets was adjusted to run through the origin to calculate the formation factor (Figure 3.3).
Figure 3.2. Formation factor ($F$) and surface conductivity ($\sigma_s$) calculated in saturated clean sand and in clayey sands containing 10% kaolinite or 10% smectite. Varied conductivities were obtained by adding KCl or NaCl to artificial groundwater. The formation factor and surface conductivity are given plus or minus the 95% confidence interval.

Table 3.2. Surface conductivity calculated in TCE oxidation samples.

<table>
<thead>
<tr>
<th>Sample Set</th>
<th>Surface Conductivity (S/m)</th>
<th>Standard Deviation</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>No TCE</td>
<td>-0.0001</td>
<td>0.0003</td>
<td>0.0006</td>
</tr>
<tr>
<td>6 mM KMnO$_4$ + 2.08 mM TCE</td>
<td>0.0009</td>
<td>0.0011</td>
<td>0.0027</td>
</tr>
<tr>
<td>10 mM KMnO$_4$ + 3.99 mM TCE</td>
<td>-0.0003</td>
<td>0.0017</td>
<td>0.0041</td>
</tr>
<tr>
<td>14 mM KMnO$_4$ + 5.82 mM TCE</td>
<td>0.0008</td>
<td>0.0010</td>
<td>0.0020</td>
</tr>
<tr>
<td>18 mM KMnO$_4$ + 7.54 mM TCE</td>
<td>-0.0002</td>
<td>0.0012</td>
<td>0.0029</td>
</tr>
</tbody>
</table>
Figure 3.3. Bulk conductivity versus pore fluid conductivity for saturated sand samples in which different TCE concentrations were oxidized by KMnO₄. Regression lines were forced through the origin. Error bars represent 95% confidence intervals for pore fluid conductivity measurements. Formation factor is reported plus or minus the 95% confidence interval.

Assuming the surface conductivity is zero for each TCE oxidation sample, formation factor can be calculated for each individual sample within the sets described in Figure 3.3. Figure 3.4 shows the formation factors calculated both by sets of samples and by individual sample as a function of oxidized TCE concentration. Examining the formation factors calculated by set, the correlation between TCE concentration and formation factor is strong ($R^2 = 0.866$). The observed formation factor increase was very small, though, approximately 0.021 for every 1
mM TCE that was oxidized. Using the individual samples yielded a very similar change in formation factor: 0.023 per mM TCE. Although the correlation between formation factor and TCE concentration is lower when examined by individual sample ($R^2 = 0.638$), the 95% confidence interval of the slope from individual samples (0.004 per 1 mM TCE) confirms that the slope is greater than zero.

Figure 3.4. Oxidized TCE concentration versus formation factor calculated in individual samples assuming no surface conductivity (small dots, dashed regression line) and calculated by sets of samples with the same TCE concentration (large open circles with 95% confidence intervals, solid regression line).

3.4.2. In-Phase Conductivity Change from TCE Oxidation

When 100 µM TCE or less was oxidized, the measured conductivity in aqueous samples corresponded well with values predicted using Equation 3.5 and PHREEQC (Figures 3.5 and 3.6). Oxidation of TCE at these concentrations was not expected to noticeably impact conductivity because of the low concentration of product ions. Observed pH was near predicted values for all samples (Figure 3.5), but small variances below the predicted pH for samples with greater than 1 mM oxidized TCE caused higher than predicted conductivities in these samples.
(Figure 3.6). However, when the measured pH values were used to predict conductivity instead of modeled pH, the measured conductivity was actually lower than predicted in all samples with the difference generally increasing as TCE concentration increased, suggesting possible adsorption of ions by MnO₂.

**Figure 3.5.** Measured versus predicted pH in fluid samples in which TCE was oxidized by 10 mM MnO₄⁻ in artificial groundwater with 2 mM HCO₃⁻. The predicted pH was calculated using PHREEQC and Equation 3.5. Error bars represent the standard deviation of three or more samples.

**Figure 3.6.** Measured and predicted electrical conductivity in fluid samples in which TCE was oxidized by permanganate. Conductivity predictions were based on Equation 3.5 using PHREEQC. All samples began with artificial groundwater with 10 mM KMnO₄ and 2 mM NaHCO₃. Error bars represent the standard deviation of at least three samples.
Clean sand, 10% kaolinite, and 10% smectite all influenced the pH of aqueous samples after adding to the porous media. Adding artificial groundwater (initial pH of 8.2) to clean sand resulted in a pore fluid pH of 7.47 to 7.75. Kaolinite samples with artificial groundwater had a pH between 6.65 and 7.05, and the smectite samples with artificial groundwater had a pH range of 8.41 to 8.75. Clean sand and 10% kaolinite displayed similar buffering capacities with TCE oxidation samples, maintaining approximately the same pH after oxidation of up to 100 µM TCE (Figure 3.7). At higher concentrations of TCE, decreases in pore fluid pH were observed as a result of the increased production of H⁺, although all pH values were still much higher than in fluid only samples. The 10% smectite displayed a much greater buffering capacity than clean sand or 10% kaolinite, with noticeable pH decreases not occurring until more than 2 mM TCE was oxidized. Even in 3.2 mM TCE samples, the pH remained above 8 in 10% smectite samples.

Figure 3.7. Observed pH in porous media samples containing artificial groundwater with 2 mM NaHCO₃ in which various TCE concentrations were oxidized by 10 mM KMnO₄. Error bars represent the standard deviation of at least two samples.
3.4.3. **In-Phase Conductivity Change from Humate Oxidation**

The decrease in permanganate concentration over time caused by the oxidant demand exerted by the humic acid coincided with a decrease in electrical conductivity (Figure 3.8). With no humic acid, the conductivity remained unchanged over time, and the measured conductivities were within 0.4% to 0.8% of the conductivities predicted using PHREEQC. Assuming two-step oxidation and first-order kinetics, rate constants of 0.003 M$^{-1}$s$^{-1}$ for the first step (humate to oxalate, determined by curve-fitting) and 0.073 M$^{-1}$s$^{-1}$ (from Yan and Schwartz, 2000) for the second step (oxalate to CO$_2$) fit the permanganate concentration data well, especially for the first 24 hours. Measured permanganate concentrations over the first 24 hours were within 3.0% of modeled values. At 48 hours, though, the model underpredicted the oxidant demand in the 300 mg/L humate set (by 10.8%) and to a lesser extent the 200 mg/L humate set (by 4.1%).

The conductivities calculated in PHREEQC based on the kinetic modeling and Equation 3.7 also fit the measured conductivities well. The predictions overestimated the measured conductivity by 1.4% to 3.6%, although only the conductivity measured at 48 hours with 300 mg/L humate was greater than 2.8% above the measured value. Generally, the error increased slightly in samples with a higher initial humate concentration.

3.4.4. **Background Quadrature Conductivity Spectra**

With artificial groundwater as the pore fluid, clean sand and 10% kaolinite display very little quadrature conductivity compared to 10% smectite (Figure 3.9). The clean sand and 10% kaolinite had no noticeable frequency-dependent quadrature conductivity peak, although the 10% kaolinite had a slightly higher quadrature conductivity than the clean sand at frequencies of 5 Hz and above. The 10% smectite displayed peak quadrature conductivity at 20 Hz. The addition of
2 mM TCE to the artificial groundwater did not have any effect on quadrature conductivity in the frequencies characteristic of Stern-layer polarization (< 100 Hz). However, 20 hours after packing, quadrature conductivity was about 30% lower at frequencies between 1 kHz and 10 kHz (Figure 3.10).

![Graphs showing conductivity and permanganate concentration over time for different humate concentrations.](image)

**Figure 3.8.** Measured permanganate concentration (triangles) and electrical conductivity (circles) in fluid samples in which 0, 100, 200, or 300 mg/L humate was oxidized by 10 mM KMnO₄ in artificial groundwater. Error bars represent the standard deviation of four samples. Long dashed lines represent kinetic modeling of permanganate reduction. Short dashed lines represent electrical conductivity calculated using PHREEQC based on the predicted product concentrations from the kinetic modeling.
3.4.5. Effects of Ion Injection on Quadrature Conductivity

In contrast to the lack of ion-dependence seen in formation factor and surface conductivity calculations, quadrature conductivity measurements were dependent on the cation that was added to the artificial groundwater. Furthermore, the response to the added cation was also frequency-dependent. In saturated clean sand, quadrature conductivity at 1 Hz decreased
slightly (about $1 \times 10^{-6}$ S/m) as KCl was added and then plateaued after approximately 10 mM (800 mg/L) KCl was added (Figure 3.11a). However, when NaCl was added, the quadrature conductivity at 1 Hz continued to increase as up to 40 mM was added. At 10 Hz, quadrature conductivity dipped slightly as 2 to 5 mM KCl was added but increased as more KCl was added (Figure 3.11b). When NaCl was added, the quadrature conductivity at 10 Hz increased at a greater rate than with KCl.

Figure 3.11. Quadrature conductivity at (a) 1 Hz and (b) 10 Hz in saturated clean sand samples after adding KCl, NaCl, and KMnO$_4$ to artificial groundwater. Error bars represent the standard deviation of duplicate samples, except for unamended groundwater (3 samples), 10 mM KMnO$_4$ (4 samples), and 30 mM KMnO$_4$ (1 sample).

Quadrature conductivity at 1 Hz for 10% kaolinite was nearly identical to the clean sand measurements (Figure 3.12a). At 10 Hz, though, 10% kaolinite had a higher quadrature conductivity until 20 mM KCl was added. At that concentration the kaolinite and clean sand quadrature conductivity curves converged (Figure 3.12b).
Figure 3.12. Comparison between quadrature conductivity change at (a) 1 Hz and (b) 10 Hz in 10% kaolinite and in clean sand after adding KCl to artificial groundwater. No error bars are shown because only single 10% kaolinite measurements were collected.

In 10% smectite samples, quadrature conductivity increased at both 1 Hz and 10 Hz as NaCl concentration increased, although the amount of increase was less with each addition of NaCl (Figure 3.13). Addition of 50 mM NaCl caused a nearly 100% increase in quadrature conductivity at 1 Hz and a 150% increase at 10 Hz over samples with unamended artificial groundwater. Addition of up to 20 mM KCl had no effect on quadrature conductivity, and further addition of KCl caused a slight decrease in quadrature conductivity. Addition of KMnO₄ had the same effect as adding KCl for all porous media compositions (Figures 3.11-3.13).

3.4.6 Effects of pH Change on Quadrature Conductivity

When TCE was oxidized by permanganate in artificial groundwater and added to clean sand or 10% kaolinite, both the sand and 10% kaolinite samples displayed similar quadrature conductivity values (Figure 3.14a). Quadrature conductivity generally decreased slightly as more TCE was oxidized with both the clean sand and 10% kaolinite at both 1 Hz and 10 Hz. In
contrast, quadrature conductivity was relatively unchanged as additional TCE was oxidized and added to 10% smectite (Figure 3.14b).

![Figure 3.13. Quadrature conductivity in saturated 10% smectite after addition of KCl, NaCl, or KMnO₄ to artificial groundwater measured at (a) 1 Hz and (b) 10 Hz.](image)

As detailed in Section 2, the pH decreases as more H⁺ is produced from TCE oxidation, and the number of negatively charged surface groups on the silica decreases as pH decreases. Because quadrature conductivity is a function of surface charge, the change in quadrature conductivity in silica sand can be estimated based on the change in pH (Table 3.3). In the saturated clean sand samples in which TCE was oxidized, the predicted and measured quadrature conductivity values at 1 Hz matched well; however, these values did not match well for quadrature conductivity measured at 10 Hz (Figure 3.15). The divergence in these comparisons indicates that the quadrature conductivity at 1 Hz in clean sand is pH-dependent, but a different physical process may dominate the quadrature conductivity value observed at 10 Hz, especially in samples with very high salinity.
Figure 3.14. Quadrature conductivity at 1 Hz and 10 Hz in saturated (a) sand and 10% kaolinite and (b) 10% smectite containing artificial groundwater in which TCE was oxidized by permanganate. Error bars represent the range of values observed in duplicate samples.

When aqueous TCE oxidation samples were added to 10% smectite, the high buffering capacity of the clay caused all of the porous media samples to have a similar pH (Figure 3.7). To further test the pH dependence of the quadrature conductivity in 10% smectite samples, three pore volumes of pH-adjusted artificial groundwater was pumped through a set of saturated samples, resulting in pore fluid pH values ranging from 3.94 to 8.07. No significant change in quadrature conductivity was measured at either 1 Hz or 10 Hz (Figure 3.16).

3.4.7. Effects of MnO₂ Production on Quadrature Conductivity

Quadrature conductivity did not appear to be influenced by the production of MnO₂ from the reduction of MnO₄⁻. Saturated clean sand samples with similar pore fluid conductivity and pH containing the reaction products of 0 to 0.72 mM TCE oxidized by permanganate showed only minor random variation in quadrature conductivity, as did samples in which 0 to 12 mM
Table 3.3. Measured and predicted quadrature conductivity ($\sigma''$) in saturated clean sand with pore fluid in which TCE was oxidized by permanganate in the presence of varying concentrations of NaHCO$_3$. The percentage of SiO$^-$ groups on the silica sand for a given pH is from Duval et al. (2002). The sample with the lowest TCE concentration in each NaHCO$_3$ group is the base measurement (indicated by *) and the predicted change in quadrature conductivity is calculated as a difference from that sample (For example, 1.96 mM TCE, 2 mM NaHCO$_3$: 14.0% / 16.4% x (3.38 x 10$^{-6}$ S/m) = 2.80 x 10$^{-6}$ S/m).

<table>
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<tr>
<th>[TCE]</th>
<th>pH</th>
<th>% SiO$^-$</th>
<th>Measured $\sigma''$, 1 Hz (S/m)</th>
<th>Predicted $\sigma''$, 1 Hz (S/m)</th>
<th>Measured $\sigma''$, 10 Hz (S/m)</th>
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<td>16.4</td>
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<tr>
<td>5 mM</td>
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<td>7.00</td>
<td>16.5</td>
<td>4.19E-06</td>
<td>*</td>
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<td>6.47E-06</td>
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Figure 3.15. Measured quadrature conductivity (symbols) compared to predicted quadrature conductivity based on pH-induced changes in SiO$^-$ percentage on silica grains (dashed line) in saturated clean sand samples in which TCE was completely oxidized by permanganate. SiO$^-$ percentage is shown in Table 3.3 and is based on Duval et al. (2002). TCE oxidation was performed in the presence of 2 mM, 5 mM, or 8 mM NaHCO$_3$. Error bars represent the range of measurements obtained in duplicate samples. Note that the predictions hold at 1 Hz but not at 10 Hz.
Figure 3.16. Quadrature conductivity of saturated 10% smectite samples with artificial groundwater pore fluid of varying pH. Error bars represent the error reported by the impedance spectroscopy instrument for a single sample derived from multiple measurements taken during a single alternating current injection series.

MnO$_2$ was extracted and resuspended in artificial groundwater (Figure 3.17). Furthermore, samples containing 10 mM KMnO$_4$ and 600 mg humic acid/L did not show any change in quadrature conductivity over a period of 48 hours during which approximately 4 mM MnO$_4^-$ was reduced to MnO$_2$ (Figure 3.18).

Figure 3.17. Quadrature conductivity at (a) 1 Hz and (b) 10 Hz versus manganese dioxide concentration in saturated clean sand samples. The pore fluid is either pH-adjusted artificial groundwater in which TCE was oxidized by permanganate (circles) or MnO$_2$ extracted from TCE oxidation samples and resuspended in artificial groundwater. The pH was between 7.5 and 7.7 for all samples. Error bars represent the range of values observed in duplicate samples. No error bar means there was only one sample.
Figure 3.18. Quadrature conductivity over time in clean sand saturated with artificial groundwater containing 10 mM permanganate and 600 mg/L humic acid (left axis). The right axis shows permanganate loss over the same time period in fluid samples with the same composition. Error bars represent the standard deviation of two porous media samples (quadrature conductivity) and four fluid samples (permanganate concentration).

3.5. Discussion

This section explains the significance of the results described in Section 2.4.

3.5.1. In-Phase (Bulk Porous Media and Fluid) Conductivity

The process of determining the pore fluid conductivity from the bulk conductivity using Equation 3.3 requires assumptions about formation factor and surface conductivity. Although the purpose of this research was not to catalog the formation factor and surface conductivity of a wide range of unconsolidated aquifer compositions, the effects of a couple different formation components can be seen in the data reported here. The clean sand had no measureable surface conductivity, while 10% kaolinite present in the sand added a small amount of surface conductivity (0.0016 ± 0.0010 S/m), and 10% smectite had a larger surface conductivity (0.0045 ± 0.0019 S/m). The change in surface conductivity is consistent with clean silica sand having the lowest CEC and smectite having the largest CEC among the porous media materials used. The
10% kaolinite and 10% smectite had the same formation factor. Neither the specific geometry of the clay particle, nor the swelling characteristics of the clay noticeably impacted the formation factor. Only the percentage of clay-size particles influenced the formation factor in these data sets.

