NUMERICAL MODELING OF THERMAL ENHANCEMENT OF IN SITU CHEMICAL OXIDATION (ISCO) AND ENHANCED IN SITU BIOREMEDIATION (EISB)

by

Sean Alexander Bryck

A thesis submitted to the Department of Civil Engineering
In conformity with the requirements for
the degree of Master of Applied Science

Queen’s University
Kingston, Ontario, Canada
(February, 2014)

Copyright © Sean Alexander Bryck, 2014
Abstract

A numerical model was utilized to assess the effects of elevated temperature on the application of in situ chemical oxidation (ISCO) and enhanced in situ bioremediation (EISB) for the subsurface remediation of trichloroethene (TCE) and tetrachloroethene (PCE). Temperature adjustment of the contaminant physicochemical properties as well as the chemical/biological reactions associated with ISCO and EISB were accounted for in the model domain. ISCO reaction rates were estimated using Arrhenius principles; microbial growth rates for EISB were estimated using non-linear fits to published literature data. The results from this study showed that temperature did provide remedial benefits to ISCO and EISB treatment during the short-term timeframe of oxidant/substrate injection. During these time periods, heated ISCO and EISB treatment exhibited greater DNAPL mass removal and mass flux reduction compared to heated abiotic dissolution. In the long term, after oxidant/substrate injection was terminated, the treatment enhancements achieved by ISCO and EISB were negated. Permeability ($k$) reduction due to rind formation (ISCO) and bioclogging (EISB) inhibited DNAPL dissolution and contributed to greater dissolution tailing effects. Tailing effects caused by ISCO were more severe compared to EISB since rind formation contributed to permanent $k$ reduction; partial $k$ recovery was observed in the EISB scenarios due to biomass decay. Even though higher temperatures were beneficial to ISCO and EISB during the short-term oxidant/substrate injection period, treatment efficacy was ultimately controlled by the detrimental by-products (rind from ISCO and biomass from EISB) formed as a result of the associative chemical/biological reactions.
Acknowledgements

Funding for this work was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada through Strategic Project Grant SPG-396730-10, scholarship funding from Queen’s University, and scholarship funding from the Ontario Graduate Scholarship Program (OGS). The contributions of Golder Associates Ltd, McMillan-McGee Corp, the Ontario Ministry of the Environment, and The Johnson Company as industrial partners to the Strategic Project Grant are acknowledged.

Numerous individuals have had a profound influence in my academic and professional life throughout the past two and a half years. I am tremendously thankful to Dr. Bernard Kueper for all of his wisdom, patience and professional guidance throughout the duration of my studies. He has always been understanding of my research issues and challenges, and has opened my eyes to the world of contaminant hydrogeology through his expertise, passion, enthusiasm, positive manner and dedication to the field (thank you very much for the opportunity to be a part of your research group). I would also like to thank Dr. Michael West for all of his help and guidance throughout my research duration. He has always shown a willingness to help me in my learning of DNAPL3D-RX and has answered every question I have ever had along the way. Dr. Kevin Mumford and Dr. Kent Novakowski also had a great influence on my studies. Dr. Mumford, thank you very much for all of your help and guidance with questions, issues, and concerns I had (especially in my learning of NOD) as well as your enthusiasm and passion towards our research group (which includes your organizing of the Darcy lectures). Dr. Novakowski, I would like to thank you for all of your help and guidance with respect to my FORTRAN programming issues, your analytical/numerical modeling course, and your positive demeanor (thank you for the squash matches as well). Additional thanks are expressed to Dr. Juliana Ramsay, Dr. Brent Sleep, and Dr. David Major for their help and guidance with regards to my education of bioremediation.
I would like to thank all of my fellow colleagues of Ellis Room 222 for all of their support and kindness they have shown me throughout the past two and a half years. Many thanks are expressed to: Paul Hegele, Owen Miles, Cindy Zhao, Eric Martin, Andrew Logan, Jonah Munholland, Jessica Worley, Richard Plourde, Shawn Trimper, Scott Hansen, Lee-Ann Sills, Obai Mohammed, Mahmudul Shojib, and Matthew McCombs (I apologize if I have forgotten to mention anyone else in this list; I extend my gratitude to everyone who I have met within the Department of Civil Engineering). Thank you very much for all of the support I have received from the technical and administrative staff: Bill Boulton, Stan Prunster, Maxine Wilson, Cathy Wagar, Debbie Ritchie, Diann King, and Phil Brown. In addition, I would like to thank my friends David McNaull, Edison Tang, and Mohamedelamin Badreldin, Andrew Bowden, Phillip Leibrecht, Kean McVeigh and Gaurav Aggarwal for all of their support over the years.

The most important people in my life are my mother Linda, and my sister Nicole. I know these past five years have been difficult for both of you, but you have always supported and encouraged me, even during the toughest of times. Nicole, you are an inspiration to me as your strong will, humour and kindness has always motivated me to be dedicated to whatever I do in life and to be the best person I can be. To my mother, you are the strongest person I have ever known in my life; thank you for being the “rock” of our family, for always going out of your way to take care of all of us, and for always believing in your children. I dedicate this thesis and all my efforts to my late father, Leon. You were always there for us, provided wisdom and lessons in life, and encouraged Nicole and I to do anything we strived for. You will always be remembered in my thoughts and you will always be the main reason I decided to pursue an education in engineering. My greatest wish in this life is that Nicole and I have made you and Mom proud to be your children. I express my deepest love and gratitude towards each of you always.

iv
"Do anything but do it with passion."
# Table of Contents

Abstract ............................................................................................................................................ ii
Acknowledgements ......................................................................................................................... iii
List of Tables .................................................................................................................................. ix
List of Figures .................................................................................................................................. x
Chapter 1 Introduction ..................................................................................................................... 1
  1.1 Research Goals............................................................................................................. .......... 4
  1.2 Organization ........................................................................................................................... 4
  1.3 References.............................................................................................................................. 6
Chapter 2 Literature Review ............................................................................................................ 8
  2.1 Water Properties ..................................................................................................................... 9
  2.2 DNAPL Properties ............................................................................................................... 10
  2.3 Mass Transfer Processes ...................................................................................................... 14
    2.3.1 Dissolution .................................................................................................................... 14
    2.3.2 Aqueous Solubility ........................................................................................................ 17
    2.3.3 Diffusion ....................................................................................................................... 19
      2.3.3.1 Molecular Diffusion Coefficient Correlations – Infinitely Dilute Binary Liquid Systems .............................................................................................................................. 21
      2.3.3.2 Diffusion Coefficient Temperature Dependence – Infinitely Dilute Binary Liquids .............................................................................................................................. ............. 23
      2.3.3.3 Molecular Diffusion Coefficient Empirical Correlations – Ionic Species ............. 24
    2.3.4 Sorption ......................................................................................................................... 26
  2.4 Permanganate ISCO ............................................................................................................. 29
    2.4.1 Oxidative Dechlorination .............................................................................................. 29
    2.4.2 Natural Oxidant Demand .............................................................................................. 32
    2.4.3 Manganese Dioxide Production .................................................................................... 36
    2.4.4 Oxidant Concentration/Dosage ..................................................................................... 38
  2.5 Biologically-Enhanced Reductive Dechlorination ............................................................... 39
    2.5.1 Temperature Effects on EISB Applications .................................................................. 43
    2.5.2 Temperature Dependence of Additional EISB Processes ............................................. 46
    2.5.3 Temperature Adjustment of Monod Kinetics Coefficients ........................................... 48
      2.5.3.1 Half-Saturation Coefficient .................................................................................... 48
      2.5.3.2 Decay Coefficient .................................................................................................. 49
4.4.1 DNAPL Source Zone Mass Removal ................................................................. 148
4.4.2 Boundary Mass Flux ......................................................................................... 153
4.4.3 Mass Flux vs Mass Removal ............................................................................. 156
4.5 Conclusions ............................................................................................................. 160
4.6 Acknowledgements ................................................................................................. 162
4.7 Notation .................................................................................................................. 163
4.8 References ............................................................................................................... 166

Chapter 5 Conclusions ............................................................................................... 178

Appendix A Literature Review Figures ...................................................................... 180

Appendix B Additional Material for Chapter 3 .........
List of Tables

Table 2.1: Physical properties of water at different temperatures (Droste, 1997) ......................... 10
Table 3.1: Virtual site characteristics of the model domains in this study ........................................ 73
Table 3.2: Schedule of ISCO treatment simulations ......................................................................... 78
Table 3.3: ISCO simulation input parameters .................................................................................. 88
Table 3.4: Mass removal enhancement factors for TCE ISCO simulations ...................................... 95
Table 3.5: Mass removal enhancement factors for PCE ISCO simulations ...................................... 96
Table 3.6: Mass flux reduction enhancement factors for TCE ISCO simulations .............................. 103
Table 3.7: Mass flux reduction enhancement factors for PCE ISCO simulations .............................. 104
Table 4.1: Schedule of EISB treatment simulations ......................................................................... 136
Table 4.2: General simulation parameters ...................................................................................... 139
Table 4.3: TCE EISB specific input parameters .............................................................................. 143
Table 4.4: Mass removal enhancement factors for the TCE EISB simulations ................................. 150
Table 4.5: Mass flux reduction enhancement factors for TCE EISB simulations .............................. 155
List of Figures