When MnO$_4^-$ oxidizes TCE or any other material, the MnO$_4^-$ is reduced to MnO$_2$, which, like clay, is a colloid-sized particle (although coagulation of MnO$_2$ can occur). Oxidation of greater concentrations of TCE, and resulting reduction of greater concentrations of MnO$_4^-$ to MnO$_2$, coincided with increased formation factor in saturated sand samples. This result, calculated with 8 mM HCO$_3^-$, was very similar to formation factor changes reported previously by Hort, et al. (2014) for unbuffered samples. The formation factor calculated in samples in which 7.5 mM (990 mg/L) TCE was oxidized by MnO$_4^-$ (4.01 ± 0.09) was still much lower than observed in 10% clay samples (4.41 ± 0.08 for kaolinite and 4.42 ± 0.11 for smectite). This concentration of TCE is near the solubility limit for TCE and would only be present near DNAPL source zones. Although statistically significant, the formation factor increase attributed to MnO$_2$ formation was only 0.02 per mM TCE (0.01 per mM MnO$_2$). TCE concentrations of less than 1 mM (130 mg/L), which are more likely to occur in most contaminant plumes, would result in negligible formation factor changes. No additional surface conductivity from TCE oxidation or MnO$_2$ formation could be detected.

The electrical conductivity of fluid TCE oxidation samples could be reasonably predicted using Equation 3.5 and PHREEQC. Manganese dioxide is known to adsorb cations, especially divalent metals, and slightly lower than expected conductivity measurements in fluid TCE oxidation samples are evidence that adsorption did occur. When accounting for actual sample pH, the measured conductivity was approximately 6% lower than predicted when 3 mM TCE
was oxidized in artificial groundwater with 2 mM HCO$_3^\text{-}$. When at least 2 mM TCE was oxidized, the pH was lower than predicted by Equation 3.5 and PHREEQC. The reduced pH had the opposite impact on conductivity predictions than adsorption, causing an increase in conductivity from the additional H$^\text{+}$. Because of the opposing effects of the two errors, using just Equation 3.5 and PHREEQC resulted in predicted conductivity that was within approximately 4% of the measured conductivity for TCE concentrations of 1 mM (130 mg/L) and higher, and within 1.5% for TCE concentrations of 100 µM (13 mg/L) and lower.

Buffering of protons both by HCO$_3^\text{-}$ and from mineral protonation impacts electrical conductivity. Carbonate buffering results in loss of both H$^\text{+}$ and HCO$_3^\text{-}$ ions, which reduces conductivity. PHREEQC can easily account for these carbonate cycle losses. On the other hand, accounting for buffering through protonation requires measured or assumed pH values. This is especially the case for higher concentrations (1 mM or greater) of TCE. Both clean sand and 10% kaolinite displayed similar buffering capacities, although they maintained different pH values based on the inherent pH of the sand and kaolinite used in the experiments. Because of its much larger surface charge density, the 10% smectite sample had a much larger buffering capacity. For example, porous media samples with 10% smectite created from artificial groundwater in which 3.2 mM TCE was oxidized still had a fluid pH above 8 despite an initial fluid pH of 2.8 prior to adding the fluid to the 10% smectite sample.

Loss of conductivity from the oxidative demand of humate over a period of 48 hours was significant, but very predictable. Assuming a two-step oxidation of humate to CO$_2$ with oxalate as the intermediate, the reduction of the MnO$_4^\text{-}$, especially for the first 30 hours, was predicted with reasonable accuracy. After 30 hours, samples with 200 to 300 mg humate / L exerted an oxidant demand greater than predicted. Because of the lack of purity of the humate that was
used (the assay provided with the product listed 50% humic acid and 15.3% water insoluble matter), it is possible that additional oxidizable material was present. Still, only a minor error in conductivity calculation resulted. The conductivities calculated in PHREEQC using the kinetic modeling of the redox reaction were within 1.4% to 2.8% of the measured values with a bias toward overprediction of the conductivity. It is possible that chelation of ions by humate at the early time stages and adsorption by MnO\textsubscript{2} at later time stages caused measured conductivity to be slightly lower than predicted. Given the small magnitude of the errors, the modeling of humate oxidation employed in this study was adequate for conductivity prediction.

3.5.2. Quadrature Conductivity

Oxidation of TCE or humate and reduction of MnO\textsubscript{4}\textsuperscript{2-} did not have a direct impact on quadrature conductivity. In formations lacking smectite clays, oxidation of TCE can lower the pore fluid pH and reduce the quadrature conductivity. However, the quadrature conductivity is extremely low in aquifers containing only silica or kaolinite, reflecting the low cation exchange capacities of these minerals. Buffering of the TCE oxidation reaction by pore fluid alkalinity and by mineral protonation limits pH changes except at very high TCE concentrations. Changes in quadrature conductivity would likely be too small to be reliably measured in field situations.

Depending on which commonly used permanganate salt is used for oxidation (sodium or potassium), injection of large quantities of the salt may measurably impact quadrature conductivity. Addition of potassium had a slight negative effect on quadrature conductivity at 1 Hz when added to artificial groundwater containing sodium as the predominant cation. On the other hand, 40 mM additional sodium caused quadrature conductivity at 1 Hz to increase by 29% in clean sand samples and nearly 100% in 10% smectite samples. Nearly identical quadrature
conductivity responses between potassium chloride and potassium permanganate indicate that the anion (Cl\(^-\) or MnO\(_4^2-\)) does not significantly affect quadrature conductivity. The increase in quadrature conductivity observed when sodium was added versus when potassium was added is consistent with a strongly hydrated ion such as sodium having a higher mobility within the Stern layer than a weakly hydrated and more strongly binding ion such as potassium.

Quadrature conductivity measurements appear to have very limited utility in relation to ISCO. Quadrature conductivity may be an indicator of general sodium permanganate plume movement and dispersion; however, sodium is conserved, while permanganate is exhausted, so quadrature conductivity would not indicate how much permanganate remains within the plume. Quadrature conductivity may also be useful for delineating where smectite clays exist, which may be helpful for determining where to adjust formation factors used in calculating pore fluid conductivities and where to expect preferential or inhibited flow.

3.6. Conclusion

Performing ISCO using permanganate to oxidize chlorinated compounds such as TCE has a direct impact on in-phase bulk conductivity and can also impact the out-of-phase, quadrature component of conductivity. Only changes in bulk conductivity, though, can be quantitatively linked to permanganate concentrations or TCE oxidation. Bulk conductivity is influenced by oxidant injection, as well as reactions between permanganate and oxidized compounds. Oxidation product formation can confound calculations to estimate remaining permanganate based on conductivity, but the products and resulting conductivity changes are predictable. At TCE concentrations found in most contaminant plumes (< 1 mM or 130 mg/L), TCE oxidation products have only a negligible impact on conductivity. Measurable changes in
quadrature conductivity in the field during ISCO may be observed if sodium permanganate (or another sodium salt) is the chosen oxidant. However, this quadrature conductivity change is the result of sodium addition and not any ISCO reaction. Quadrature conductivity may be useful for detecting smectite clays during pre-ISCO characterization.

This research demonstrates that resistivity measurements can provide additional information to help track the movement and exhaustion of permanganate during ISCO applications. Resistivity would be most useful in time-lapse applications as a complement to traditional groundwater and core sampling. Combined with solute transport models, the type of chemical modeling demonstrated here could produce conductivity calculations useful for constraining inversion results and improving tomogram accuracy. Additional research is needed at the tank and field scales employing improved 4-D inversion techniques (Karaoulis et al., 2011) and application of physical models to resistivity inversions (such as described by Day-Lewis et al., 2005) to fully demonstrate the potential of resistivity tomography for monitoring ISCO.

However, with recent improvements to resistivity measurement system speed and inversion resolution, time-lapse resistivity measurements may provide a promising tool for monitoring permanganate fate and transport at time-scales that cannot be achieved with traditional sampling alone.

Acknowledgements
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CHAPTER 4. TWO-DIMENSIONAL ANALYSIS OF PERMANGANATE PLUME
MOVEMENT AND INTERACTION WITH TCE THROUGH VISUAL EVIDENCE, WATER
SAMPLING, AND TIME-LAPSE ELECTRICAL CONDUCTIVITY TOMOGRAPHY

Abstract. While electrical conductivity can be accurately predicted in homogeneous samples after permanganate injection during trichloroethene (TCE) oxidation, modeling changes in conductivity in a two- or three-dimensional space caused by a discrete plume of injected permanganate solution is much more complicated. In this study, the movement, dispersion, and extent of loss during TCE oxidation were examined for an injected permanganate plume during advection-dominated flow conditions in a two-dimensional tank with saturated sand. During iterations with and without TCE dissolved in artificial groundwater, an injected 50 mM permanganate plume moved as a mass at the same velocity as the flow of the groundwater, with dispersion and diffusion only evident at the edges of the plume. No residual permanganate could be identified behind the plume. Based on comparative mass balances of recovered permanganate between the two iterations, approximately the same volume of TCE was oxidized as the volume of permanganate injected. Knowledge of the ISCO reactions and solute movement can be used to improve inversions of electrical conductivity survey data and improve the effectiveness of conductivity tomography as a tool for monitoring permanganate distribution during chemical remediation.

4.1. Introduction

Trichloroethene (TCE) can be mineralized to carbon dioxide quickly using permanganate as an oxidant. The effectiveness of this reaction as an in situ groundwater treatment, however, is
dependent on contact between the oxidant and the groundwater contaminant (TCE). Traditionally, delivery of permanganate has been monitored using water samples from wells. Monitoring wells provide accurate oxidant and contaminant concentration data at the point of monitoring, but interpolating the data between wells in heterogeneous aquifers is not always easy or accurate. Preferential flow paths may cause injected permanganate to move in unexpected directions.

The ionic nature of permanganate makes it a good candidate for monitoring using electrical conductivity measurements. Such measurements have been used numerous times to track the movement of injected solutes within aquifers (Cassiani et al., 2006; Kemna et al., 2002; Singha and Gorelick, 2005). The method has also recently been used to track the movement of permanganate during in situ chemical oxidation (ISCO) (Halihan et al., 2012; Harte et al., 2012). Generally, however, electrical conductivity has only been applied during ISCO in a qualitative manner.

In previous work (Hort et al., 2014 and Chapter 3 of this dissertation), I demonstrated that conductivity change as a result of oxidation of TCE and natural organic matter by permanganate can be modeled accurately in porous media batch reactors with both clean sand and sand/clay mixtures as the granular material. However, inverse modeling of permanganate concentrations from conductivity measurements yields multiple possible solutions that must be constrained with additional information, such as initial TCE concentrations. The problem becomes more complex in a non-homogeneous two- or three-dimensional setting in which a solution of permanganate is injected into an extensive aquifer. The electrical conductivity within the injected MnO$_4^-$ plume depends on the transport properties of the oxidant, the contaminant, and the oxidation products.
How much of the plume actually contacts the TCE, where it contacts the TCE, and for how long all potentially impact the electrical conductivity distribution.

Furthermore, calculation of MnO$_4^-$ concentration is further hampered by the difficulty in recovering actual subsurface conductivities at a high resolution using common inversion techniques such as Tikhonov regularization. One issue is that conductivity resolution drops with distance from the electrodes (Day-Lewis et al., 2005). Secondly, Tikhonov regularization introduces smoothness that may be unrealistic and cause underestimation of the actual conductivity at the plume (Zhou et al., 2014). Inversions can be improved, however, by constraining the inversion results with known data points and other knowledge of plume or hydrologic characteristics (Irving and Singha, 2010; Jardani et al., 2013). Using two-dimensional tanks, this study examines the flow characteristics of MnO$_4^-$ plumes and their interaction with TCE in order to improve the ability to model conductivity changes that occur during ISCO and relate them to actual MnO$_4^-$ concentrations.

4.2. Theoretical Background

TCE is oxidized by permanganate to carbon dioxide (CO$_2$) through various carboxylate intermediates. Depending on pH, the most abundant form of carboxylate is either formate or oxalate (Yan and Schwartz, 2000). Equations 4.1 and 4.2 describe the formate pathway, while Equations 4.3 and 4.4 describe the oxalate pathway.

$$\frac{8}{3} \text{H}_2\text{O} + C_2\text{HCl}_3 + \frac{2}{3} \text{MnO}_4^- \rightarrow 2 \text{HCOO}^- + 3 \text{Cl}^- + \frac{13}{3} \text{H}^+ + \frac{2}{3} \text{MnO}_2$$  \hspace{1cm} (4.1)

$$2 \text{HCOO}^- + \frac{10}{3} \text{H}^+ + \frac{4}{3} \text{MnO}_4^- \rightarrow 2 \text{CO}_2 + \frac{4}{3} \text{MnO}_2 + \frac{8}{3} \text{H}_2\text{O}$$ \hspace{1cm} (4.2)

$$\frac{4}{3} \text{H}_2\text{O} + C_2\text{HCl}_3 + \frac{4}{3} \text{MnO}_4^- \rightarrow (\text{COO})_2\text{O}^- + 3 \text{Cl}^- + \frac{11}{3} \text{H}^+ + \frac{4}{3} \text{MnO}_2$$ \hspace{1cm} (4.3)

$$(\text{COO})_2\text{O}^- + \frac{2}{3} \text{MnO}_4^- + \frac{8}{3} \text{H}^+ \rightarrow 2 \text{CO}_2 + \frac{2}{3} \text{MnO}_2 + \frac{4}{3} \text{H}_2\text{O}$$ \hspace{1cm} (4.4)
Independent of pathway, the overall reaction is described by

$$C_2\text{HCl}_3 \text{ (TCE)} + 2 \text{MnO}_4^- \rightarrow 2 \text{MnO}_2(s) + 2 \text{CO}_2(g) + 3 \text{Cl}^- + \text{H}^+.$$  \hspace{1cm} (4.5)

Both pathways result in intermediate ions that could potentially cause an increase in conductivity that is greater than the final oxidation products.

The oxidation of TCE and carboxylate intermediates and the reduction of MnO$_4^-$ are first order with respect to each other. The second-order rate constant for the transformation of TCE to the carboxylate between pH 4 and 8 is in the range of 0.65 to 0.68 M$^{-1}$s$^{-1}$. The rate constants for formate and oxalate oxidation range from 0.075 to 0.35 M$^{-1}$s$^{-1}$ and from 0.073 to 0.11 M$^{-1}$s$^{-1}$, respectively, with rate increasing as pH decreases between pH 4 and 8 (Yan and Schwartz, 2000). Figure 4.1 shows the degradation of TCE and a carboxylate (oxalate) when 2 mM TCE is oxidized by 10 mM MnO$_4^-$, assuming second order rate constants of 0.65 M$^{-1}$s$^{-1}$ for TCE and 0.11 M$^{-1}$s$^{-1}$ for oxalate. In reality, some formate would be formed instead of all oxalate, though this only slightly changes the rate of intermediate degradation. The overall reaction is essentially complete within two hours.

**Figure 4.1.** Oxidation of 2 mM TCE by 10 mM MnO$_4^-$ assuming oxalate as an intermediate. Second order rate constants are 0.65 M$^{-1}$s$^{-1}$ for TCE and 0.11 M$^{-1}$s$^{-1}$ for oxalate.
The measured in-phase bulk electrical conductivity ($\sigma'$) within a saturated granular media (such as an aquifer) is a combination of both the flow of electrical charge through the liquid media (pore fluid conductivity, $\sigma_f$) and the flow across the mineral surfaces (surface conductivity, $\sigma_s$). This relationship can be described by the following linear equation (Revil et al., 2013):

$$\sigma' = \frac{1}{F} \sigma_f + \sigma_s$$  \hspace{1cm} (4.6)

where $F$ is the formation factor of the aquifer formation, a power law function of porosity described by Archie (1942). In ISCO situations where concentrated solutes such as potassium or sodium permanganate are added to the aquifer, $\sigma_f$ is much larger than $\sigma_s$ and $\sigma_s$ becomes negligible (Hort et al., 2014; Chapter 3 of this dissertation). Therefore, $F \approx \sigma_f / \sigma'$.

When a concentrated solute such as potassium permanganate is injected into the subsurface, the plume will move and spread out based on advection, mechanical dispersion, and diffusion. The center of mass of the plume will generally move through advection along with the flow of the groundwater, although adsorption can attenuate the rate of plume movement. Additionally, the plume will spread and mix with the surrounding groundwater as a result of mechanical dispersion and diffusion (molecular dispersion). Because mechanical dispersion and diffusion cannot be differentiated based solely on observation of solute movement, the two forces are often described together by the term hydrodynamic dispersion.

Diffusion is mixing that occurs as a result of concentration gradients. The rate of diffusion for ions is described in units of $m^2 \cdot s^{-1}$ by a diffusion coefficient ($D_i$) (see Table 2.1). The apparent rate of diffusion within porous media ($D_i^*$) is a fraction of the diffusion coefficient, and can be estimated by

$$D_i / D_{i}^* = 1/(F \phi),$$  \hspace{1cm} (4.7)

where $F$ is the formation factor and $\phi$ is the porosity (Perkins and Johnston, 1963). The actual
diffusion distance is a Gaussian function whereby 95.4% of the solute mass lies within two standard deviations on either side of the plume’s center of mass. One standard deviation is equal to \((2Dt)^{1/2}\) where \(t\) is equal to the time in seconds.