Figure 2.1: DNAPL density versus temperature................................. 11
Figure 2.2: DNAPL dynamic viscosity versus temperature................ 12
Figure 2.3: PCE interfacial tension versus temperature..................... 13
Figure 2.4: TCE aqueous solubility versus temperature..................... 18
Figure 2.5: PCE aqueous solubility versus temperature..................... 19
Figure 2.6: Estimation of free-water diffusion coefficients for both TCE and PCE.................................................. 24
Figure 2.7: Estimation of free-water diffusion coefficients for lactate, chloride and permanganate .......................................................... 26
Figure 2.8: Organic carbon partitioning coefficient versus temperature. 28
Figure 2.9: Distribution coefficient versus temperature (experimentally measured)......................................................... 28
Figure 2.10: Experimentally measured reaction rate coefficients versus temperature......................................................... 31
Figure 2.11: Arrhenius correlation-determined reaction rate coefficients versus temperature................................. 32
Figure 2.12: Estimated OAM-MnO$_4^-$ reaction rate coefficients ...... 35
Figure 2.13: Maximum substrate utilization rate of TCE/PCE dechlorinators as a function of temperature .......................................................... 45
Figure 2.14: Maximum substrate utilization rate of lactate fermenters as a function of temperature .......................................................... 46
Figure 2.15: Maximum substrate utilization rate of methanogens as a function of temperature ................................. 48
Figure 3.1: Base case DNAPL saturation ($S_{NW}$) and permeability ($k$) fields................................................................. 72
Figure 3.2: Cross-section cut-out of the model domain at A-A’.................. 75
Figure 3.3: TCE aqueous solubility versus temperature..................... 82
Figure 3.4: PCE aqueous solubility versus temperature..................... 83
Figure 3.5: DNAPL source zone mass removal versus time for TCE ISCO and TCE abiotic dissolution simulations after 50 years........................................ 93
Figure 3.6: DNAPL source zone mass removal versus time for PCE ISCO and PCE abiotic dissolution simulations after 50 years........................................ 94
Figure 3.7: Total DNAPL mass removed at the end of the MnO$_4^-$ injection period......................................................... 95
Figure 3.8: DNAPL mass removal rate versus time for TCE ISCO and TCE abiotic dissolution simulations after 50 years. .......................................................... 98
Figure 3.9: DNAPL mass removal rate versus time for PCE ISCO and PCE abiotic dissolution simulations after 50 years. .......................................................... 99
Figure 3.10: Downgradient boundary mass flux versus time for TCE ISCO and TCE abiotic
dissolution simulations after 50 years. .......................................................... 102
Figure 3.11: Downgradient boundary mass flux versus time for PCE ISCO and PCE abiotic
dissolution simulations after 50 years. .......................................................... 103
Figure 3.12: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus
normalized DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. ............ 106
Figure 3.13: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus
normalized DNAPL source zone mass ($M_n$) for the ISCO treatment simulations. ............. 107
Figure 3.14: Normalized PCE mass flux ($F_n$) and PCE solute concentration ($C_n$) versus
normalized DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. ............ 108
Figure 3.15: Normalized PCE mass flux ($F_n$) and PCE solute concentration ($C_n$) versus
normalized DNAPL source zone mass ($M_n$) for the ISCO treatment simulations. ............. 109
Figure 4.1: Base case DNAPL saturation ($S_{NW}$) and permeability ($k$) fields .................. 130
Figure 4.2: Cross-section cut-out of the model domain at A-A’ ............................................. 133
Figure 4.3: TCE aqueous solubility versus temperature ......................................................... 138
Figure 4.4: DNAPL source zone mass removal versus time for TCE EISB and TCE abiotic
dissolution simulations after 50 years. ............................................................................. 149
Figure 4.5: Total DNAPL mass removed at the end of the 2.5 year pulse lactate injection period
for the TCE EISB scenarios. ......................................................................................... 150
Figure 4.6: DNAPL mass removal rate versus time for TCE EISB and TCE abiotic dissolution
simulations after 50 years. ......................................................................................... 153
Figure 4.7: Downgradient boundary mass flux versus time for TCE EISB and TCE abiotic
dissolution simulations after 50 years. ............................................................................. 154
Figure 4.8: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized
DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. ......................... 157
Figure 4.9: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized
DNAPL source zone mass ($M_n$) for the EISB treatment simulations. .............................. 158
Figure A.1: Maximum utilization rate of TCE/PCE dechlorinators as a function of temperature
........................................................................................................................................ 181
Figure A.2: Maximum utilization rate of lactate fermenters as a function of temperature ...... 182
Figure A.3: Maximum utilization rate of methanogens as a function of temperature .......... 183
Figure A.4: PCE reductive dechlorination half-saturation coefficients as a function of temperature
........................................................................................................................................ 184
Figure A.5: TCE reductive dechlorination half-saturation coefficients as a function of temperature ................................................................. 185
Figure A.6: H₂ utilization half-saturation coefficients as a function of temperature .................. 186
Figure A.7: Lactate fermentation half-saturation coefficients as a function of temperature ...... 187
Figure A.8: Methanogenic half-saturation coefficients as a function of temperature................. 187
Figure A.9: Biomass decay coefficients as a function of temperature................................. 188
Figure A.10: Dechlorinator biomass yield coefficients as a function of temperature............. 189
Figure A.11: Methanogenic biomass yield coefficients as a function of temperature............. 190
Figure A.12: Lactate-fermentative biomass yield coefficients as a function of temperature..... 190
Figure B.1: Saturation (SNW) and TCE/MnO₂(s) concentration fields for 20°C TCE ISCO and abiotic dissolution at 10 years at z = 5m. ................................................................. 194
Figure B.2: Saturation (SNW) and TCE/MnO₂(s) concentration fields for 40°C TCE ISCO and abiotic dissolution at 10 years at z = 5m. ................................................................. 195
Figure B.3: Saturation (SNW) and TCE/MnO₂(s) concentration fields for 60°C TCE ISCO and abiotic dissolution at 10 years at z = 5m. ................................................................. 196
Figure B.4: Saturation (SNW) and TCE/MnO₂(s) concentration fields for 80°C TCE ISCO and abiotic dissolution at 5 years at z = 5m. ................................................................. 197
Figure B.5: Permanganate (MnO₄⁻) oxidant preferential migration pathways at a) 1 month, b) 1 year, and c) end of the injection period for the 40°C TCE ISCO scenario at z = 5m. ............... 198
Figure D.1: Fitting of maximum utilization (for TCE reductive dechlorination) rate data from literature. .......................................................................................................................... 204
Figure D.2: Fitting of maximum utilization (for lactate fermentation) rate data from literature. 205
Figure D.3: Fitting of maximum utilization (for methanogenesis) rate data from literature. ...... 206
Figure D.4: Fitting of TCE reductive dechlorination half-saturation coefficient data from literature. .......................................................................................................................... 207
Figure D.5: Fitting of methanogenic half-saturation coefficient data from literature.............. 207
Figure D.6: Fitting of H₂ utilization half-saturation coefficient data from literature.............. 208
Figure D.7: Fitting of lactate fermentation half-saturation coefficient data from literature. ...... 208
Figure D.8: Dechlorinator biomass yield coefficient data from literature. ................................ 209
Figure D.9: Methanogenic biomass yield coefficient data from literature. ................................ 210
Figure D.10: Lactate-fermentative biomass yield coefficient data from literature. ................. 210
Figure D.11: Biomass decay coefficient data from literature. ................................................. 211
Chapter 1

Introduction

Contamination of groundwater resources from the past use and disposal of chlorinated organic solvents remains a significant environmental issue. The most common of chlorinated solvents, trichloroethene (TCE) and tetrachloroethene/perchloroethene (PCE), were utilized in military, industrial, and commercial practices for chemical manufacturing, metal cleaning/degreasing and dry cleaning applications (Pankow and Cherry, 1996). These fluids are classified as dense non-aqueous phase liquids (DNAPLs) and can persist in the subsurface for time periods ranging from decades to centuries due to their low aqueous solubilities. TCE/PCE can migrate downward within subsurface systems and redistribute as pools (connected, potentially mobile DNAPL) and ganglia/blobs (disconnected DNAPL); the source zone is composed of both of these distributions. The extent of DNAPL movement, both laterally and vertically, is strongly controlled by geologic heterogeneity (Kueper et al., 1993). This physical phenomenon makes it difficult to characterize source zones and hence, to remediate contaminated sites.

TCE and PCE are classified as probably carcinogenic and carcinogenic, respectively, and pose a significant risk to human health and safety. Human exposure pathways for these types of contaminants include ingestion, inhalation, and dermal contact (ATSDR, 2011ab). Even though the aqueous solubilities of TCE and PCE are low (approximately 200 to 1100 mg/L), they are significantly greater than the maximum contaminant level (MCL) of 5 ppb (0.005 mg/L) specified for both compounds (US EPA, 2013). This particular property of both compounds makes it difficult to remediate sites to within these compliance limits. Removal/destruction of the...
contaminant mass is essential to reducing downgradient contaminant concentrations and terminating the contributing source in order to mitigate/prevent harmful impact to the public.

In the past few decades, there has been greater emphasis allocated towards developing *in situ* reactive transport methods for subsurface remediation. Other remediation technologies such as pump-and-treat, soil vapour extraction (SVE), and steam injection involve significant operational/maintenance costs and energy input. *In situ* chemical oxidation (ISCO) and enhanced *in situ* bioremediation (EISB) are two of the most optimistic *in situ* technologies that have been applied for the remediation of contaminant source zones. ISCO and EISB rely on an enhanced dissolution scheme to accelerate the rate of contaminant mass removal. Both *in situ* technologies reduce contaminant aqueous phase concentrations, thereby driving the gradient towards greater dissolution.

A number of different chemical oxidants have been applied for the ISCO treatment of DNAPLs. Persulfate, ozone, hydrogen peroxide, and permanganate have been utilized for subsurface contaminant remediation. Permanganate (MnO₄⁻) ISCO has been applied in numerous laboratory and field studies. It is a selective oxidant capable of reacting with chlorinated solvents (in their aqueous phase), yielding chloride ions. In addition to aqueous phase contaminants, MnO₄⁻ will also react with subsurface materials, which is classified as the natural oxidant demand (NOD). NOD can be a detriment to MnO₄⁻ ISCO as it represents a non-productive sink; oxidant can be consumed through these reactions thereby preventing oxidation of contaminants. The formation of manganese dioxide (MnO₂(s)) and carbon dioxide (CO₂(g)) due to MnO₄⁻ ISCO reactions can
also inhibit contaminant treatment. Both MnO$_2$(s), an insoluble precipitate, and CO$_2$(g) can reduce subsurface permeability and contribute to significant flow bypassing (Siegrist et al., 2011).

EISB treatment of subsurface contaminants has been extensively studied at both the laboratory and field scales. There are various microbial cultures capable of anaerobic reductive dechlorination (RD) of chlorinated solvents (Holliger et al., 1993; Neumann et al., 1994; Gerritse et al., 1996), but few are capable of complete dechlorination to ethene (Maymó-Gatell et al., 1997). Similar to ISCO, dechlorinators can utilize (convert to a less toxic daughter compound) the contaminant in the aqueous phase as part of its metabolic activity. The addition of an organic substrate (biostimulation) can assist in facilitating greater dechlorination activity as these compounds can be fermented to provide a source of hydrogen (H$_2$) electron donor. However, competition for the H$_2$ electron donor from other microbial cultures (methanogenic, sulfate-reducing, iron-reducing) can severely inhibit dechlorinator growth. The degree of biocompetition will be dependent on factors such as concentration thresholds, redox conditions, as well as the selection of organic substrate. The biomass populations produced can also deposit within subsurface pores, which can contribute to significant flow bypassing and consequently inhibit EISB treatment.

Thermal treatment involves the application of heat to enhance/accelerate contaminant removal from the subsurface. Thermal conductive heating (TCH), electrical resistive heating (ERH), steam injection and radio frequency (RF) heating are thermal treatment technologies capable of generating subsurface temperatures to at or above the boiling point of water ($100^\circ$C), depending on local pressures (USACE, 2009). Higher temperatures generally correspond to an increase in
the aqueous solubility, volatility, diffusivity and desorption of TCE and PCE. Enhancement in
dissolution can also be attained since at higher temperatures, the density and viscosity of both
fluids decrease.

1.1 Research Goals

The focus of this research was to assess the effects of elevated subsurface temperature on the
application of the in situ technologies ISCO and EISB by utilizing the numerical model,
DNAPL3D-RX (West, 2009; West and Kueper, 2012). Changes in temperature will have an
impact on groundwater flow and solute transport, fluid properties, and associative
chemical/biological reaction rates. These mass removal technologies were simulated over a finite
timescale for active treatment (oxidant/substrate injection period); at times following termination
of injection, only dissolution was simulated. Both ISCO and EISB were evaluated against
corresponding abiotic dissolution scenarios to assess the remedial enhancements of employing
these treatment technologies. Evaluation metrics utilized for each treatment/dissolution scenario
included DNAPL mass removal and mass flux reduction.

1.2 Organization

The remaining Chapters and Appendices of this thesis were organized in the following manner:

- Chapter 2 was written as a literature review that provides background knowledge
  necessary to conducting this research project.
• Chapters 3 and 4 were written in stand-alone manuscript format, intended for publication in peer reviewed journals. S. Bryck is the first author and Dr. Bernard H. Kueper and Dr. Michael R. West are the co-authors for both of these Chapters.

• Chapter 5 was written as a Conclusions Chapter that summarized the material presented in Chapters 3 and 4.

The following Appendices contain supporting material pertaining to Chapters 2, 3, and 4; they were organized as follows:

• Appendix A – Literature Review Figures which include parameters used, measured, and estimated by numerous bioremediation studies.

• Appendix B – Additional Material for Chapter 3 which includes a list of the DNAPL3D-RX multiphase flow and solute transport equations (ISCO) and additional chapter figures.