Mechanical dispersion is caused by pore-scale velocity differences (microscopic dispersion) and larger-scale differences in hydraulic conductivity (macroscopic dispersion). It is a function of both the distance that a solute travels and the level of heterogeneity within the porous media. The dispersion inherent to an aquifer formation is usually described using dispersivity terms in the longitudinal (parallel to flow, \(\alpha_L\)) and transverse (perpendicular to flow, \(\alpha_T\)) directions in units of length. Transverse dispersivity is often estimated to be a fraction (about 0.3) of the longitudinal dispersivity. The dispersion coefficient, which is analogous to the diffusion coefficient is then calculated by \(D_L = \alpha_L v\) (or \(D_T = \alpha_T v\)) where \(v\) is the flow velocity. Dispersion distance is calculated in the same manner as diffusion distance.

After examining longitudinal (parallel to flow) dispersions (\(\alpha_L\)) reported at numerous sites for distances up to 100 m, Neuman (1990) found that \(\alpha_L\) could be estimated by the equation

\[
\alpha_L = 0.0169 L^{1.53}.
\]  

However, homogeneous porous media samples in laboratory-scale experiments may have dispersivities much lower than described in many of the studies examined by Neuman, which included field-scale experiments. Bacri et al. (1987) found that longitudinal dispersion was also a function of the ordering and heterogeneity of the flow paths. They observed a relatively low longitudinal hydrodynamic dispersion in homogeneous glass beads (200 µm diameter, \(\phi = 0.40\)) compared to sandstone and brick. The hydrodynamic dispersion in the glass beads was approximately 5 times the pore length times flow velocity at Péclet numbers less than or equal to
0.1 and 0.5 times the pore length times flow velocity at Péclet numbers greater 10 or greater. Between Péclet numbers of 0.1 and 10, the multiplier value decreased with Péclet number.

4.3. **Methods**

Time-lapse bulk electrical conductivity measurements were collected in two types of saturated sand samples: homogeneous batch reactors and two-dimensional tanks. The materials and procedures used for both types of tests are described in this section.

4.3.1. **Materials**

The granular media used in all experiments was Unimin #70 industrial crushed quartz sand. The sand was sieved twice with a Tyler #80 sieve, muffled at 550°C to remove organic content, and rinsed with deionized water until the rinsate was clear and had a conductivity less than 3 µS/cm to remove ions and additional fine-grained material associated with the sand. After preparation, the sand was very well sorted with a $d_{10}$ grain size of approximately 0.175 mm and a $d_{50}$ grain size of approximately 0.21 mm (#70 mesh size). The sand grains were predominantly angular. The connected porosity of the sand was estimated to be 0.42 by measuring the volume of water displaced by 50 ml of sand. The formation factor of the sand was approximately 3.83 (Chapter 3). Artificial groundwater consisted of 4 mM Na$^{+}$, 0.2 mM Ca$^{2+}$, 0.1 mM Mg$^{2+}$, 2.4 mM Cl$^{-}$, 2 mM HCO$_3^-$, and 0.1 mM SO$_4^{2-}$ in deionized water. Granular KMnO$_4$ (RemOx, Carus Chemical) was added to the artificial groundwater at concentrations described in the subsections below. TCE was added to samples in the form of deionized water saturated with TCE.
4.3.2. Permanganate and TCE Concentration Measurements

Permanganate (MnO$\text{}_4^-$) concentration in solution was measured by centrifuging an aqueous sample for 8 minutes at a force of 3000 times gravity to remove precipitate and measuring the absorbance of the aqueous fraction at 525 nm in a Hach spectrophotometer, similar to Standard Method 4,500-KMnO$_4$ (Eaton et al., 2005). The aqueous fraction was diluted prior to measuring with the spectrophotometer in order to achieve an absorbance between 0.2 and 1.0.

Samples containing TCE were prepared in a fume hood, which can potentially accelerate volatilization. To account for volatilization, TCE concentration in samples was measured based on its oxidant demand on MnO$_4^-$. For batch samples with TCE oxidation, residual permanganate was measured spectrophotometrically (as described in the paragraph above) in fluid extracted from the sample after bulk conductivity measurements were completed. The reduced MnO$_4^-$ concentration (initial minus remaining MnO$_4^-$) was then divided by two to calculate the amount of TCE that was present in accordance with Equation 4.5. TCE concentration in the tank reservoirs during the iteration with TCE was measured just prior to KMnO$_4$ injection and just before permanganate reached the downstream reservoir by mixing 5 ml of reservoir solution with 5 ml of 10 mM KMnO$_4$ dissolved in artificial groundwater. The solutions were then allowed to react overnight, and TCE concentration was calculated the same way as for the batch reactions.

4.3.3. Conductivity Estimation from Pore Fluid Composition

Conductivity predictions were calculated using PHREEQC, 3.0.6 from the U.S. Geological Survey (Parkhurst and Appelo, 2013), using the PHREEQC database provided with the software with slight modification to add permanganate to the database. The diffusion
coefficient for permanganate was from the *CRC Handbook of Chemistry and Physics, 93rd Edition* (Vanýsek, 2012). Coefficients \( a^o \) and \( b \) for determining ionic activity, \( \gamma \), by the equation

\[
\log \gamma = \left(\frac{-Az_e^2\sqrt{\mu}}{1 + Ba_0\sqrt{\mu}}\right) + b\mu
\]

(where \( A \) and \( B \) are constants at a given temperature and pressure, \( z_e \) is the number of equivalents of exchanger in the exchange species, and \( \mu \) is the ionic mobility) was transferred from the WATEQ database (also provided with the PHREEQC program).

### 4.3.4. Batch Samples

Porous media samples were wet-packed immediately after mixing the aqueous part of the samples. The fluid was added first to the sample holder, and then sand was added. The sample holder was vibrated with a vortex mixer after each scoop of sand was added to aid compaction. The sample holder was cylindrical in shape and designed for collecting bulk resistivity and phase measurements with two copper current injection electrodes on the outside and two silver-silver chloride electrodes potential measurement electrodes on the inside in a Wenner array (Hort et al., 2014). Bulk resistance and phase were measured starting 10 minutes after packing the samples using the SIP-Lab-2 impedance spectrometer from Radic Research, using a 3-volt alternating current applied across the outer electrodes at frequencies from 10 Hz to 100 mHz. The bulk resistance measurements were repeated periodically (the phase measurements were not used in this study).

Bulk conductivity was calculated by dividing the conductance (the reciprocal of the bulk resistance) by the geometric factor for the sample holder, which was calculated from a calibration curve (shown in dissertation Appendix A) using various KCl solutions of known conductivity. The 1 Hz measurement is used for to calculate the bulk conductivity for the batch
samples. From 100 mHz to 10 Hz, the bulk conductivity is not frequency dependent (Hort et al., 2014). Sample temperature was measured to the nearest 0.1°C prior to bulk resistance measurement by inserting a Thermoworks RT600C-N temperature probe through the upper valve of the sample holder (when vertically oriented). After completing all bulk resistance measurements, fluid was extracted from each sample using a vacuum pump for pH and fluid conductivity measurements. Fluid conductivity was measured using a calibrated conductivity probe (calibration in dissertation Appendix A).

4.3.5. Adsorption Correction for Batch Samples

Because the sand was rinsed repeatedly with deionized water during preparation, many of the exchange sites on the sand were likely free of non-proton cations. Therefore, any subsequent solution added to the sand would likely exhibit loss of cations from solution through adsorption onto negatively charged mineral surface groups. To measure adsorption after packing a saturated sand sample, two samples were created with pore fluid containing artificial groundwater amended with 10 mM KMnO$_4$. Bulk electrical conductivity was measured starting 10 minutes after packing and then periodically for 20 hours in one sample, and 44 hours in the other sample. Conductivity decreased logarithmically due to adsorption of ions for the first 90 minutes (Figure 4.2). After that time, conductivity was relatively stable.

Using pore fluid conductivity measurements collected after all bulk conductivity measurements were completed, a formation factor of 3.85 was calculated in both samples, neglecting surface charge (fluid conductivity / bulk conductivity). Assuming an initial bulk conductivity of 0.0418 S/m based on the initial measured fluid conductivity (0.1611 ± 0.0001 S/m) and the formation factor, the bulk conductivity decreased 0.0021 S/m over the first 1.5
hours. Over the next 18.5 hours, the bulk conductivity decreased by only 0.0001 S/m. Based on the calculated formation factor, the total loss of fluid conductivity over 1.5 hours was 0.0083 ± 0.0000 S/m, and over 20 hours it was 0.0086 ± 0.0006 S/m.

Figure 4.2. Change in bulk conductivity at 22.0°C over 44 hours after packing artificial groundwater amended with 10 mM KMnO₄ with silica sand at pH 7.68. The error bars represent the range of values observed in duplicate samples. The regression line is a logarithmic fit of measurements taken in the first 1.5 hours (first 4 measurements).

To create a rough adsorption correction, the conductivity loss over the first 1.5 hours was plotted over time, and a logarithmic regression curve was calculated (Figure 4.3a). After 1.5 hours, a constant loss of 0.0083 S/m in pore fluid conductivity from the initial conductivity was assumed. However, while the fluid pH measured at the end of the bulk conductivity sampling was 7.68, the pH in the TCE reaction samples (presented in Section 4.1) for which correction is needed was 5.75. Because the number of negatively charged surface sites on silica decreases as pH decreases, the adsorption correction was adjusted as follows for a pH of 5.75. The percentage of deprotonated silanol groups (SiO⁻) as a total of overall silanol groups can be calculated based on the equation % SiO⁻ = 6.4033 × e⁽⁽0.1352 pH⁾⁾, derived from Duval et al. (2002).
At pH 7.68, approximately 18.1% of silanol groups are deprotonated. At a pH of 5.75, only 13.9% are deprotonated. The adsorption potential at 5.75, therefore, would be 77% of that at pH 7.68. Figure 4.3b shows the resulting adsorption correction for pH 5.75. The maximum conductivity loss from adsorption at pH 5.75 was assumed to be 0.0064 S/m at pH 5.75.

![Figure 4.3](image_url)

**Figure 4.3.** Loss of pore fluid conductivity at 22.0°C over the first 1.5 hours after packing duplicate saturated clean sand samples with artificial groundwater amended with 10 mM KMnO$_4$ (a) at pH 7.68 and (b) adjusted for pH 5.75.

### 4.3.6. Tank Experiments

An acrylic tank was used to monitor MnO$_4^-$ movement through saturated sand two-dimensionally over time (Figure 4.4). The total outer dimensions of the tank were 22 inches (55.9 cm) long by 3 inches wide (7.6 cm) by 8 inches (20.3 cm) tall. Inside the tank were two 0.25-inch (0.64-inch) thick permeable walls placed 3 inches (7.6 cm) from each end. Each wall was constructed of two individual 1/8-inch (0.32 cm) thick acrylic pieces with holes drilled in them and a woven nylon mesh with 150 μm diameter openings between the two acrylic pieces. The two outer sections were used as fluid-only reservoirs, while the inner section contained saturated sand. The inner length and width for both reservoirs was 6.2 cm by 6.5 cm. The inner
length and width for the center section was 39.4 cm by 6.5 cm. A series of 32 small stainless-steel electrodes were fixed to one of the long walls on the inside of the sand-carrying section of the tank along lines A, B, C, and D shown in Figure 4.4, with wires leading to an external board that connected the electrodes to an ABEM LS resistivity data collection system. Lines A and B contained six electrodes each, while lines C and D contained 12 electrodes. All electrodes were spaced 3.0 cm apart.

Figure 4.4. Tank used for two-dimensional time-lapse experiments. Dashed lines A – D represent the electrode array lines. Sample Tube 2 is shown in its location during the no-TCE iterations. For the TCE iteration, the bottom of the tube was located at the same elevation as Sample Tube 1.

Two separate iterations of tank measurements were performed, one with artificial groundwater containing no TCE and one with artificial groundwater containing dissolved TCE. For both iterations, the tank was wet-packed by first adding the pre-mixed solution (either unamended artificial groundwater or artificial groundwater with dissolved TCE) and then adding the sand into the center section of the tank. The sand was repeatedly tapped with a glass rod while packing in order to remove bubbles and aid compaction. The sand was filled to a height of 17.8 cm for both iterations with an initial static fluid head of 16.7 cm. Three Viton tubes with an
inner diameter of 1/8 inch (0.318 cm) were emplaced in the sand approximately 7.0 cm from each reservoir and in the center of the tank (19.7 cm from either edge). The upstream tube was used for permanganate solution injection and the other two tubes for water sample collection. The bottom of the injection tube was 6.7 cm below the sand, and the bottom of the center sampling tube was 8.2 cm below the sand. During the non-TCE iteration, the downstream sampling tube was 9.7 cm below the sand. Because no permanganate reached that depth during the non-TCE iteration, the tube was moved to 8.2 cm below the sand for the TCE iteration. After packing, the tank was covered with plastic wrap for the no-TCE iteration and Parafilm and plastic wrap for the TCE iteration to limit evaporation and volatilization. For the TCE iteration, the tank was packed and maintained within a fume hood.

After filling the tank, fluid was pumped from the downstream reservoir to the upstream reservoir at a rate of 6.3 ml/min using two tubes connected to an Ismatec IPC peristaltic pump. Pumping resulted in an upstream head of 17.4 cm and a downstream head of 16.0 cm (gradient of 0.035 cm/cm). The heads stabilized after approximately 20 minutes. Based on a combined diffusion coefficient of $1.78 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ for KMnO$_4$ (Vanýsek, 2012) and an estimated pore size of 0.175 mm (because of the angular nature of the grains, the d$_{10}$ grain size was used to give a rough estimate), a pore-scale Péclet number of 2.2 was calculated. This Péclet number indicates that both diffusion and dispersion would impact the spread of the plume.

Background bulk conductivity measurements were collected a day after packing and starting the pump for the no-TCE iteration. For the TCE iteration, though, initial measurements were collected about 2.5 hours after packing and starting the pump to reduce volatilization. After collecting background measurements, 50 ml of artificial groundwater amended with 50 mM KMnO$_4$ was injected into the sand through the injection tube. Electrical conductivity data
were collected through the ABEM system immediately after injection and then every half-hour after injection for 5.5 hours during the non-TCE iteration and 4.5 hours during the TCE iteration. These data were inverted using Tikhonov regularization within COMSOL Multiphysics software in order to calculate a discretized conductivity over a three-dimensional matrix (performed by Dr. Deqiang Mao of the Colorado School of Mines Geophysics Department). The tomograms presented here are two-dimensional cross sections of the discretized data set representing the plane 10 cm from the wall with the electrodes.

4.4. Results

The evolution of electrical conductivity in saturated sand after TCE oxidation by MnO$_4^-$ was examined first in homogeneous batch samples and then in a two-dimensional tank after injection of a MnO$_4^-$ solution into pore fluid with and without TCE. The measurements and observations in each sample are described below.

4.4.1. Batch Experiments

As with the adsorption correction samples detailed in Section 3.4, measured bulk conductivity decreased after packing duplicate aqueous samples containing 10 mM KMnO$_4$ and 1.8 mM TCE in artificial groundwater that had just been mixed before packing. However, when the conductivity loss from adsorption was removed, no change in conductivity over the 8-hour time period was evident in both samples (Figure 4.5). Over that time period, the $2^{nd}$ order rate constants of Yan and Schwartz (2000) imply that the oxidation of TCE by MnO$_4^-$ should be complete. Although no reaction evidence was seen during 8 hours in the TCE oxidation samples, the bulk conductivity was significantly higher than the non-TCE oxidation values at all
measured time points, indicating the reaction occurred in less than 10 minutes. In the TCE oxidation sample that was measured for 23 hours, a secondary decrease in bulk conductivity not related to adsorption of ions into sand was evident starting at approximately 3.5 hours (Figure 4.6). This conductivity decrease occurred after most of the TCE oxidation reaction was complete.

![Graph](graph.png)

**Figure 4.5.** Change in bulk conductivity at 22.0°C over 8 hours in sand saturated with artificial groundwater mixed with 10 mM KMnO₄ and 1.8 mM TCE immediately before packing. The error bars represent the range of values observed in duplicate samples.

The formation factor measured in the TCE oxidation saturated sand samples was 3.875 ± 0.085. Based on this formation factor, the pore fluid conductivity between 20 minutes and 196 minutes after accounting for adsorption was 0.1734 ± 0.0011 S/m. This time period is relevant for the tank experiments shown in Section 4.4.2, which lasted approximately 4 hours. This fluid conductivity value compares favorably with the conductivity of 0.1745 S/m predicted using PHREEQC, assuming the measured pH of 5.75.
Figure 4.6. Change in bulk conductivity at 22.0°C over 23.3 hours in saturated sand, packed immediately after mixing artificial groundwater, 10 mM KMnO$_4$, and 1.8 mM TCE. Effect of ionic adsorption has been removed. Measurements are from one sample.

4.4.2 Tank Experiments

After injecting a MnO$_4^-$ solution into the two-dimensional tank described in Section 4.3.6, movement of the injected plume was observed, water samples were collected, and two-dimensional electrical surveys were performed. Each type of data are described in separate subsections below.

4.4.2.1 Visual Data

Because MnO$_4^-$ is purple in color, the movement of the plume was possible to visibly track beginning shortly after injection. In the non-TCE experiment, the KMnO$_4$ solution was injected slightly closer to the electrode side of the tank. The photographs were initially taken from the non-electrode side, but then photographs were taken on the electrode side (Figure 4.7). Only the electrode side photographs are displayed in Figure 4.7. Photographs of the TCE iteration were taken from the non-electrode side (Figure 4.8). During both iterations, the plume
moved as a mass in the direction of the gradient, with some hydrodynamic dispersion evident. In
the TCE iteration, the longitudinal hydrodynamic dispersion in one direction was observed to be
approximately 2.2 cm after 3 hours. Dispersion could not be accurately calculated in the non-
TCE iteration because an initial photograph was not available from the electrode side of the tank,
and dispersion on the electrode side may have been influenced by the electrode assembly.