• Appendix C – Additional Material for Chapter 4 which includes a list of the DNAPL3D-RX multiphase flow and solute transport equations (EISB).

• Appendix D – EISB/Monod Parameter Estimation Fitting which includes the hypothetical mesophilic fits from select literature data. The estimated parameters from these fits are utilized for the numerical models described in Chapter 4.
1.3 References


United States Environmental Protection Agency. (2013, May 29). Water: Basic Information about Regulated Drinking Water Contaminants and Indicators. *United States Environmental Protection...


Chapter 2

Literature Review

The past disposal of dense non-aqueous phase liquids (DNAPLs) in military, commercial and industrial practices, without awareness of environmental implications, continues to negatively impact subsurface water systems throughout North America. In situ chemical oxidation (ISCO) and enhanced in situ bioremediation (EISB) are technologies capable of complete contaminant destruction and have been implemented in past site remedial applications. The focus of this research is on the effects of elevated, sub-boiling subsurface temperatures (20 to 80°C for ISCO, 10 to 40°C for EISB) on permanganate (MnO$_4^-$) ISCO and lactate-augmented EISB for remediation of trichloroethene (TCE) and tetrachloroethene (PCE). The subsurface temperature can be elevated using thermal treatment methods such as electrical resistance heating (ERH), thermal conductive heating (TCH), and radio frequency heating (USACE, 2009).

Elevated temperatures will alter the physicochemical properties of both the ambient groundwater and subsurface contaminant. Mass transfer processes are greatly influenced by temperature as aqueous solubility (of TCE/PCE), diffusivity, and desorption generally increases at higher temperatures. For ISCO applications, the reactions that occur between the oxidant and target (i.e. TCE/PCE) and non-target (organic aquifer material (OAM)) compounds are enhanced as reaction rates increase with increases in temperature, in accordance with Arrhenius principles. The biological processes involved in EISB reductive dechlorination of TCE/PCE are also significantly affected due to changes in temperature. Most microorganisms utilized for dechlorination are mesophilic in nature, and their activity/affinity is extremely sensitive to temperatures.
below/above their temperature optima. Increases in temperature will impact associative biological processes (other than dechlorination) such as substrate fermentation (for \( \text{H}_2 \) electron donor production) and EISB-competing hydrogenotrophic reactions, primarily methanogenesis.

### 2.1 Water Properties

The physicochemical properties of water will change with respect to increasing temperatures, based on the characteristics of hydrogen bonds. The maximum liquid density of water is 1000 kg/m\(^3\) at the approximate temperature of 4°C (39°F) (Droste, 1997). This property of water can be attributed to the nature of hydrogen bonds. At sub-melting temperatures (below 0°C), the hydrogen bonds between water molecules are organized in a fixed but relatively open structure (in the solid form of ice). Increasing the temperature causes fractional breaking of hydrogen bonds, which collapses the structure and increases the density. This process continues past the melting point until water density reaches its maximum (water molecules are arranged in its most organized structure) at 4°C. After this point, water behaves similar to most other liquids as increases in temperature decreases the liquid density. Heating of liquid molecules provides kinetic energy for greater molecular activity and reduces the organization of the molecular structure due to the increases in bond breaking (Petrucci et al., 2007). Table 2.1 outlines the density of water at different temperatures.
Table 2.1: Physical properties of water at different temperatures (Droste, 1997).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (kg/m³)</th>
<th>Dynamic Viscosity (Pa•s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>999.8</td>
<td>1.78E-03</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>1.52E-03</td>
</tr>
<tr>
<td>10</td>
<td>999.7</td>
<td>1.31E-03</td>
</tr>
<tr>
<td>15</td>
<td>999.1</td>
<td>1.14E-03</td>
</tr>
<tr>
<td>20</td>
<td>998.2</td>
<td>1.00E-03</td>
</tr>
<tr>
<td>25</td>
<td>997.0</td>
<td>8.90E-04</td>
</tr>
<tr>
<td>30</td>
<td>995.7</td>
<td>7.98E-04</td>
</tr>
<tr>
<td>40</td>
<td>992.2</td>
<td>6.53E-04</td>
</tr>
<tr>
<td>50</td>
<td>988.0</td>
<td>5.47E-04</td>
</tr>
<tr>
<td>60</td>
<td>983.2</td>
<td>4.66E-04</td>
</tr>
<tr>
<td>70</td>
<td>977.8</td>
<td>4.04E-04</td>
</tr>
<tr>
<td>80</td>
<td>971.8</td>
<td>3.54E-04</td>
</tr>
<tr>
<td>90</td>
<td>965.3</td>
<td>3.15E-04</td>
</tr>
<tr>
<td>100</td>
<td>958.4</td>
<td>2.82E-04</td>
</tr>
</tbody>
</table>

Fluid flow resistance tends to decrease at higher temperatures. Viscosity is related to the degree of the intermolecular forces within the fluid. Increasing the temperature provides the kinetic energy required to break the intermolecular bonds that form the fluid structure. Table 2.1 outlines the viscosity values of water at different temperatures. Like other fluids, water viscosity decreases as the temperature increases. The strength of hydrogen bonds are reduced due to the higher kinetic energy obtained at higher temperatures (Petrucci et al., 2007).

2.2 DNAPL Properties

The physicochemical properties of dense non-aqueous phase liquids (DNAPLs) will be influenced by variation in temperature. The strength of the intermolecular forces of fluids tends to decrease with elevated temperatures. Increased kinetic energy decreases the organizational
structure of the intermolecular bonds. Viscosity and density are properties that are directly correlated to the degree of intermolecular structure. As intermolecular bond structure decreases (due to increased temperature/kinetic energy), the viscosity and density of most fluids will decrease (Petrucci et al., 2007). Figures 2.1 and 2.2 display the variation in the density and viscosity of TCE/PCE due to variations in temperature (Sleep and Ma, 1997; NOAA, 1999; Lide, 2012).

Figure 2.1: DNAPL density versus temperature. Sleep and Ma’s (1997) PCE temperature-dependent density correlation is also presented.
The interfacial tension (IFT) that exists between organic solvents and water is expected to
decrease with increasing temperature (Imhoff et al., 1997). The rate of decrease of the interfacial
tension is specific to the physicochemical properties of the individual compound. Non-aqueous
phase liquids (NAPLs) with greater impurities have lower interfacial tensions in comparison to
pure-phase immiscible fluids (Sleep and Ma, 1997). Sleep and Ma (1997) studied the effects of
temperature on the interfacial tension of NAPLs: Voltesso 35 and PCE. For the temperature range
of 24.3°C-89.9°C, the interfacial tension of PCE did not vary significantly; approximately a 6%
decrease within this temperature range. Imhoff et al. (1997) observed an approximately 7%
decrease in PCE-water interfacial tension from 5°C to 40°C (decrease in interfacial tension was
not significant). In contrast, Sleep and Ma (1997) found that the interfacial tension of Voltesso 35
was more affected by elevated temperatures (within this temperature range) as it decreased by
approximately 39%. Voltesso 35 was more representative of a multi-component NAPL and was more sensitive to changing temperature (Sleep and Ma, 1997). Even though interfacial tension decreases with increasing temperature, it has been suggested from past literature that the effect is minor (USACE, 2009).

![Figure 2.3: PCE interfacial tension versus temperature.](image)

The decreases in the physicochemical properties of both non-wetting (TCE, PCE) and wetting fluids will have an impact on subsurface flow. From Table 2.1, the decrease in water viscosity is more drastic in comparison to the decrease in density at increasing temperatures. Subsurface hydraulic conductivity will increase due to elevated temperatures (assuming the intrinsic permeability remains constant) in accordance with Equation 2-1 (Fetter, 2001):

\[
K = \frac{k \rho g}{\mu}
\]  

(2-1)
where $K$ is the hydraulic conductivity {L$^1$T$^{-1}$}, $k$ is the intrinsic permeability {L$^2$}, $\rho$ is fluid density {M$^1$L$^{-3}$}, $g$ is the gravitational constant {L$^1$T$^{-2}$}, $\mu$ is the fluid viscosity {M$^1$L$^{-1}$T$^{-1}$}.

Similar to water, NAPL mobilization will also increase with temperature as both viscous and interfacial (tension) resistance is reduced (O’Carroll and Sleep, 2007). The simulations conducted by West and Kueper (2012) utilized post-hydraulic displaced (HD) NAPL saturation fields prior to ISCO treatment. The NAPL source zone was subjected to HD after release, migration, and redistribution within the porous media domain. For these particular modeling scenarios, the impact of mobile NAPL pools are minimized; residual NAPL saturations are increased as a result of HD (Richards et al., 2012).

### 2.3 Mass Transfer Processes

#### 2.3.1 Dissolution

Dissolution between the non-aqueous and aqueous phases is enhanced by increases in temperature. It is an endothermic process, in which the addition of heat should allow for a more favourable/greater reaction, in accordance with Le Châtelier’s principle (Grant, 2005; Petrucci et al., 2007). Dissolution at the macroscopic scale has been commonly represented in past literature studies using the steady-state approximation of the thin stagnant film model, as shown in Equation 2-2 (Miller et al., 1990):

$$ J = k_i a_{ma} (C_s - C) = K_i (C_s - C) $$

$$ (2-2) $$
where $J$ is the solute mass flux from the immiscible liquid phase to the aqueous phase $\{M^1 L^{-2} T^{-1}\}$, $k_i$ is the mass transfer coefficient $\{L^1 T^{-1}\}$, $a_{in}$ is the interfacial area between NAPL and aqueous phases $\{L^{-1}\}$, $C_s$ is the thermodynamic equilibrium phase concentration (solubility) in which the non-aqueous phase is present $\{M^1 L^{-3}\}$, $C$ is the bulk-solution aqueous phase solute concentration $\{M^1 L^{-3}\}$, $K_i$ is the lumped mass transfer rate coefficient $\{T^{-1}\}$.

The use of this single boundary layer description of mass transfer shows that dissolution is controlled by both the mass transfer coefficient and the concentration gradient which exists between both non-aqueous and aqueous phases (rate-limited process). Increased temperatures will have a direct effect on mass transfer coefficients. Past studies have related the lumped mass transfer coefficient to experimentally-determined dimensionless parameters such as the Reynolds (Re), Schmidt (Sc), and modified Sherwood (Sh) numbers (Miller et al., 1990). These parameters will be affected by temperature as they are a function of the fluid properties. The diffusivity, density, viscosity, and the interfacial tension of both non-aqueous and aqueous phase fluids will vary with temperature. Imhoff et al. (1997) studied the effects of hot water flushing on PCE mass transfer processes. It was observed that the lumped mass transfer coefficient for the PCE-water system increased by a factor of approximately 2 from 5 to 40°C. The experimental results suggested that mass transfer was enhanced due to the significant decrease in PCE viscosity at higher temperatures; mobile resistance for mass transfer was reduced. Within this temperature range, PCE-water interfacial tension decreased by approximately 7% and was found to have a minimal effect on mass transfer. However, depending on the properties of the immiscible fluid, the magnitude of interfacial tension reduction may have a significant effect on mass transfer.
Interfacial tension is inversely proportional to the interfacial area; lowered interfacial tensions should result in greater interfacial areas for mass transfer (Bradford and Abriola, 2001; Seo and McCray, 2002). Higher temperatures can significantly enhance DNAPL mass transfer as reduction of viscosities and interfacial tensions as well as increases in diffusivity have a direct effect on the mass transfer coefficient. The magnitude of the mass transfer enhancement for an immiscible fluid will be dependent on its unique physicochemical properties. For immiscible fluids whose solubility greatly increases with temperature or which have significant mass transfer resistance due to high viscosities, these fluids may experience greater dissolution enhancement (Imhoff et al., 1997).