The extent of diffusion predicted within 3 hours was 0.8 cm based on Equation 4.7, a
formation factor of 3.83 and porosity of 0.42, and a combined diffusion coefficient of \(1.78 \times 10^{-9}\)
m\(^2\)s\(^{-1}\) for KMnO\(_4\). The diffusion coefficients of the other dissolved ions were considered
negligible given the much larger concentration of KMnO\(_4\) compared to other solution
components. The remaining 1.4 cm of hydrodynamic dispersion (longitudinal) could then be
attributed to mechanical dispersion. This mix of diffusion and mechanical dispersion is
consistent with the Péclet number of 2.2 calculated in Section 4.3.6. While this mechanical
dispersion value is much smaller than the distance predicted using Equation 4.8 (6.1 cm), the
total observed hydrodynamic dispersion (2.2 cm) is reasonably close to the value predicted using
the Bacri et al. (1987) dispersion relationship observed at a Péclet number of 2 (\(D_L \approx \text{pore length}\)
\(\times v\), where \(D_L\) is hydrodynamic dispersion). This relationship yields a predicted hydrodynamic
dispersion of 2.0 cm.

The leading edge of the permanganate plume first reached the downstream reservoir
(32.4 cm from the injection point) approximately 3 hours and 40 minutes after injection for the
non-TCE iteration and 3 hours and 35 minutes after injection for the TCE iteration. The center
of mass took approximately 4 hours in either case to reach the edge. Based on a flow rate of 6.3
cm\(^3\)/min applied by the pump, a porosity of 0.42, and a cross-sectional area of 110 cm\(^2\), the
plume moved horizontally at about the same rate as the flow of water. During that time, the
Figure 4.7. Time lapse photography and electrical conductivity tomography of the permanganate plume as it moved across the tank during the no-TCE iteration. Photographs were taken approximately 15 minutes after the conductivity measurements. No electrode-side photograph was taken at injection. The tomograms were provided by Dr. Deqiang Mao, Colorado School of Mines Geophysics Department.
Figure 4.8. Time lapse photography and electrical conductivity tomography of the permanganate plume as it moved across the tank during the TCE iteration. Photographs were taken at about the same time as the conductivity measurements. The tomograms were provided by Dr. Deqiang Mao, Colorado School of Mines Geophysics Department.
plume (center of mass) sank approximately 2 cm during each run. Upon excavation of the tank samples, there was no evidence of any MnO$_4^-$ remaining in the sand except for a small concentrated zone immediately at the injection point caused by KMnO$_4$ solution that remained in the tube after injection.

4.4.2.2. Water Sampling

The TCE concentration in the reservoirs was calculated to be 1.60 ± 0.37 mM immediately prior to injecting KMnO$_4$ solution and 1.30 ± 0.10 mM just before the KMnO$_4$ solution reached the downstream reservoir (about 3.5 hours after injection). Although some of this loss may have resulted from back-diffusion of TCE into areas where it was oxidized by the MnO$_4^-$ plume, most of this measured TCE loss was likely from volatilization. Fluid conductivity remained consistent in the two reservoirs throughout both iterations (0.0461 to 0.470 S/m in the non-TCE iteration and 0.464 to 0.470 S/m in the TCE iteration). In both runs the conductivity increased by 0.002 to 0.004 S/m from injection to finishing the run, but this increase could be attributed to a slight increase in temperature. A small temperature gradient of 0.2 to 0.7°C developed between the two reservoirs from the pump heating the water (upstream reservoir warmer than downstream), resulting in a gradient of 0.0002 to 0.0009 S/m between the two reservoirs.

Water samples were collected as the plume crossed the sampling ports (Table 4.1). Samples taken at 2 hours in both iterations still had very high concentrations of MnO$_4^-$: 46.7 mM for the non-TCE iteration and 47.5 mM for the TCE iteration. A sample taken at 3 hours during the no-TCE run missed the plume because the tubing was set too low. The sample at 3 hours during the TCE iteration may have missed the center of the plume, but it still had a relatively
high TCE concentration (35.3 mM). These values are in agreement with visual observations that indicate that some hydrodynamic dispersion occurred, but the plume remained relatively concentrated toward the center. The TCE iteration sample taken from the first (centrally located) port at 4 hours and 45 minutes had no detectable TCE and the pH at that location had rebounded to the background level.

<table>
<thead>
<tr>
<th>Sample Tube</th>
<th>Time After Injection</th>
<th>[MnO₄⁻] (mM)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>No TCE</td>
<td>1</td>
<td>2 Hours</td>
<td>46.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3 Hours</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3 Hours</td>
<td>0</td>
</tr>
<tr>
<td>TCE</td>
<td>1</td>
<td>2 Hours</td>
<td>47.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3 Hours</td>
<td>35.3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.75 Hours</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4.1. Water samples collected from Sample Tubes 1 and 2.

Comparative mass balances between injected and recovered MnO₄⁻ are presented in Tables 4.2 and 4.3 for both tank iterations. The differences in reservoir volumes reflect that sampling occurred while still pumping for the non-TCE iteration and after pumping was shut off for the TCE iteration. Approximately 96.8% of the injected molar mass of MnO₄⁻ was accounted for in the tank when no TCE was present. After the TCE iteration, approximately 90.6% of the original molar mass was calculated to be present. If 50 ml of MnO₄⁻ solution is assumed to have contacted 50 ml of 1.6 mM TCE (0.08 mmol TCE), that would equate to a loss of 0.16 mmol MnO₄⁻, assuming complete reaction. Adding that 0.16 mmol to the MnO₄⁻ recovered from the tank would result in a recovery of 97.0%, nearly identical to the recovery from the non-TCE iteration.
Table 4.2. Permanganate recovery at the end of pumping with no TCE in the artificial groundwater.

<table>
<thead>
<tr>
<th>Location</th>
<th>$[\text{MnO}_4^-]$ (mM)</th>
<th>Volume (mL)</th>
<th>Mass (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream Reservoir</td>
<td>0.047</td>
<td>713.3</td>
<td>0.034</td>
</tr>
<tr>
<td>Downstream Reservoir</td>
<td>3.277</td>
<td>648.8</td>
<td>2.126</td>
</tr>
<tr>
<td>Injection Tube</td>
<td>50</td>
<td>0.14</td>
<td>0.007</td>
</tr>
<tr>
<td>Water Removed from Tube 1, 2 Hrs</td>
<td>46.7</td>
<td>3.82</td>
<td>0.187</td>
</tr>
<tr>
<td>Water Remaining in Tube 1, 2 Hrs</td>
<td>46.7</td>
<td>0.18</td>
<td>0.008</td>
</tr>
<tr>
<td>Water Removed from Tube 1, 3 Hrs</td>
<td>0.28</td>
<td>3.82</td>
<td>0.001</td>
</tr>
<tr>
<td>Water Remaining in Tube 1, 3 Hrs</td>
<td>0.28</td>
<td>0.18</td>
<td>0.000</td>
</tr>
<tr>
<td>Pumping Tubes</td>
<td>3.277</td>
<td>20.1</td>
<td>0.066</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Total Recovered Mass (mmol)</th>
<th>Injected Mass (mmol)</th>
<th>% Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.42</td>
<td>2.50</td>
<td>96.8%</td>
</tr>
</tbody>
</table>

Table 4.3. Permanganate recovery at the end of pumping with TCE in the artificial groundwater.

<table>
<thead>
<tr>
<th>Location</th>
<th>$[\text{MnO}_4^-]$ (mM)</th>
<th>Volume (mL)</th>
<th>Mass (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upstream Reservoir</td>
<td>0</td>
<td>669</td>
<td>0.000</td>
</tr>
<tr>
<td>Downstream Reservoir</td>
<td>2.88</td>
<td>669</td>
<td>1.927</td>
</tr>
<tr>
<td>Injection Tube</td>
<td>50</td>
<td>0.14</td>
<td>0.007</td>
</tr>
<tr>
<td>Water Removed, Port 1</td>
<td>47.5</td>
<td>3.82</td>
<td>0.181</td>
</tr>
<tr>
<td>Water Remaining in Port 1 Tube</td>
<td>47.5</td>
<td>0.18</td>
<td>0.009</td>
</tr>
<tr>
<td>Water Removed, Port 2</td>
<td>35.3</td>
<td>3.82</td>
<td>0.135</td>
</tr>
<tr>
<td>Water Remaining in Port 2 Tube</td>
<td>35.3</td>
<td>0.18</td>
<td>0.006</td>
</tr>
<tr>
<td>Pumping Tubes</td>
<td>0</td>
<td>20.1</td>
<td>0.000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Total Recovered Mass (mmol)</th>
<th>Injected Mass (mmol)</th>
<th>% Recovered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.27</td>
<td>2.50</td>
<td>90.6%</td>
</tr>
</tbody>
</table>

4.4.2.3. Bulk Conductivity Tomography

As expected, increased bulk electrical conductivity occurred in the same general location as the visually observed purple plume (Figures 4.7 and 4.8). Although the electrical conductivity tomograms corresponded well with the visible movement of the plume, the conductivities reported in the tomograms for the plume area are not very close to the actual conductivities. For the no-TCE iteration, where no reaction affected the conductivity, the fluid conductivity calculated from the water sample was approximately 0.559 S/m. Based on an estimated
formation factor of 3.8, the bulk conductivity should be around 0.147 S/m. The highest conductivity in the tomogram, however, was only 0.0092 S/m. Background conductivities were 0.0025 S/m in the tomogram and 0.012 S/m estimated by fluid conductivity measured in the reservoirs. The tomograms also show a bias toward higher conductivity values as the plume crosses the two vertical electrode lines. Although the inversion could not resolve the absolute conductivity, the tomograms do show that the conductivities returned to background values as the plume passed by an area. This lack of residual elevated conductivity indicates that no residual MnO$_4^-$ or reaction products were left behind and is in agreement with visual and water sample evidence.

4.5. Discussion

The batch samples confirmed that the oxidation reaction between TCE and MnO$_4^-$ occurs too quickly for reaction progress to be monitored with conductivity measurements at any sampling rate that would be relevant in a field situation. The end result of the reaction on conductivity could, however, be detected. The loss of electrical conductivity that appears to begin around 3.5 hours occurs too late to be explained by oxidation of carboxylate or protonation. Instead, the loss is most likely the result of adsorption of ions by MnO$_2$, which forms as the MnO$_4^-$ is reduced. Because of the short duration of the tank experiments presented here, adsorption of ions by MnO$_2$ can be assumed to have a negligible effect on conductivity. This loss could be significant, though, in field applications where monitoring is likely to occur over a period of days or weeks. Additional experiments would be needed to verify that ionic adsorption onto MnO$_2$ is the source of the conductivity loss and to determine concentration or mass-dependent adsorption isotherms.
Based on the combination of visual inspection, water sampling, and electrical measurements, the MnO$_4^-$ plume appeared to move as a mass with the groundwater flow with about 2.2 cm of hydrodynamic dispersion (mechanical dispersion plus diffusion) observed after three hours. The low dispersion compared to most values observed at larger scales (even after removing the distance effect of dispersivity) is a result of the porous media in the tank being very homogeneous. Therefore, mechanical dispersion would be dominated by microscopic-scale dispersion. No significant heterogeneity was present to introduce macroscopic-scale dispersion except at the wall containing the electrode assembly. In a more heterogeneous formation, longitudinal hydrodynamic dispersion over three hours would likely approach the 6.9 cm calculated in Section 4.4.2.1, leading to a total plume length of nearly 15 cm. Sinking of MnO$_4^-$ from the density gradient may have had some impact on plume enlargement, as well, and may be a significant factor in plume dispersal under much slower natural groundwater gradients.

The discrepancy between fluid conductivities estimated by water sampling and the conductivities calculated in the inversion results highlights the shortcomings of Tikhonov regularization. The boundary between the plume and the surrounding groundwater appears sharper in the photographs than in the tomograms. Also, the apparent electrical conductivity increases as the plume approaches each vertical electrode set and decreases when the plume is at the farthest point between the two vertical electrode sets (in the middle of the tank). Coupling the raw resistivity data with additional information, such as point fluid conductivities or permanganate concentrations, would be necessary to improve the conductivity resolution in the tomograms. However, the tomograms did have sufficient resolution to accurately depict the movement of the permanganate plume.
The tomography, along with visual plume inspection and water sampling, did provide insight into how plume movement and the TCE oxidation reaction proceeds. The cores of the MnO$_4^-$ plumes during both the non-TCE and TCE iterations had similarly high MnO$_4^-$ concentrations (93-95% of the injected concentration) two hours after injection. The measured MnO$_4^-$ concentration was actually slightly higher during the TCE iteration. Most TCE oxidation likely occurred at the edges of the plume. The injection appeared to displace the TCE plume and replace it with injectate. H$^+$ ions were able to diffuse into the plume core based on water sample pH, though. A larger-scale experiment enabling water samples of sufficient size to measure fluid conductivity and ion concentrations would be needed to fully determine where within the plume oxidation did occur.

Based on the MnO$_4^-$ mass balance, the same volume of TCE was oxidized as solution was injected, assuming a TCE concentration of 1.6 mM (the approximate TCE concentration in the tank at the time of MnO$_4^-$ injection). Furthermore, based on the quick pH recovery observed in the TCE iteration, the TCE oxidation reaction products generally appear to have moved with the MnO$_4^-$ plume. Therefore, at the time-scale of the tank experiment, the plume resembled in many ways a plug-flow reactor. Based on an assumption of plug flow, an average electrical conductivity for the plume may be estimated in the same manner as in batch reactors, with a correction based on plume size growth.

The following is a proposed estimation of the average conductivity within the plume using the TCE iteration as an example. During the experiment, about 1.6 mM TCE was oxidized by 50 mM MnO$_4^-$, and the pH was around 5.75 based on water sampling. The average plume content after reaction, then, would be as listed in Table 4.4. Based on this aquifer composition, the average conductivity should be around 0.605 S/m, not accounting for hydrodynamic
dispersion. If the plume were to grow in volume by about 20% because of hydrodynamic dispersion, then the average bulk conductivity may be around 0.506 S/m \((1 \times 0.605 \text{ S/m} + 0.2 \times 0.012 \text{ S/m}) / 1.2\). Adsorption is neglected because injection occurred more than two hours after the sand was in contact with the pore fluid, so adsorption sites would already be full. In fact, the reduction of pH could cause a slight increase in conductivity of about 0.002 S/m from desorption of ions from the sand based on the adsorption corrections calculated in Section 3.4. This impact is negligible compared to the estimated plume conductivity.

**Table 4.4.** Estimated average groundwater composition within the plume after injection of artificial groundwater amended with 50 mM KMnO\(_4\) into artificial groundwater containing 1.6 mM TCE.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>(2.09 \times 10^{-6})</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>(1.18 \times 10^{-3})</td>
</tr>
<tr>
<td>K(^+)</td>
<td>(5.00 \times 10^{-3})</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>(9.90 \times 10^{-3})</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>(1.98 \times 10^{-4})</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>(1.18 \times 10^{-3})</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>(7.20 \times 10^{-3})</td>
</tr>
<tr>
<td>MnO(_4^-)</td>
<td>(4.68 \times 10^{-2})</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>(8.57 \times 10^{-5})</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>(4.01 \times 10^{-3})</td>
</tr>
</tbody>
</table>

Because of the small scale and limited duration of the experiments, open questions remain related to modeling where conductivity changes would occur within the plume and the actual extent of mixing that occurs between the plume and surrounding aquifer. In the tank experiment, interaction between MnO\(_4^-\) and TCE appeared to be limited to the outside portion of the plume and a small zone surrounding the plume where hydrodynamic dispersion occurred. The movement of the MnO\(_4^-\) plume did not appear to significantly increase the amount of TCE.
exposed to MnO$_4^-$ because all dissolved groundwater constituents moved at the same rate as the general groundwater flow.

4.6. Conclusion

Although the inversion of the electrical conductivity data from the tank experiment using Tikhonov regularization was unable to resolve the actual conductivity values within the MnO$_4^-$ plumes, the tomograms were effective in tracking the location and movement of the MnO$_4^-$.

Using the combination of visual inspection, water sampling, and electrical conductivity imagery, it was possible to estimate the growth of the plume from diffusion and dispersion and to determine the mass of TCE that was oxidized by the plume as a whole. Consequently, an average conductivity for the plume as a whole was possible to estimate. However, conductivity distribution within the plume could not be determined.