Dissolution will also be enhanced at higher temperatures as the aqueous solubility of chlorinated solvents increase (see Section 2.3.2). Increases in the aqueous solubility will increase the concentration gradient between the non-aqueous and aqueous phases. Higher temperatures will also increase the rate of ISCO reactions and EISB processes within certain temperature ranges. In the absence of thermal input (increased temperatures), ISCO/EISB reactions enhance NAPL dissolution by reacting with aqueous phase concentrations (Siegrist et al., 2011). Increases in temperature will increase the reaction rate between NAPL and permanganate/microorganisms, thereby further lowering/reducing aqueous phase concentrations. ISCO/EISB coupled with thermal treatment could significantly increase dissolution of NAPLs through increased aqueous solubility and decreased aqueous phase concentrations (within the bulk solution) at higher temperatures.
The ISCO/EISB simulations conducted by West (2009) modeled dissolution using the local equilibrium assumption \((C_s = C)\), an instantaneous, non-rate limited process occurring between the non-aqueous and aqueous phases. The applications of both equilibrium and non-equilibrium (rate-limited) approaches to model dissolution are greatly dependent on domain scale (Grant, 2005). Field scale dissolution has been considered to be rate-limited as solute concentrations measured have been found to be lower than the solubility limit in heterogeneous subsurface environments (Rivett and Feenstra, 2005). This difference in solute concentrations has been strongly related to advective-dispersive transport effects such as flow bypassing due to subsurface heterogeneity (Sale and McWhorter, 2001). However, equilibrium dissolution was found to be sufficient for local scale domains, for scenarios in which the complexities of the contaminant distribution and the porous media were considered (Brusseau et al., 2002). This was the premise used by West (2009) to justify the use of the local equilibrium assumption for field scale modeling applications. The local equilibrium assumption of mass transfer is primarily dependent on the change in the solubility limit of the specific compound with temperature. Similar to the rate-limited expression of dissolution (Equation 2-2), equilibrium dissolution should increase with temperature (refer to Section 2.3.2).

2.3.2 Aqueous Solubility

Elevated temperatures will increase the solubility of numerous organic compounds. Past laboratory studies have determined that the solubility of both TCE and PCE increase at higher temperatures (Imhoff et al., 1997; Sleep and Ma, 1997; Heron et al., 1998b; Knauss et al., 2000; Chen et al., 2012). Both compounds also exhibited a minimum solubility limit within sub-boiling
temperature ranges (with reference to water’s boiling point). Imhoff et al. (1997) observed that there was a slight drop in PCE solubility from 5°C to around 20°C, but steadily increased for greater temperatures past this minimum point. Chen et al. (2012) found that PCE solubility decreased to a minimum of 197 mg/L at 21°C, but increased from 21°C to 75°C thereafter. For TCE, Knauss et al. (2000) found that solubilities increased from temperatures of 21°C to 117°C, with no evidence of a minimum solubility within this range. However, Chen et al. (2012) observed a minimum TCE solubility of 1310 mg/L at 35°C, but increased at higher temperatures. Heron et al. (1998b) also found that TCE solubility was at a minimum at approximately 30°C. Figures 2.4 and 2.5 summarize the literature data on TCE/PCE solubility dependence with temperature. The figures display the fact that both solubilities increase exponentially at temperatures above the normal boiling point of water (USACE, 2009). Both experimentally determined solubilities and empirical correlations (as determined by the authors) are presented.

Figure 2.4: TCE aqueous solubility versus temperature. Data points represent laboratory measured solubilities.
2.3.3 Diffusion

Diffusion is a mass transfer process that occurs in the absence of bulk flow and/or mixing. It is greatly dependent on concentration, temperature, and pressure gradients which exist within the chemical system; for binary liquid systems, the general expression of diffusive flux is shown in Equation 2-3 (Poling et al., 2001):

\[ J_{AB} = -D_{AB}^o \frac{\partial C_A}{\partial z} \]  

where \( J_{AB} \) is the diffusive flux of solute A diffusing into solvent B \( \{M^1L^{-2}T^{-1}\} \), \( D_{AB}^o \) is the binary free-water molecular diffusion coefficient of solute A diffusing into solvent B in dilute solutions.
\{L^2T^{-1}\}, \ C_A is the concentration of solute A \ \{M^1L^{-3}\}, \ z is the vertical transverse distance/direction \ \{L^1\}.

Diffusion coefficients are sensitive to changes in temperature, which can significantly impact mass transfer processes. Within the temperature range of 10°C to 80°C, both TCE and PCE are assumed to be present within the liquid phase (Lide, 2012). Section 2.3.3 focuses on the diffusion of liquid/aqueous solutes in water (the solvent) for infinitely dilute solute concentrations. In infinitely dilute binary liquid diffusion, contaminants and products of reaction are present in an essentially pure water system; it is assumed that there is minimal to no concentration gradient for water to diffuse into the solute (Poling et al., 2001).

The molecular diffusion coefficient of liquid solutes (i.e. subscript \(A\)) into liquid solvents (i.e. subscript \(B\)) can be represented through the application of the Stokes-Einstein equation under no-slip conditions (Poling et al., 2001; Bird et al., 2002); see Equation 2-4:

$$D_{A\beta}^* = \frac{RT}{6\pi \mu_B r_a}$$  \hspace{1cm} (2-4)

where \(R\) is the universal gas constant (8.3144621 J/mol K), \(T\) is the reference temperature (°K), \(\mu_B\) is the dynamic viscosity of solvent B at reference temperature \(\{M^1L^{-1}T^{-1}\}\), \(r_a\) is the radius of spherical-shape solute A \(\{L^1\}\).
This equation was derived through hydrodynamic theory and the manipulation of the Nernst-
Einstein equation for a spherical solute particle. The equation has been found to be applicable for
representing the diffusion of large spherical solute particles in dilute, low molecular weight
solutions (Bird et al., 2002). From Equation 2-4, it can be observed that molecular (solute)
diffusion coefficients are inversely related to the viscosity of the solvent and directly related to
the temperature of the system. The viscosity of fluids decrease with increasing temperatures, as
previously discussed. Less restriction of molecular movement allows for greater mass transfer via
diffusion. The effects of rising temperatures and the corresponding decreases in solvent viscosity
will increase molecular diffusivity (Delle Site, 2001).