Modeling of the expected conductivity within the plume in a similar manner to what is described in Chapters 2 and 3 would likely improve the inversion of the conductivity data, allowing more realistic recovery of actual conductivities at a given location. Future tank experiments should be performed combining the electrical conductivity measurements with both forward modeling of the redox chemistry and solute transport modeling to attempt to improve the inversion results. Additionally, larger scale tank experiments allowing more fluid sampling are recommended to test the results of the inversion and enable further examination of fluid conductivity and oxidation product distribution across a plume. Eventually, tank experiments should be performed in heterogeneous media to test the effectiveness of the improved time-lapse conductivity tomography and inversion in a system more representative of field conditions.
CHAPTER 5. EVALUATING THE SUCCESS OF THE SUPERFUND COMMUNITY ADVISORY GROUP PROGRAM THROUGH EFFECTS ON CLEANUP TIME AND ACHIEVEMENT OF SOCIAL GOALS

Abstract. The United States Environmental Protection Agency (U.S. EPA) started its Superfund Community Advisory Group (CAG) program in 1994, largely as a response to an increasing number of community protests against the agency’s hazardous waste site cleanup decisions. CAGs have represented approximately 67 sites on the agency’s National Priority List (NPL) since the program began. Despite the EPA’s motivation to reduce delays due to community protest, there has been a correlation between CAG involvement and increased time needed to reach final remedy selection, construction completion, and deletion from the NPL. However, case studies of seven CAGs demonstrate that CAGs may still benefit from the program through the achievement of social goals. Five out of the seven CAGs in the study substantially achieved five social goals originally proposed by Thomas Beierle: informing and educating the public, incorporating public values into decision-making, improving the substantive quality of the decisions, increasing trust in institutions, and reducing conflict. While these five successful CAGs varied in size and composition, they each were able to extend the reach of their influence beyond their organization members and the cleanup site to provide benefits to the community that otherwise would not be achieved through technological solutions alone.

5.1. Introduction

Opportunity for public input into Superfund site cleanup has been mandated since the original writing of the Comprehensive Emergency Response, Compensation, and Liability Act
(CERCLA) in 1980, which created the Superfund program. Section 117 of CERCLA requires notice of remedial plans, an opportunity for public response, and public meetings. Throughout the history of the program, both Congress and the EPA have instituted reforms designed to increase community involvement. As part of the Superfund Amendments and Reauthorization Act (SARA) of 1986, Congress authorized technical assistance grants (TAGs) to give communities financial assistance to help them participate in cleanup decision-making. In 1994, the EPA began officially recognizing community advisory groups (CAGs). At that time, the EPA also assigned regional staff to the position of Community Involvement Coordinator and issued *Guidance for Community Advisory Groups at Superfund Sites* (U.S. EPA, 1995). By 1997, the EPA had sanctioned 33 community advisory groups (U.S. EPA, 1998a). Currently, approximately 67 of the 1,674 sites that have been added to the National Priority List (including sites that have been deleted) currently have or once had CAGs (U.S. EPA, 2011, 2000, 1998b, 1996).

The Superfund CAG program was largely a response to two different issues that arose in the early 1990s: an increase in citizen protest against EPA-accepted cleanup plans and an increasingly active environmental justice movement. In 1993, the EPA stated in its *Superfund Administrative Improvements* report that lack of support for cleanup operations from citizen groups was a critical problem in the Superfund program (U.S. EPA, 1993). Residents of New Bedford, Massachusetts demonstrated just how large this problem could be. In 1990, the EPA signed a record of decision (ROD) accepting dredging and incineration of PCB-contaminated harbor sediments as the method of cleaning New Bedford Harbor (U.S. EPA, 1990). However, in 1991 protesters threatened to block construction of the incinerator, and in 1993 the town itself passed a bylaw preventing further cleanup operations (Finney and Polk, 1995). Prior to the
EPA’s decision to sign the ROD, the New Bedford mayor’s office had actually formed its own citizen group that accepted the remedy. That group was criticized, though, as not being representative of the community (Finney and Polk, 1995). Eventually, another community advisory group was formed, which participated in mediation proceedings with the EPA to agree on a treatment plan. It took until 1999 for the EPA to sign an amended ROD (U.S. EPA, 1999).

Concurrently, the EPA was being pressured by a growing environmental justice movement. Throughout the 1980s and 1990s a growing body of research suggested that minority and low income communities had greater exposure to hazardous waste sites and toxic chemicals than the general population (Brown, 1995; Commission for Racial Justice, 1987; Cutter, 1995). In July 1990, the EPA created an environmental equity workgroup to review the evidence of environmental inequity and to review and suggest changes to EPA policies that might have contributed to such inequity (Roque, 1993). In February 1994, President Clinton signed Executive Order 12898, which directed federal agencies to address environmental justice in minority and low-income populations. That same month, the EPA co-sponsored the Environmental Justice Conference with the Centers for Disease Control, the National Institute for Environmental Health Sciences, the National Institute for Occupational Safety and Health, and the Agency for Toxic Substances and Disease Registry. Community activists seized control of the conference, staging a walkout and opening the microphone to citizens who then criticized the EPA and other government agencies for their roles in perpetuating environmental injustice toward minorities (McFarling, 1994).

While the growing citizen involvement in Superfund site decision making could be seen as a positive in terms of increased democratic governance, from the EPA’s perspective, citizen groups were becoming a disruptive force to the progress of site cleanup. For the EPA to
continue its mission of cleaning the country’s most hazardous contamination sites, the Superfund program needed to become a partner to communities instead of an adversary. The EPA hoped that the establishment of the community advisory group program would open up communications with local communities and allow issues to be worked out sooner, avoiding long-term delays (U.S. EPA, 1993). Although a number of studies have measured the success of environmentally-related community advisory processes (Finney and Polk, 1995; Lynn and Busenberg, 1995; Murdock et al., 2005; Santos and Chess, 2003), most have looked at the immediate outcomes. However, because this program has been in existence for twenty years, it is now possible to examine the long-term benefits that participation in the EPA’s community advisory group program may have brought to both the communities and to the EPA.

5.2. Measuring the Success of Community Advisory Groups

The success of the CAG program could be measured in numerous ways. From the point of view of the EPA, the most obvious method may be to consider how cleanup progress has been affected at sites for which CAGs have been formed. Has the cleanup progressed more quickly than at non-CAG sites? Has cleanup been more effective? These questions are largely a matter of efficient and effective technology implementation. While contaminant removal may be the EPA’s primary focus and is certainly an important concern for impacted residents, such questions may not fully address the needs and values of the community. For community members, successful CAG participation may depend on more than simply selecting the most effective technology to remove waste. Residents may have concerns about how a certain remedy may impact their communities during implementation, or they may have final goals for the site that go beyond achieving specific cleanup levels. This study examines not only the effects of
CAG involvement on site cleanup progress, but also whether CAG participation has provided broader benefits beyond removal of hazardous waste.

5.2.1. Measuring Cleanup Progress

Measuring progress at Superfund sites can be difficult. The EPA defines six major site cleanup milestones: proposal to the National Priority List (NPL), final NPL listing, first cleanup action completion, final remedy selection, construction completion, and deletion from the NPL (U.S. EPA, 2014a). These milestones are defined in Table 5.1. Progress is often nonlinear, with activities toward multiple milestones usually occurring simultaneously. Initial cleanup actions such as contaminated soil removal may occur before final listing and while remedial investigations and remedy designs are being performed. Also, once listed on the NPL, many sites are divided into operable units (OUs) based on location and/or contaminated media. Different OUs at a single site often reach these milestones at different times. Furthermore, a remedy can be found to be ineffective after final remedy selection or after construction completion, and a new remedy may be selected and installed. While imperfect, however, these milestones offer the best available measurement of cleanup progress reached at Superfund sites. In Section 3, achievement of the EPA site cleanup milestones will be compared among sites that have CAGs and sites that do not have CAGs.

5.2.2. Evaluating the Public Participation Processes

Measuring the success of community involvement in Superfund decision making is even less concrete than measuring the progress of cleanup at a contamination site. Judging public participation depends upon the framework that is used to evaluate the forum. Such frameworks
Table 5.1. Major site cleanup milestones as defined by the U.S. EPA (2014a).

<table>
<thead>
<tr>
<th><strong>Milestone</strong></th>
<th><strong>Definition</strong></th>
</tr>
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<tbody>
<tr>
<td>Proposal to National Priority List (NPL)</td>
<td>Sites are proposed to the NPL through the issuance of a proposed rule in the Federal Register. EPA accepts and responds to comments on a site, and if a site continues to meet criteria for Final listing, will be listed as Final on the NPL.</td>
</tr>
<tr>
<td>Final Listing on NPL</td>
<td>A site that has been proposed to National Priorities List is &quot;final&quot; when it has been formally added to the National Priorities List.</td>
</tr>
<tr>
<td>First Cleanup Action Initiated</td>
<td>The first physical cleanup action underway at a site, consisting of either a removal or remedial activity.</td>
</tr>
<tr>
<td>Final Remedy Selection</td>
<td>The final remedy selected is a cleanup milestone which focuses on the measure(s) that EPA has determined will best address, correct, or remediate the contamination concerns at the site. The final remedy is documented in the last planned Record of Decision (ROD) document at the site. The ROD provides the justification for the remedial action (treatment) chosen at a Superfund site. It also contains site history, site description, site characteristics, community participation, enforcement activities, past and present activities, contaminated media, the contaminants present, scope and role of response action, and the remedy selected for cleanup.</td>
</tr>
<tr>
<td>Construction Completion</td>
<td>A site is categorized as Construction Completion by meeting one of the following criteria: any necessary physical construction is complete, whether or not final cleanup levels or other requirements have been achieved; EPA has determined that the response action should be limited to measures that do not involve construction; or the site qualifies for Deletion from the NPL.</td>
</tr>
<tr>
<td>Deletion from NPL</td>
<td>Deletion of sites from the National Priorities List (NPL) may occur once all response actions are complete and all cleanup goals have been achieved. EPA has the responsibility for processing deletions with concurrence from the State. EPA can also delete portions of sites that meet deletion criteria.</td>
</tr>
</tbody>
</table>

can often be classified based on whether the evaluation focuses on the processes that were used or instead the outcomes that resulted from the community involvement (Chess and Purcell, 1999). Additionally, both process and outcome goals may differ depending on whether they are based on theory or based on the preferences of the participants (Santos and Chess, 2003).
Because each framework has its own strengths and weaknesses, the use of multiple frameworks can improve the evaluation of community group participation (Santos & Chess, 2003).

Participation process frameworks focus on how public participation should occur. Users of such frameworks judge public forums based on whether these forums use procedures that advance or inhibit certain ideals. Many common theoretical frameworks for judging public participation draw from Habermas’s theories of ideal speech and communicative action (Santos and Chess, 2003; Webler and Tuler, 2000). Habermas (1990) proposed that the following conditions must be present for ideal speech to occur:

1. Every subject with the competence to speak and act is allowed to take part in a discourse.
2a. Everyone is allowed to question any assertion whatever.
2b. Everyone is allowed to introduce any assertion whatever into the discourse.
2c. Everyone is allowed to express his or her attitudes, desires and needs.
3. No speaker may be prevented, by internal or external coercion, from exercising his or her rights as laid down in (1) and (2).

Two main principles that arise in the ideal speech situation are fairness and competence. Renn et al. (1995) and Webler and Tuler (2000) adopt these principles in their normative theory of participation, but modify the idea of competence to be a characteristic of the participation process rather than of the individual participant. Fairness entails that all stakeholders are allowed to attend, initiate discourse, participate in the discussion, and participate in the decision making (Webler and Tuler, 2000). Competence requires that all participants have equal access to information so that Habermas’s (1985) validity claims of comprehensibility, factual trueness,
objectivity, and sincerity can be investigated (Webler and Tuler, 2000). Implied in the idea of competence is that participants have access to the tools necessary to understand and process the information they are given.

Participants themselves may have different views of what defines an appropriate participation process. Webler and Tuler (2006) identify four disparate viewpoints that may influence what participants would want out of a participation process: science-centered stakeholder consultation, egalitarian deliberation, efficient cooperation, and informed collaboration. A science-centered stakeholder consultation seeks to consistently progress toward achieving practical outcomes through a science-led process and de-emphasizes or ignores building trust or social capital. An egalitarian deliberation attempts to even out power among participants by giving equal access to information and control over the agenda. Efficient cooperation begins with the assumption that agencies already possess legitimacy. Focus is on strong leadership and establishing rules for participation that ensure an efficient process. An informed collaboration is characterized by the opposite initial assumption of efficient cooperation. In an informed collaboration, agencies aim to develop trust and obtain legitimacy while providing equal access to high quality information. Rather than discrete viewpoints, these process preferences represent a spectrum of preference emphases toward efficiency, equality of control and influence, science-centrism, and value-centrism. Emphasizing one ideal requires tradeoffs of others (Webler and Tuler, 2006).

In addition to looking at the participation process, citizen forums can be evaluated based on the results that they produce. Stakeholders themselves may be more interested in the outcomes of a public participation forum than in the processes (Santos and Chess, 2003). Outcome goals can often differ depending on the stakeholder’s interests or expectations of the
Citizens usually want to have the ability to influence the decisions being made, while agencies might be motivated by gaining community acceptance for a specific proposal or fostering trust in the agency (Murdock et al., 2005). Beierle (1999) argues that rather than look at results based on stakeholder interests, public participation should be judged based on the achievement of broader social goals. He suggests six goals for public decision-making forums:

1. informing and educating the public;
2. incorporating public values into decision-making;
3. improving the substantive quality of the decisions;
4. increasing trust in institutions;
5. reducing conflict; and
6. maintaining cost-effectiveness of the public participation process (Beierle, 1999).

Although oriented toward the achievement of specific results, Beierle’s social goals framework incorporates aspects of Renn, Webler and Tuler’s framework for successful participation processes, especially in goals one and two. Goal #1, informing and educating the public, mirrors the idea of competence. A concerted effort to inform and educate the public is usually necessary to develop a competent citizen group capable of influencing the decision-making process (Hartley, 2005). Goal #2 of incorporating public values, assumptions, and preferences into decision-making is very similar to the process goal of fairness. Webler and Tuler (2000) refer specifically to the full participation of the public in meetings, while Beierle (1999) envisions that decisions fully account for the wishes of the public. While many frameworks for assessing community advisory processes are short term in focus, looking at the mechanics of the meetings themselves, Beierele’s social goals framework is suitable for examining long-term impacts of the community advisory processes. In addition to examining the effect of CAGs on site cleanup progress (Section 3), an evaluation of the achievement of Beierele’s social goals by a selection of EPA-sanctioned CAGs is presented in Section 4.
5.3. **Milestone Completion at Superfund Sites With and Without CAG Involvement**

Using information from the EPA’s Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) (U.S. EPA, 2013a), a database was created containing all sites on the NPL and the dates on which each site was listed on the NPL, had the first cleanup activities initiated, had the final remedy selected, reached construction completion, and was deleted from the NPL. The number of days taken to reach four cleanup milestones (initial cleanup activities, final remedy selection, construction completion, and deletion from the NPL) was calculated for each site with a start date of final listing on the NPL. At the time of this study, the EPA was in the process of instituting a new database system (the Superfund Enterprise Management System), and data in the CERCLIS system was last updated November 12, 2013 (U.S. EPA, 2013).

Superfund sites that have EPA-sanctioned CAGs and sites that do not have CAGs were compared to see if the presence of a CAG affected the amount of time it took to reach the cleanup milestones. CAGs were initially identified from the EPA’s Community Advisory Group website (http://www.epa.gov/superfund/community/cag). However, since this site only lists CAGs that are currently active, additional CAGs were identified through case studies published by the EPA and its regional offices (U.S. EPA, 2000, 1998b, 1996). While it is possible that a few CAGs have been missed, it is unlikely that this number is very large. The EPA states that 66 CAGs are currently active (U.S. EPA, 2011), although some of these CAGs are for sites that were not yet listed on the NPL as of the final CERCLIS update.

Two different data sets were examined to compare the amount of time it took to reach cleanup milestones. First, the times were compared using the entire data set of NPL sites. Looking at all Superfund sites could bias the comparison, however, because the first CAGs were
not recognized by the EPA until 1994. Sites that began cleanup activities before this time, especially in the 1980s, would have longer to reach cleanup milestones. The average listing date for all sites on the NPL is August 1990, whereas the average listing date for sites with CAGs is July 1996. For this reason, a second comparison was made using only sites that were listed on the NPL starting in 1991. This brings the average listing date closer for the two groups, giving the non-CAG sites an average listing date of July 2001 and the CAG sites an average listing date of August 2002. Although the EPA began officially certifying CAGs in 1994, 21 Superfund sites with CAGs have NPL listing dates prior to 1991. Therefore, both the full and abridged sample sets are examined below.

Of the 1,606 hazardous waste sites without a CAG that have been added to the NPL, 1,171 sites (73%) have reached final remedy selection, 1,123 sites (70%) have reached construction completion, and 355 sites (22%) have been deleted from the NPL. The overall percentage of sites with CAG involvement that have reached these milestones is much smaller; 25% have reached construction completion and only three sites out of the 67 have been deleted from the NPL (Figure 5.1). When only sites listed after 1990 are examined, a larger percentage of sites without CAGs still have reached those three milestones when compared to sites with CAGs (Figure 5.2). However, the difference between CAG and non-CAG sites is smaller, especially for the percentage of sites reaching final remedy selection. The EPA has selected the final remedy at 43% of sites without a CAG and 33% of sites with a CAG. The percentage of sites listed after 1990 reaching construction completion is much greater for sites that did not have CAG involvement even when the adjustment for date is made (35% of sites without a CAG compared to 14% of sites with a CAG for sites listed after 1990). Of the sites that reached each of the cleanup milestones, sites without CAGs reached final remedy selection and construction
completion in fewer days on average than sites with CAGs (Figures 5.3 and 5.4). The variation in the number of days needed to reach the cleanup milestones from site to site was large, though, so the difference in time between sites with and without CAGs cannot be determined to be significant. This variance indicates that factors beyond whether or not a site has a CAG may influence the amount of time it takes for a cleanup site to reach the progress milestones.

**Figure 5.1.** Percentage of Superfund sites attaining cleanup milestones (full sample set).

![Graph showing percentage of Superfund sites reaching cleanup milestones](image1)

**Figure 5.2.** Percentage of Superfund sites listed on the NPL after 1990 attaining cleanup milestones.

![Graph showing percentage of Superfund sites listed on the NPL after 1990 reaching cleanup milestones](image2)
Figure 5.3. Average number of days elapsed between NPL site listing and attainment of site cleanup milestones (full sample set). Error bars represent one standard deviation. Only sites that reached the given milestones are considered.

Figure 5.4. Average number of days elapsed between NPL site listing and attainment of site cleanup milestones for sites listed after 1990. Error bars represent one standard deviation. Only sites that reached the given milestones are considered. No sites listed after 1990 with a CAG have been deleted from the NPL.

While most milestones were reached more quickly when no CAG was involved, it is interesting to note that the one milestone that was reached more quickly at sites with CAGs was the initial cleanup action. On average, NPL sites that have registered CAGs had cleanup actions initiated two days prior to the site being added to the NPL. On the other hand, non-CAG sites
had an initial cleanup action performed 1,067 days after NPL listing (Figure 5.3). Because of the large variability among sites, this statistic on its own may not be an indicator of much. In most cases, CAGs did not form until after this first cleanup action, so they cannot be credited with increasing the speed at which it occurred. The speed of the first cleanup action was also not linked to the site’s hazard ranking system (HRS) score, an estimate of the potential hazard of the site developed by the EPA prior to listing the site on the NPL. Sites with a CAG have an average hazard ranking score of 49.6 compared to 42.9 for sites that did not have a CAG (Figure 5.5), but this may not be a significant difference based on the overlapping standard deviations.

![Figure 5.5. Comparison of average hazard ranking system (HRS) scores between NPL sites that have CAG involvement and sites that do not have CAG involvement. Error bars represent one standard deviation.](image)

Based on Figures 5.1 through 5.4, it can be concluded that CAGs as a whole did not improve the speed at which cleanup occurred. To the contrary, it is possible that they had a negative influence on cleanup rate; however, given the large standard deviations for the times to reach all cleanup milestones, how much of a factor CAG involvement was in the observed slowdown is difficult to determine. Given that CAGs do not positively influence the speed of Superfund site cleanup, it is necessary to look at other possible long-term benefits that may have resulted from CAG involvement.
5.4. Social Goals Achieved Through CAG Involvement

This section examines how well seven CAGs (Table 5.2) achieved five of Beirele’s six social goals: incorporation of public values, improvement of the substantive quality of decisions, conflict resolution, institutional trust building, and public education. Cost effectiveness of the participation processes were not evaluated in this study. Five of these CAGs (Sebasticook Committee for a Clean Environment, Waukegan Harbor Citizens Advisory Group, Omaha Lead Site Community Advisory Group, Pine Street Barge Canal Coordinating Council, CCI Concerned Citizens Group) were largely successful in achieving the five social goals, while two (Aerojet Community Advisory Group, Raymark Advisory Committee) were less successful. Communities represented by these CAGs varied in size, as did the size of the CAGs themselves.

5.4.1 Eastland Woolen Mill, Corinna, Maine

The Eastland Woolen Mill Superfund site is located in Corinna, Maine, at the former location of a wool mill that served as the largest employer for the town until it closed in 1996. The mill had disposed of wastewater containing chlorobenzenes into floor drains that led into the soil and into the East Branch of the Sebasticook River, which flowed beneath the mill. The site was listed on the NPL in July 1999. The Sebasticook Committee for a Clean Environment first assembled in 1999 with the help of a Technical Assistance Grant (TAG) from the EPA and consisted of members of the community, including a member of the town’s Revitalization Committee (Seekins, 1999). The TAG made it possible for the committee to hire an outside consultant to interpret EPA documents and represent the committee at EPA meetings.

One of the major obstacles for cleaning the mill site also proved to be an opportunity for the community to have an important role in the cleanup. The former mill occupied much of
Table 5.2. Community Advisory Groups discussed in this study.

<table>
<thead>
<tr>
<th>Community Advisory Group Name</th>
<th>Superfund Site(s) Represented</th>
<th>Location</th>
<th>Year Listed on the NPL</th>
<th>Last Milestone Reached</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sebasticook Committee for a Clean Environment</td>
<td>Eastland Woolen Mill</td>
<td>Corinna, Maine</td>
<td>1999</td>
<td>Construction Complete</td>
</tr>
<tr>
<td>Omaha Lead Site Community Advisory Group</td>
<td>Omaha Lead</td>
<td>Omaha, Nebraska</td>
<td>2003</td>
<td>Final Remedy Selected</td>
</tr>
<tr>
<td>Pine Street Barge Canal Coordinating Council</td>
<td>Pine Street Canal</td>
<td>Burlington, Vermont</td>
<td>1983</td>
<td>Final Remedy Selected</td>
</tr>
<tr>
<td>CCI Concerned Citizens Group</td>
<td>Chemical Commodities, Inc.</td>
<td>Olathe, Kansas</td>
<td>1994</td>
<td>Construction Complete</td>
</tr>
<tr>
<td>Aerojet Community Advisory Group</td>
<td>Aerojet General Corp.</td>
<td>Rancho Cordova, California</td>
<td>1983</td>
<td>1st Cleanup Action Initiated</td>
</tr>
<tr>
<td>Raymark Advisory Committee</td>
<td>Raymark Industries, Inc.</td>
<td>Stratford, Connecticut</td>
<td>1995</td>
<td>1st Cleanup Action Initiated</td>
</tr>
</tbody>
</table>
Main Street in the center of town. In order to help make cleanup easier, this road would need to be rerouted along with part of the East Branch of the Sebasticook River. The town coordinated with the EPA as well as the Maine Department of Environmental Protection and the Maine Department of Transportation to develop a plan for the relocation. Additionally, the town needed to decide how the site would be redeveloped because that would determine how the soil, which was excavated and treated on site, would be replaced after treatment (Mack, 2003). One community member commented about the opportunity to change the downtown landscape by saying, “We have a clean sheet of paper to start planning a new village center and this is a unique opportunity...some of us envision a New England village center with retail services, antiques and crafts, home or micro businesses, possible B&Bs and offices for professional services, all overlooking a river/lakeside environment.” (U.S. EPA, 2002).

The CAG’s main role at this site was to administer the TAG and also to act as a liaison between all of the different groups involved in the cleanup process. The group was initially chaired by Lynn Chianchette (Seekins, 1999), but soon after the group’s formation the chairperson and voice to the community became Ken Dow. He used his blog website, The Cattail Press, to chronicle the history of the cleanup and provide information to the Corinna population (Dow, 2003). A full archive of Superfund site articles and photos posted from September 1999 to November 2003 is still available at http://cattailpress.com/Archive/archive.htm. Dow posted numerous photos of the cleanup as it progressed, as well as weekly progress reports from the contractor performing the cleanup. The website also informed the public about opportunities for comment and input on the town’s redevelopment plans.

The CAG was successful in achieving most if not all of the five social goals. The community was allowed to influence the result of the cleanup throughout the process through
their opportunity to comment on options for site redevelopment. An example of the influence that community members had was in changing a trail that crossed Main Street near the Superfund site. When a community member complained about limited visibility for snowmobiles as they crossed the highway, the CAG contacted the EPA, who had the contractor move the trail so that snowmobiles would cross at a safer location (Seekins, 2001). Through the Cattail Press site, the CAG was able to educate the community on the progress of the cleanup and how the cleanup would affect the future of their town. The photo journal of the cleanup progress and regular contractor progress reports gave a high level of transparency to the remediation project and likely added to the level of trust. Ken Dow gave further evidence of the level of trust by stating, “The EPA has been very responsive. They’ve given us some good, solid answers to our questions” (Seekins, 2001). Little conflict was evident throughout the cleanup.

5.4.2 Omaha Lead, Omaha, Nebraska

The Omaha Lead Superfund site consists of a 27-square-mile area with over 125,000 residents within the site boundary in eastern Omaha, Nebraska. Elevated soil lead levels found in properties in this area are suspected to originate from the ASARCO lead refinery that operated from the 1870’s to 1997 (U.S. EPA, 2010). Cleanup at this site has consisted of removal of surface soils at all properties with lead levels above 400 ppm and replacement with new soil and new grass sod. On October 23, 2011, the EPA completed cleanup of its 10,000th residential yard within the site boundaries. Two separate community groups are associated with this Superfund site. The Lead Safe Omaha Coalition formed in 1999 to address the problem of childhood lead poisoning in the area. In 2004 the Union Pacific Railroad facilitated the formation of the Omaha Lead Site Community Advisory Group to interact directly with the EPA to provide community
input on studies and remedial actions. The CAG is composed of members of various organizations representing local government, neighborhood groups, potentially responsible parties (PRPs), health professionals, and other stakeholders (Black & Veatch and U.S. EPA, 2004). The community advisory group produced a web site to update residents on CAG meetings and provide a repository for meeting minutes, plans, and comments from residents. Although updating of the website ended in 2009, the CAG still met with EPA officials on a regular basis as of 2013 (France-Isetts, 2013).

The main concerns that residents in the affected area had were the length of time between sampling of their properties and receiving results, difficulty in understanding the meaning of results once they received them, and the length of time it took for their yards to be decontaminated once their properties were determined to be contaminated (Black & Veatch and U.S. EPA, 2004). The community group alerted the EPA to sites where large numbers of children played, allowing the EPA to adjust its sampling plans to better address the health risks that were present. Also, the groups successfully petitioned the EPA to establish two public information centers, which opened in November 2005, to perform public outreach and educate the community on the site, sources of lead contamination, and health impacts. The CAG has also provided a forum for the community to provide input on the quality of the work performed by the contractors and subcontractors. Although some concerns existed over unsafe work practices and inferior replacement soils, in general the community was satisfied with the work being performed and the EPA’s response to complaints (OLS CAG, 2008). The CAG’s largest success, however, is arguably its creation of the Omaha Healthy Kids Alliance (OHKA), which focused its efforts on educating the public on the hazards of lead exposure, not just from the contaminated soils, but also from lead-based paints and other sources. In 2014, OHKA received
a $200,000 grant from the EPA to establish a program targeting lead education for the city’s Spanish-speaking population (Kaarre, 2014).

The Community Advisory Group for the Omaha Lead Site was successful in achieving multiple social goals. They were able to educate the public not only about the Superfund site, but also on the issue of lead poisoning in general through the public information centers and OHKA. The CAG was able to inject public values into decision-making and improve the quality of decision-making through its influence on sampling plans. Additionally, the CAG was able to provide a forum that addressed conflict. The lack of negative articles found in researching this site suggests that conflict was minimal and the public generally trusted the EPA. However, the pace of cleanup at this site was generally quick compared to other Superfund sites, which may also contribute to low conflict and increased trust.

5.4.3 Outboard Marine Corporation / Johns-Manville / Yeoman Creek Landfill, Waukegan, Illinois

The Outboard Marine Corporation (OMC) Superfund site was listed on the NPL in 1983 and is situated on Waukegan Harbor on the shore of Lake Michigan in Waukegan, Illinois. OMC produced outboard boat motors until its bankruptcy and closure in 2000. The company used hydraulic fluids with polychlorinated biphenyls (PCBs) in the 1960s and 1970s, which it sometimes discarded through floor drains leading to sewers and into the harbor. It also used trichloroethene (TCE) for degreasing that leaked into the soil and migrated into the groundwater. The site also includes the location of the former Waukegan Coke Plant (WCP) which operated until the 1940s and contaminated the soil and groundwater with tars, creosote, arsenic, ammonia, and phenol (U.S. EPA, 2014b). After the OMC bankruptcy, the City of Waukegan purchased the land with the intent of revitalizing the harbor area. The Johns-Manville Superfund site is an
asbestos cleanup site located about a mile north of the OMC site and was also listed on the NPL in 1983. Yeoman Creek Landfill is an unlined landfill that leached PCBs into Yeoman Creek, a tributary of the Waukegan River, which flows into the Waukegan Harbor. This Superfund site was listed on the NPL in 1989. In addition to being the location of three Superfund sites, the harbor as a whole has been identified as an area of concern as part of the U.S.-Canada Great Lakes Water Quality Agreement for its high PCB content.

The Waukegan Harbor Citizens Advisory Group was formed by the Illinois EPA in 1990 as a government-community partnership for creating the remedial action plan for the harbor as a whole and represents all three Waukegan Superfund sites. It is a large organization with membership consisting of people from 34 member organizations and 17 associate member organizations representing area businesses, government, non-governmental organizations, and the local community (Waukegan Harbor CAG, 2014a). The CAG meets monthly, and participants in the meetings hear presentations on site progress, as well as educational presentations on a variety of environmental topics related to harbor and river ecosystems. Future presentation topics are posted on the CAG’s website (http://waukeganharborcag.com). Attendance at meetings continues to be robust given that the CAG has been in existence since 1990. The June 2014 meeting had 28 people in attendance (Waukegan Harbor CAG, 2014b).

The CAG claims a number of successes, including an award from the United States and Canadian governments presented at the 1998 State of the Lakes Ecosystem Conference for its role in preparing the remedial action plan for harbor cleanup (Bukro, 1998). The CAG actively works to achieve the social goal of public education through a number of programs that complement its presentations and publishing of progress updates. Its citizen scientist initiative engages residents in the monitoring of a variety of plant and animal species within the watershed,
and the CAG website updates anglers on fish consumption advisories due to PCB contamination (complete with color photographs of what each fish looks like and written in both English and Spanish).

Because the CAG itself was tasked with completing the remedial action plans for the three Superfund sites, public values were considered in producing the remedial action plan. This heavy community involvement may have come at a cost of time, as it took four years to produce (Spencer, 1994). The citizen group expanded the study area to include other industrial sites that the EPA did not originally consider (Spencer, 1992). The commitment of everyone involved, though, appears to have led to effective decision making and ultimately cleanup. The final dredging of the harbor for cleanup purposes occurred in July 2013, and the PCB concentration in the harbor was less than the harbor water quality limit of 0.1 ppm as of 2013 (U.S. EPA, 2013b). Conflict was reduced and trust appeared to be gained through the widespread involvement in making the remediation plan. A spokesperson for the Illinois EPA referred to this lack of conflict in stating after the plan was created, “You don't normally see companies coming forward in a setting like this and saying that we have a problem and trying to solve it” (Spencer, 1994).

### 5.4.4 Pine Street Canal, Burlington, Vermont

The Pine Street Canal Superfund site is a 38-acre site at the former location of a coal gasification plant that operated from 1895 to 1966. The site contains a canal built in the mid-1800s to serve lumberyards in the area as well as a former pond and a wetland area (Soos, 2011). Wastes containing coal tar, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) and metals from the coal gasification plant were discharged into the wetland and spread through the soil and groundwater and into the canal (U.S. EPA, 2014c). The site was
added to the NPL in 1983. In 1992, the EPA proposed a cleanup plan that included removal of 175,000 cubic yards of canal sediments and surface soils and placing them in an on-site disposal facility (Hartley, 2005). This plan, however, was canceled after strong community opposition.

After the release of the original remedial plan proposal in 1992, the potentially responsible parties (PRPs) formed a meeting group and invited members of the Vermont government and the EPA to attend. The following year, the EPA suggested the PRPs form a formal organization to negotiate a remedial action plan with the condition that they accept a neutral facilitator hired by the EPA and accept community members representing a broad stakeholder interest. In addition to the facilitator, the newly formed Pine Street Barge Canal Coordinating Council also received a technical assistance grant (TAG) to hire an outside consultant to explain technical information (U.S. EPA, 2000). The coordinating council was split into four subcommittees: Ecological Risk, Contaminant Fate and Transport, Human Health Risk, and Community Involvement (U.S. EPA, 2000). The first year was spent determining goals and operating procedures for the coordinating council. The goal they agreed upon was “to reach consensus on the scope of work for further studies of the Pine Street site, recommendation of a remedy that is both acceptable to the community and satisfies EPA’s and the State of Vermont’s statutory and regulatory obligations, and such other subjects as the Council may by consensus agree to consider” (U.S. EPA, 2000). By 1998, the council agreed to a remediation plan, which consisted of capping the contaminated sediments. This plan became the basis for the EPA’s record of decision (ROD) for the site.

The Pine Street Barge Canal Coordinating Council successfully achieved most if not all of the five social goals. The members of the public who were involved in the coordinating council quickly learned enough about the technical details of the remediation to ask meaningful
questions about the site studies and cleanup options (Hartley, 2005). One community member stated that the TAG was essential because it allowed them to be equal members in the deliberation process (U.S. EPA, 2000). However, it is difficult to determine if the public as a whole became better educated through the process. No specific outreach programs were established by the coordinating council, although council members did report that they regularly met with their constituency groups outside of the council meetings to disseminate information and gather feedback (U.S. EPA, 2000). The fact that the coordinating council’s final decision became the basis for the EPA’s ROD shows that public values were incorporated into the decision making. Several community members were present at most council meetings (U.S. EPA, 2000). The council was able to produce a higher quality plan that the community as a whole could accept. Additionally, the council’s plan included measures that went beyond contaminant removal, including business and community development (Hartley, 2005). It could be argued that the resulting remediation plan was not optimal because contaminants have periodically been found to have escaped the cap. However, the plan was much more acceptable to the community and therefore an improvement over the original EPA plan. Trust in the EPA was initially low. After the EPA announced its initial plan, several negative newspaper stories contained statements by Vermont state officials claiming the EPA produced an inadequate study of the contamination and presented an inappropriate and environmentally unsound plan (Hartley, 2005). The EPA admitted that the initial cleanup plan “left the Agency’s credibility with the community in tatters” (U.S. EPA, 2000). At the end of the process, though, community members thanked the EPA for their commitment to the consensus process (U.S. EPA, 2000). In the end, the conflict between the EPA and the community was reduced enough to allow implementation of a viable remediation plan.
5.4.5 Chemical Commodities, Inc., Olathe, Kansas

Chemical Commodities, Inc. (CCI) was a chemical recycling facility in central Olathe, Kansas, from 1951 to 1989. Poor chemical storage practices allowed contaminated rain runoff to leave the site and also caused nearby soil and groundwater to be contaminated with metals, volatile and semi-volatile organic compounds, and pesticides (U.S. EPA, 2012a). The site was added to the NPL in May 1994. Although the site is only 1.5 acres in size, it is adjacent to residential properties. In 2002, indoor air samples of residences up to two blocks away had elevated levels of various volatile organic compounds including carbon tetrachloride, chloroform, methyl chloride, and trichloroethylene (Kansas State University, 2014).

The CCI Concerned Citizens Group formed in 2001 and incorporated as a non-profit organization in 2003. The core members of the group consisted of 11 residents whose homes were near the CCI site and required ventilation systems to protect them from indoor air contamination (Andrews, 2003). The community group received assistance from Kansas State University through the EPA’s Technical Outreach Services for Communities (TOSC) program. The goals for the group included gaining a unified community voice, determining what homeowners expected during the cleanup process, monitoring testing and cleanup plans, disseminating information to the community, and obtaining a just and equitable resolution from PRPs (Andrews, 2003). The CAG met on an as-needed basis to get community comments for cleanup proposals and other site-related activities. Twenty-five residents attended one such meeting in August 2004 to give their input on a set of proposals that the EPA had developed for the site cleanup (Chen, 2004a). The CAG also published a newsletter that they distributed to keep the community updated on progress.
The community group sent representatives to meetings with the EPA, state regulators, and PRPs to give the community a voice in the cleanup decisions. After the EPA developed a plan in 2004, the CAG presented specific changes to the plan that they wanted such as additional soil removal and the lengthening and addition of interceptor trenches (Chen, 2004b). As a result of input from both the CAG and the Kansas Department of Health and Environment, the EPA adjusted their proposed remediation plan to make it more aggressive (Andrews and McVeigh, 2005). The CCI Concerned Citizens Group was also involved in planning the future of the site after it reached construction completion in 2012. With input from the community, the group developed a plan for turning the former hazardous waste site into an educational park designed to attract pollinators. After remedial activities on the site were completed in 2012, the community group organized over 100 volunteers to plant the pollinator gardens (U.S. EPA, 2013c). The community group received an award from the EPA in 2012 for its work as a liaison between the EPA and the community (U.S. EPA, 2012b).

CCI Concerned Citizens Group was successful in achieving many of the social goals. They kept the public informed and educated on site progress through both their meetings and newsletters. The newsletters explained all of the processes that were occurring on site including non-cleanup activities such as getting the PRPs to sign consent decrees, which would otherwise appear to the public as inactivity. The large turnout achieved at important meetings and events demonstrated their ability to communicate with the public. The CAG also influenced the decisions that were made both during remediation and after cleanup activities were completed by pushing for more aggressive cleanup and being a partner in the design of the new city park. The CAG’s influence ensured that public values were incorporated into the decision making. The community’s involvement led to high quality decision making, changing what was once a foul-
smelling eyesore (Chen, 2004c) into a community-built wildlife habitat. Involvement of the community in the project undoubtedly built trust in the EPA and other regulatory institutions. In 2004, many in the community felt that the site would never be cleaned up within their lifetimes (Chen, 2004b, 2004c). By 2012, cleanup activities had been completed. The CAG was also able to work with the EPA and state regulators to reduce conflict. In 2004, the CAG suggested that lawsuits may be necessary (Chen, 2004b); however, through talks with the EPA, state regulators, and the PRPs, the CAG was able to successfully negotiate a better remedy and avoid litigation.

5.4.6 Aerojet General Corporation, Rancho Cordova, California

Aerojet General Corporation is a manufacturer of liquid and solid rocket propellant. In the past the company disposed of its chemicals through surface impoundments, landfills, deep injection wells, leachate fields, and open burning (U.S. EPA, 2014d). The EPA added the site to the NPL in 1983 after TCE contamination was found in shallow groundwater. At that time, Aerojet treated the groundwater by pumping the contaminated water out of the shallow aquifer and reinjecting the water after treatment into a deeper aquifer system (Lamb, 2006). Although perchlorate from the plant was widely known to have infiltrated into the groundwater since the 1950s, poor detection limits and disputes over the health effects of perchlorate allowed the company to largely ignore the perchlorate contamination (Waldman, 2002). However, after improved methods of detecting perchlorate were developed in 1997, off-site wells were confirmed to be contaminated with perchlorate (Waldman, 2002). The perchlorate contamination forced the shutdown of many city- and county-operated drinking water wells, which prompted Sacramento County to file lawsuits against Aerojet and Boeing to recover costs
for developing alternate water supplies (Kalb, 2012). The county negotiated a $35 million settlement with the companies in 2012.

The Aerojet Community Advisory Group (Aerojet CAG) was established in 2001 (U.S. EPA, 2014d). The CAG does not have a website and does not appear to have any method for widespread dissemination of information throughout the community. The CAG does meet bimonthly, and its meeting notes are posted on the EPA’s webpage for the Aerojet General Corp. Superfund site (http://yosemite.epa.gov/r9/sfund/r9sfdocw.nsf/vwsoalphabetic/Aerojet+General+Corp.). Generally, the meetings are dominated by members of various California regulatory agencies and water service providers with very few residents present other than the CAG chairperson, Janis Heple. Table 5.3 illustrates the makeup of attendees at a typical Aerojet CAG meeting.

Table 5.3. Attendance at the Aerojet CAG meeting, November 16, 2004 (Aerojet CAG, 2004).

<table>
<thead>
<tr>
<th>Name</th>
<th>Organization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charles Berrey</td>
<td>U.S. EPA</td>
</tr>
<tr>
<td>Don Hodge</td>
<td>U.S. EPA</td>
</tr>
<tr>
<td>Monica Brown</td>
<td>California Cancer Registry</td>
</tr>
<tr>
<td>Alex MacDonald</td>
<td>Regional Water Quality Control Board</td>
</tr>
<tr>
<td>George Waegell</td>
<td>Southern California Water Service</td>
</tr>
<tr>
<td>Paul Schubert</td>
<td>Southern California Water Service</td>
</tr>
<tr>
<td>Jean Young</td>
<td>Sacramento County</td>
</tr>
<tr>
<td>Ed Cargile</td>
<td>California Department of Toxic Substances Control</td>
</tr>
<tr>
<td>Ed Winkler</td>
<td>Sacramento Groundwater Authority</td>
</tr>
<tr>
<td>Michael Girard</td>
<td>Aerojet</td>
</tr>
<tr>
<td>Tim Murphy</td>
<td>GenCorp (parent company of Aerojet)</td>
</tr>
<tr>
<td>Janis Heple</td>
<td>CAG Chairperson</td>
</tr>
<tr>
<td>John B. Hervey</td>
<td>Gold River resident</td>
</tr>
<tr>
<td>Tricia Carter</td>
<td>Recorder, CH2M HILL</td>
</tr>
</tbody>
</table>

The lack of community involvement with the CAG is not likely to be a result of a lack of community interest in the groundwater contamination or its cleanup. Instead, residents have
found other means to express their opinions and attempt to influence remediation efforts. Residents filed a toxic tort class action lawsuit against the company in 1998 (Waldman, 2002), and developers have also sued the company (Turner, 2012). Residents also communicate with officials directly through community web forums, such as *Gold River Online*. For example, a complaint from a community member regarding the installation of a monitoring well was answered by employees of Aerojet and the Regional Water Quality Control Board (Gold River Online, 2013). Public meetings are held in the different communities surrounding the site to announce cleanup and monitoring plans. At one such meeting in Fair Oaks, the Fair Oaks Water District and Aerojet announced their plans to drill a monitoring well. Residents objected and delayed installation (Allagree, 2008); however, the monitoring well installation eventually occurred at the disputed site with some concessions made to an adjacent property owner to minimize the construction impacts (Aerojet CAG, 2009).

Unlike the previous five CAGs discussed above, the Aerojet CAG appears to have been less successful at achieving the five social goals. While much useful information has been disseminated at CAG meetings, hardly any community members have been in attendance to receive it. Other than posting meeting notes on the EPA website, the CAG does not organize any community outreach activities. While community members have expressed their opinions on cleanup issues such as monitoring well placement, they have had very little influence on decision making. The predominant decision-making mode has been for regulators and Aerojet to make decisions and then defend those decisions at public meetings, explaining why a certain option is the only feasible option. Given the lack of community involvement in the CAG, it is difficult to argue that the existence of the CAG has led to better decisions related to site cleanup. The CAG
has done little to reduce conflict, as community protest has led to delays in remediation activity such as monitoring well emplacement.

5.4.7 Raymark Industries, Stratford, Connecticut

The Raymark facility in Stratford, CT, produced gaskets, clutches, and brake components for the automotive industry from 1919 to 1989 (Town of Stratford, 2008). Manufacturing wastes from the factory were used as fill material at the Raymark facility and also at other locations throughout Stratford such as commercial properties, parks, several wetlands near the Housatonic River, and at least 46 residential properties. These wastes contained polychlorinated biphenyls (PCBs), asbestos, lead, and copper. Additionally, volatile organic compounds from solvents used in the manufacturing process have contaminated the soil and groundwater at the factory site (U.S. EPA, 2014e). Because waste from the facility was spread throughout the town, the Superfund site consists of nine operable units (OUs). The site was listed on the NPL in April 1995. Although the company no longer exists, a trust fund for site cleanup was established as part of the company’s bankruptcy settlement (Raymark Advisory Committee, 2007a). Establishment of the fund guaranteed that some money would be available for cleanup, but it also capped the liability of the defunct Raymark company. As of 2007, the account for the Superfund Site Cleanup had approximately $21 million (Raymark Advisory Committee, 2007a).

The Stratford Town Council established the Raymark Advisory Committee in June 2000 after residents of Stratford strongly opposed all options proposed by the EPA a year earlier for cleanup of the Shore Road area (OU 5). The committee had approximately 20 residents consisting of owners of property within or adjacent to contaminated areas, small business owners, and other interested residents (Raymark Advisory Committee, 2007a; U.S. EPA, 2001).
Members of the Raymark Advisory Committee were appointed to a two-year term by Town Council members and agreed to attend all monthly meetings. Using funding provided by the EPA, the committee hired a facilitator to manage meetings and a technical consultant to assist in reviewing the site documents (U.S. EPA, 2001). It took three years for the Raymark Advisory Committee to agree to the goals of the committee, drafting a consensus agreement in September 2003 (Raymark Advisory Committee et al., 2003).

The main point of contention that instigated the formation of the Raymark Advisory Committee was the community’s disapproval of the EPA’s plan to move contaminated soil from OU 5 to OU 4 (Raybestos Ballfield). Earlier, in 1994 as an interim measure, the EPA overlaid contaminated soil at OU 5 with a geotextile fabric with 6 inches of woodchips over the fabric. By 1999, parts of the fabric had become exposed and were failing. The EPA’s original plan to fix this area included moving some of the soil to OU 4. However, because of the community objections, the EPA limited its actions at OU 5 to conducting more tests to determine the extent of contamination, moving utilities to where they could be accessed without exposing contaminants, paving or repaving traffic areas, and recapping exposed contamination areas (LePage, 2002). As of 2014, no additional work had been done at OU 5, and no plans had been accepted for a permanent remedy.

After the interim work was completed at OU 5, most of the committee’s focus was on OU 6. This operable unit consists of 24 commercial, residential, and recreational properties throughout Stratford that contain fill material from Raymark (Tetra Tech, 2005; U.S. EPA, 2014e). While the feasibility study was being produced, the EPA presented the Raymark Advisory Committee with preliminary treatment options. Because of the nature of the contaminants found in the soils in OU 6, the only feasible option for permanent treatment would
be removal of the soils. While transfer of all soils to a facility outside the town would permanently remove contamination from Stratford, this option would cost approximately $70 million (Raymark Advisory Committee, 2007b), well above the $21 million left in the site’s cleanup fund. Removal of all contaminated soil and consolidation of the soil at sites within Stratford would cost approximately $14 million, not counting the cost of developing and capping the consolidation sites. However, acceptable sites for contaminated soil storage would have been very difficult to identify (Raymark Advisory Committee, 2007b). For some sites, partial soil removal and capping would also be an option, but this would limit property use and require property owners to be responsible for cap maintenance (Raymark Advisory Committee, 2007a). The advisory committee strongly opposed consolidation of contaminated soils anywhere within Stratford. They also demanded that either the EPA or the State of Connecticut pay the cost of cap maintenance (Raymark Advisory Committee, 2007a). In 2007, the Raymark Advisory Committee disbanded, citing a loss of funding for the facilitator and technical advisor as the reason for discontinuing (Town of Stratford, 2014). Before disbanding, however, the committee produced a document for the Stratford Town Council outlining its successes, the limitations posed by the Superfund site, and its recommendations for future treatment options (Raymark Advisory Committee, 2007a).

The Raymark Advisory Committee had very few successes when examined in the context of Beierle’s social goals. Unlike at other sites, such as Pine Street Canal, where community members became knowledgeable enough in the technical cleanup aspects that they were able to ask questions on their own, the Raymark committee members remained reliant on their technical assistants and could not continue without them. Furthermore, it does not appear that any effort was made to educate the community as a whole about the project. In fact, many residents living
above the contaminated groundwater or whose yards still contained contaminated soils were unaware of the contamination until told by neighbors or the media (Lyte, 2011). The committee did attempt to incorporate public values into decision making by holding firm on their stand against consolidating waste within the town. They also created a prioritized list of the OU 6 properties, recommending the order in which they should be cleaned. However, as of 2014, there was only a plan to clean up 4 of the 24 OU 6 properties with no agreement on how to proceed with cleanup of the remaining 20 (Rainone, 2014). The quality of the decisions did not improve because few decisions were ever made. Rather than building trust, one committee member blamed the EPA in a *New York Times* article stating, “While the E.P.A. and the D.E.P. should have long ago developed a plan to remediate the waste on all these local properties, they always seem to come up with another big testing project or study they have to do first” (Weizel, 2004). Conflict continues to prevent any cleanup from occurring. The EPA and the Town of Stratford essentially remain at a stalemate. The EPA insists that contaminated soil must be consolidated in town because of a lack of funding to take the soil elsewhere, and the town will not accept that option.

5.5. Discussion

The EPA’s CAG program was developed largely as a reaction to delays in implementing cleanup plans at Superfund sites as a result of community protests. After examining the cleanup rate at all sites listed on the NPL, it appears that the presence of CAGs has not generally resulted in faster cleanup times. A smaller percentage of sites with CAGs have reached the EPA cleanup milestones of final remedy selection, construction completion, and deletion when compared to sites without CAGs. Likewise, the average number of days starting from NPL listing to reach
these three milestones is greater for sites that have had EPA-recognized CAGs. Given the overlap of the large standard deviations for the amount of the time needed to reach cleanup milestones at both CAG and non-CAG Superfund sites, it cannot be stated that the presence of CAGs has significantly increased the amount of time needed to proceed through the steps of Superfund site cleanup. The large variation in time needed to achieve cleanup milestones throughout Superfund sites indicates that factors other than CAG presence influence cleanup time. This is consistent with the findings of other research that has linked cleanup time to factors such as multiple PRPs, high levels of contamination, and site characterization complexity, in addition to community involvement (Daley and Layton, 2004).

While the presence of CAGs has not resulted in quicker cleanup of Superfund sites, many communities have clearly benefitted from the program. Using Beirele’s (1999) framework of social goal achievement, this study examines five CAGs that have fully achieved those social goals and two CAGs that had less success. The five successful CAGs (Eastland Woolen Mill, Omaha Lead, Outboard Marine Corp., Pine Street Canal, and Chemical Commodities, Inc.) achieved the goals of informing and educating the public, incorporating public values into decision making, improvement of decision quality, increased institutional trust, and reduced conflict. The other two CAGs in the study (Aerojet Community Advisory Group and Raymark Advisory Group) failed to achieve those goals to the extent identified in the other five examples.

It is beyond the scope of this research to determine how many sites have had successful CAG involvement versus unsuccessful CAG involvement. The sites featured in this study merely illustrate examples of highly successful and less successful CAG involvement. The information presented here came from material published by the EPA, CAGs, organizations assisting CAGs, and the news media. Restricting the discussion to Superfund site CAGs with
readily available public information likely leads to a bias toward either CAGs that were more effective at informing and educating the public or toward Superfund sites with a high level of conflict that attracted media attention. It is worth noting that only about half of the CAGs recognized by the EPA had much readily available information beyond the cursory information found on EPA webpages. If a researcher specifically looking for information about a CAG cannot find much information on its activities, then it may follow that many community members may miss out on the opportunity to participate in the CAG or benefit from its existence. Many CAGs should consider improving their outreach to the communities they serve.

The need for some CAGs to improve their community outreach is further illustrated by the Aerojet General and Raymark site CAGs. The Aerojet General CAG meetings resembled interagency regulatory meetings more than community meetings. While many of the meetings featured speakers that presented good information for community members, such as the November 16, 2004 meeting with an epidemiologist from the California Cancer Registry, almost no community members were present to see the presentation. Without community input into the planning of remediation and monitoring plans, community members responded by protesting the plans that were presented by the regulators. Furthermore, lack of community outreach can lead to individuals continuing to expose themselves to health risk. At the Raymark site, well after the plume had been delineated, individuals continued to purchase homes overlying the groundwater TCE plume with no knowledge of vapor intrusion hazards. If the previous owner had refused a vapor intrusion mitigation system, then new owners were on their own to learn that a hazard even existed and were forced to bear the costs of installing such a system (Lyte, 2011). Lack of a concerted effort to reach out to the community members that do not attend CAG meetings can greatly restrict the benefits that a CAG can achieve.
As long as CAGs have community representation, they can vary in makeup and size and still be successful. Like the Aerojet General CAG, the Waukegan Harbor CAG was heavily represented by government agencies. By far the largest organization in this study, however, the Waukegan Harbor CAG had significant community representation and created specific community outreach programs. Much smaller CAGs have been successful, too. The Sebasticook Committee for a Clean Environment and the CCI Concerned Citizens Group had much smaller core memberships, but still proved effective as they reached out to the larger community. CAGs such as the Waukegan Harbor CAG, Pine Street Barge Canal Coordinating Council, and Omaha Lead had regulators as official CAG members, while the Sebasticook and CCI CAGs only had residents as members. The specific goals for each of these CAGs also differed slightly, although the overarching goal of allowing community input in decision-making existed for each CAG. The Waukegan Harbor CAG and the Pine Street Barge Canal Coordinating Council were tasked with actually writing the remedial action plans. Other CAGs served more as liaisons between the community and the EPA.

The key similarity in all of the CAGs that successfully achieved Beirele’s social goals, though, was that they made a concerted effort to extend their reach outside of the meetings. For example, the Omaha Lead CAG created the Omaha Healthy Kids Alliance, which worked to educate the city about lead hazards regardless of source. The Waukegan Harbor CAG has engaged residents through its citizen scientist program, and the CAG has also involved schools by having students assist in making fish advisory signs. The CCI Concerned Citizens Group recruited over 100 volunteers to help create a park and pollinator habitat on what used to be a contaminated property. In addition to maximizing community input in cleanup decisions, outreach programs give CAGs an opportunity to make positive changes in the community out of
the negative impacts of a Superfund site. Such opportunities may energize CAGs and create goals that keep CAGs engaged in the cleanup process.

5.6. Conclusion

While the EPA’s Community Advisory Group program has not resulted in faster cleanups at most Superfund sites, it has been successful in other ways. CAGs have allowed site administrators to make cleanup decisions that are more appropriate for the communities. In many cases CAGs have reduced conflict and increased the communities’ trust in the officials charged with protecting their health. CAGs have also provided a forum for teaching community members about health hazards resulting from environmental pollutants and about the science behind cleaning up contamination. Most importantly, though, CAGs have provided opportunities for citizens to improve their communities.

While not all CAGs have been succeeded in producing the social goals proposed by Beirele, many communities have benefitted immensely from the program. The greatest successes in the CAG program have been the result of the hard work and dedication of the community members within these CAGs. While a few successful CAGs have been large organizations with strong government backing, many smaller CAGs have been equally successful due to the persistence and vision of just a few people. Just as removing contaminants from hazardous waste sites can be difficult, obtaining meaningful input from the community can be just as difficult. The most successful CAGs have been able to extend their reach outside the walls of the meeting room. Successful community involvement in cleanup decisions leads to much more than just removal of hazardous materials and chemicals. It allows citizens to determine the future of their community.
CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

Significant changes in both in-phase and quadrature conductivity were observed in homogeneous aqueous and porous media samples as a result of processes related to permanganate-based in situ chemical oxidation (ISCO). In-phase conductivity could be accurately predicted using known reaction equations to determine reaction products and PHREEQC to calculate conductivity based on the product concentrations. On the other hand, ISCO reactions caused only small quadrature conductivity changes that are not likely to be measureable in the field. However, injection of sodium permanganate (but not potassium permanganate) causes a significant increase in quadrature conductivity that may be useful for monitoring plume movement and estimating level of plume mixing.

6.1. In-Phase (Bulk and Pore Fluid) Conductivity

The following physical processes occurring during ISCO were found in this study to significantly influence the in-phase component of conductivity (bulk or pore fluid conductivity):

- Addition of permanganate salts (sodium or potassium) increases conductivity.
- Reaction between permanganate and TCE increases conductivity.
- Reaction between permanganate and natural organic matter such as humate decreases conductivity.
- Protonation of mineral surfaces decreases conductivity.

Hypothesis 1 (Chapter 1) postulated that in-phase conductivity changes after oxidation of TCE or natural organic matter are possible to predict with reasonable accuracy based on the
equations for TCE oxidation and humate oxidation by permanganate (Equation 1.5). Using the geochemistry software PHREEQC, fluid conductivity could be predicted to within 6% after oxidation of TCE. Error generally increased as TCE concentration increased. Conductivity change from humate oxidation could be predicted by using equations proposed for oxidation of humate to oxalate and then to carbon dioxide and combining those equations with first order kinetic modeling of humate degradation. The combination of those components with PHREEQC yielded conductivities in aqueous samples within 3% of measured conductivity values.

Hypotheses 2a – 2c predicted that granular media such as silica, kaolinite, and smectite would remove protons produced during ISCO from the pore fluid, moderating pH and conductivity changes. Significant removal of protons from the pore fluid occurred simply through adsorption onto silica grains in saturated clean sand samples with no other buffering present. Protonation of silica occurred quickly with pH increasing and pore fluid conductivity increasing logarithmically, reaching near completion within three hours. The loss of pore fluid ions resulted in removal of 94.7% of the conductivity that would have been attributed to protons produced during oxidation of 8 mM TCE. Presence of bicarbonate in the pore fluid further increases this removal of protons. The buffering capacity of 10% kaolinite was similar to clean sand. Addition of 10% smectite to clean sand, on the other hand, increased the buffering capacity significantly. In saturated 10% smectite samples with artificial groundwater pore fluid, pH remained above 8 after oxidation of 3 mM TCE, compared to pH 4.8 with clean sand. Because protonation and carbonate reactions both influence pH within the subsurface, it may be difficult to predict with great certainty pH values. Consequently, measured pH values help improve conductivity predictions.
Additionally, adsorption of pore fluid ions by manganese dioxide solids produced during permanganate reduction may decrease conductivity. Additional research is needed, though, to determine to what extent this will occur. In aqueous samples with lightly buffered artificial groundwater as the background fluid, measured conductivity was 1.5% to 6% lower than predicted after oxidation of TCE by permanganate; however, when potassium chloride solution was the background fluid, measured conductivity was 2.1% to 5.5% higher than predicted. Manganese dioxide is known to adsorb divalent cations (Brûlé et al., 1980; Kanungo et al., 2004), and the groundwater composition may have a large influence on how much adsorption impacts pore fluid conductivity.

Hypothesis 3 predicted that formation factor would increase in a predictable manner such that pore fluid conductivity could be easily calculated from bulk conductivity and vice versa. The results demonstrated that formation factor and surface conductivity are important considerations when calculating bulk conductivity from pore fluid conductivity or the other way around. The composition of the aquifer sediments may significantly impact both formation factor and surface conductivity, especially if significant smectite clays are present. However, manganese dioxide precipitation during TCE oxidation did not cause a large increase in formation factor. The observed increase was only approximately 0.02 per mole of TCE oxidized. Furthermore, no increase in surface conductivity could be detected during TCE oxidation.

6.2. Quadrature Conductivity

The following processes influence quadrature conductivity during ISCO with permanganate:

158
• Reduction in pH lowers quadrature conductivity in clean sand and sand/kaolinite mixes, but only if no significant smectite is present in the granular material.

• Addition of sodium increased quadrature conductivity rather significantly; however, addition of potassium caused a slight decrease in quadrature conductivity or had no effect in samples with artificial groundwater containing sodium as the dominant cation.

Hypothesis 4 predicted that TCE itself would not have a measurable quadrature conductivity signature at soluble concentrations. Indeed, saturated sand samples containing artificial groundwater with 2 mM TCE did not exhibit a change in quadrature conductivity in the frequency range attributed to Stern layer polarization or membrane polarization (frequencies below 100 Hz). However, 20 hours after sample creation, reduced quadrature conductivity was observed at 500 Hz and above with a 29% to 34% decrease in quadrature conductivity at frequencies between 1 and 10 kHz, though no significant decrease had been observed 3 hours after sample creation. The difference increased at higher frequencies, suggesting that changes in the Maxwell-Wagner polarization were involved. Further testing is required to conclusively determine if TCE itself is detectable through quadrature conductivity measurements, especially at low frequencies related to Stern layer polarization.

Hypothesis 5 predicted that manganese dioxide production would cause an increase in quadrature conductivity. No increase in quadrature conductivity was observed either as a result of either TCE oxidation or humate oxidation. Furthermore, saturated sand samples containing extracted manganese dioxide resuspended in artificial groundwater did not exhibit significantly different quadrature conductivity than porous media samples with artificial groundwater alone.
The lack of measureable Stern layer polarization for manganese dioxide should not be unexpected in light of the low polarization observed with the silica sand. The cation exchange capacity of manganese dioxide, $4 \times 10^{-13}$ mol/kg (Murray, 1974), is significantly less than the value for silica sand, 1.5 to $6.2 \times 10^{-5}$ mol/kg (Revil, 2012).

Hypothesis 6 predicted that reduced pH from TCE oxidation would reduce quadrature conductivity. Indeed, reduced quadrature conductivity at 1 Hz was observed in saturated sand samples after TCE oxidation. The lower quadrature conductivity compared well with theoretical reductions in the number of negatively charged silica surface groups at reduced pH. The comparison between theoretical negative surface charge density and quadrature conductivity diverged significantly at 10 Hz, though, especially in samples with higher salinity (containing 5 mM or 8 mM NaHCO$_3$ instead of 2 mM). Because the comparison held up well at 1 Hz, the increase in polarization was more likely from Maxwell-Wagner polarization, which generally occurs at higher frequencies than Stern layer polarization (although the two may overlap), than membrane polarization, which generally occurs at the same frequencies as Stern layer polarization. No significant change in quadrature conductivity was observed in samples with 10% smectite, owing to smectite’s largely non-pH dependent cation exchange capacity. Because quadrature conductivity in sand or sand/kaolinite mixes without smectite is already near detection limits, it is unlikely that reduction in quadrature conductivity from pH reduction could be reliably observed in field measurements.

Hypothesis 7 predicted that increased salinity as a result of injection of permanganate salts would cause an increase in quadrature conductivity. While increased quadrature conductivity was observed as salinity increased, this increase was dependent on the cation that was added to the pore solution. Adding 40 mM sodium to artificial groundwater (equivalent to
5.7 g sodium permanganate per liter) caused a 29% increase in quadrature conductivity in saturated clean sand and a 100% gain in quadrature conductivity in saturated 10% smectite at 1 Hz. However, addition of potassium to artificial groundwater caused no change to a slight decrease. Addition of permanganate ion had no effect on quadrature conductivity, which was expected as only cations should be found within the Stern layer at circumneutral pH. Because sodium is conserved and permanganate is transformed during ISCO, quadrature conductivity would not be an indicator of how much permanganate was present, though. On the other hand, changes in quadrature conductivity may be an indicator of the level of mixing of an injected sodium permanganate plume.

6.3. Time Lapse Conductivity Tomography of Permanganate Plume Movement and TCE Oxidation

Permanganate plume movement was captured well in time-series two-dimensional snapshots of electrical conductivity using Tikhonov regularization to invert measured conductivity measurements. However, the inversion returned localized conductivities that were much lower than the actual conductivities calculated from background fluid conductivities and measured permanganate concentrations (0.0025 S/m compared to 0.012 S/m for the background bulk conductivity and 0.0092 S/m compared to 0.14-0.15 S/m for the center of the plume). Furthermore, the plume conductivity appeared to increase when the plume was immediately near electrodes and decrease when it was further away from electrodes. Both problems are typically encountered during inversion of electrical resistivity data using Tikhonov regularization (Day-Lewis et al., 2005). Further constraint of the inversion model with actual fluid conductivity and/or permanganate concentration measurements or additional physical and chemical modeling would be necessary to return accurate conductivity measurements throughout the survey space.
Visual plume inspection, water sampling, and electrical conductivity tomography all produced evidence of minimal mixing of permanganate plume with the surrounding pore fluid. After passing by a given location, no residual permanganate was left behind. The permanganate plume moved at the same velocity as the velocity of the groundwater whether TCE was present or not. Comparisons of the mass balances between injected and recovered permanganate with and without TCE present indicated that the same volume of TCE was oxidized (assuming the TCE concentration present in the pore fluid at injection) as the volume of permanganate that was injected.

6.4. Application of Results

Because of the accuracy by which in-phase conductivities could be modeled after oxidation of both TCE and humate in homogeneous systems, the potential exists to use electrical conductivity tomography, especially time-lapse, to monitor permanganate concentrations over time and space after injection. However, it may currently only be possible to monitor overall permanganate plume movement in a qualitative manner using common inversion techniques. With limitations on monitoring well density common at many remediation sites, however, qualitative mapping of the permanganate plume is still an improvement over monitoring well data alone.

Both in-phase and quadrature conductivity measurements may be useful as indicators of the level of mixing that occurs between the injected solution and the surrounding groundwater. Monitoring of the size of the permanganate plume with in-phase time-lapse measurements may be an effective method for determining the rate of dispersion of the permanganate plume. Furthermore, if sodium permanganate is used, quadrature conductivity measurements over time
could help determine changes in sodium concentration and distribution, which would be further indicators of plume mixing. However, improvements to tomography accuracy and resolution are needed to fully realize this application.

Studying the movement of injected permanganate also gives insights into the most efficient and effective means of delivering the oxidant. Injection of large concentrations of permanganate under advection-dominated conditions may not be an efficient manner of remediation if the target area for contaminant removal is extensive. Other methods for delivery should be considered to improve efficiency. Multiple injections of low permanganate concentrations or insertion of slow-release permanganate delivery devices (Christenson et al., 2012) may result in similar concentrations of TCE being removed with less permanganate used. Alternately, engineered injection and extraction designed to create chaotic advection (Neupauer et al., 2014) may be considered to improve mixing and increase contact between the oxidant and contaminant.

Possibly, the most effective application of the results presented in this dissertation, though, would be the use of the chemical modeling described in Chapters 2 and 3 to constrain the inversion of conductivity surveys during ISCO. The largest limitation of the research presented in this dissertation was the difficulty in recovering accurate conductivity distributions from two- and three-dimensional surveys. Although more work is needed to combine solute transport properties with ISCO redox chemistry to produce an accurate distribution of conductivity across a reactive permanganate plume, the use of such modeling could make it possible to obtain accurate conductivity distributions throughout the aquifer and make inverse modeling of permanganate concentrations possible where physical sampling is not feasible.
6.5. **Recommendations for Further Study**

This study showed that the change of fluid conductivity in homogeneous batch samples was possible to accurately predict; however more work needs to be done before conductivity can be modeled across a heterogeneous permanganate plume within a two- or three-dimensional space. Future work should focus on additional two- and three-dimensional experiments that combine the chemical modeling described in Chapters 2 and 3 with solute transport (advection, dispersion, and diffusion) modeling. Larger scale tank experiments that allow for more fluid samples are needed so that actual permanganate and oxidation reaction product concentrations as well as fluid conductivities can be measured across the plume. These values could then be compared to the values predicted in the reactive transport modeling.

Successful predictive modeling of conductivity could then be used in conjunction with time-lapse tomography to constrain inversions and improve recovery of electrical conductivities within the measured aquifer space. These improved inversions could then be tested to determine how accurately they model conductivity distribution throughout the measured aquifer space. Once accurate tomography of electrical conductivity measurements is achieved, experiments focused on the inverse problem of recovering permanganate concentrations from electrical conductivities can be performed. Additionally, experiments should be performed under various flow conditions and with heterogeneous granular materials to simulate a wider range of aquifer conditions.
REFERENCES CITED


APPENDIX A. CALIBRATION DATA

This appendix shows calibrations for the porous media conductivity sample holders, electrical conductivity probe, and permanganate spectrophotometer measurements that were used throughout this dissertation (Figures A.1 – A.3).

**Figure A.1.** Geometric factor calculation for the porous media sample holders. Samples consisted of solutions (fluid only) of different concentrations of KCl.

**Figure A.2.** Fluid conductivity probe calibration. Measurements are for different concentrations of KCl. Theoretical conductivity was calculated using PHREEQC.
Figure A.3. Calibration of permanganate ($\text{MnO}_4^-$) concentration versus absorbance at 525 nm.