2.3.3.1 Molecular Diffusion Coefficient Correlations – Infinitely Dilute Binary Liquid Systems

The application of liquid diffusion state theories for estimation of molecular diffusion coefficients
of liquid solutes in dilute binary liquid systems remains difficult since these theories consider
ideal conditions (Poling et al., 2001; Bird et al., 2002). Calculation of molecular diffusion
coefficients is strongly dependent on empirical correlations in order to capture the effects of
increasing temperature. One of the earliest empirical correlations (Equation 2-5) was proposed by
Wilke and Chang (1955), which is still commonly used to estimate diffusion coefficients for
excess water solvent systems:

\[
D_{AB}^* = \frac{7.4 \times 10^{-8} \sqrt{\phi M_B T}}{\mu_B V_A^{0.6}}
\]

(2-5)
where $\phi$ is the association factor of solvent B (for water $\phi = 2.6$), $M_B$ is the molecular weight of solvent B $\{M^1\text{mol}^{-1}\}$, $V_A$ is the molar volume of solute A at its normal boiling point $\{L^2\text{mol}^{-1}\}$.

The Wilke-Chang (1955) empirical expression has been found to be suitable (average error of about 10%) for systems in which water is the solvent. It is recommended that other empirical correlations be applied for other infinitely dilute binary liquid cases (Poling et al., 2001). Studies conducted by Tyn and Calus (1975) and Hayduk and Minhas (1982) proposed the following empirical expressions (Equations 2-6 and 2-7, respectively) for estimating diffusion coefficients for infinitely dilute binary liquid systems:

\[
\frac{D_{AB}^*}{V_B} = 8.93 \times 10^{-8} \left( \frac{V_A}{V_B^2} \right)^{1/6} \left( \frac{P_B}{P_A} \right)^{0.6} \frac{T}{\mu_B}
\]  

(2-6)

\[
D_{AB}^* = 1.25 \times 10^{-8} \left( V_A^{-0.19} - 0.292 \right) T^{1.52} \mu_w^{\epsilon^*}
\]

(2-7)

\[
\epsilon^* = (9.58 / V_A) - 1.12
\]

where $V_B$ is the molar volume of solvent B at its normal boiling point $\{L^2\text{mol}^{-1}\}$, $P_A/P_B$ is the parachor of solute A / solvent B $\{M^{1/4}L^{3/2}T^{-1/2}\text{mol}^{-1}\}$, $\mu_w$ is the dynamic viscosity of water (solvent) at reference temperature $\{M^1L^{-1}T^{-1}\}$.

The Tyn-Calus method requires input values of the parachors of both the solute and solvent. The parachor of a fluid is dependent on the surface tension and molar volume, which vary with temperature. For practical purposes, it can be assumed that the parachors of the solute and solvent are relatively independent of temperature; parachor values can be estimated using tabular values.
found in literature (Quayle, 1953; Poling et al., 2001). Both the Tyn-Calus and Hayduk-Minhas
correlations are more computationally intensive and require more solute/solvent property inputs
than the Wilke-Chang equation. Even though there is a level of uncertainty and error associated
with all correlations, the Tyn-Calus and Hayduk-Minhas correlations are more preferred as they
yield lower errors than the Wilke-Chang correlation (Poling et al., 2001).

2.3.3.2 Diffusion Coefficient Temperature Dependence – Infinitely Dilute Binary Liquids

The empirical correlations described in Section 2.3.3.1 are suitable in estimating diffusion
coefficients for infinitely dilute binary liquid systems over small temperature ranges (Skelland,
1974; Poling et al., 2001). Estimating diffusion coefficients over greater temperature ranges can
be approximated either graphically or from Tyn’s (1981) proposed correlation (Equation 2-8):

\[
\frac{D_{AB(T_2)}}{D_{AB(T_1)}} = \left( \frac{T_c - T_1}{T_c - T_2} \right)^n
\]  

(2-8)

where \(T_c\) is the critical temperature of the solvent (°K), \(T_1/T_2\) are reference temperatures (°K).

Tyn’s (1981) temperature-dependent expression is suitable and is not associated with significant
error (i.e. about 10%) for temperature ranges 10 degrees Kelvin above/below the normal
freezing/boiling point (Poling et al., 2001). Figure 2.6 displays the estimates of free-water
diffusion coefficients for both TCE and PCE. The Hayduk-Minhas correlation was utilized to
calculate the free-water diffusion coefficient of both chlorinated solvents at 10°C; Equation 2-8
was used afterwards to estimate the diffusion coefficients at higher temperatures. The Tyn-Calus correlation and Equation 2-8 were also used to estimate the free-water diffusion coefficients of TCE/PCE. This method resulted in similar values in comparison to the Hayduk-Minhas correlation (values not shown).

![Figure 2.6: Estimation of free-water diffusion coefficients for both TCE and PCE for the temperature range of 10°C to 80°C.](image)

\[ \text{Free-Water Diffusion Coefficient (cm}^2/\text{s}) \]

\[ \text{Temperature (°C)} \]

\[ \text{TCE} \quad \text{PCE} \]

2.3.3.3 Molecular Diffusion Coefficient Empirical Correlations – Ionic Species

For MnO$_4$-ISCO applications, assuming potassium permanganate completely dissociates in solution, ionic diffusion at infinite dilution needs to be considered. Chloride (Cl$^-$) is produced via permanganate ISCO reactions with TCE/PCE and will also diffuse in the aqueous system. Free ion diffusion is governed by the individual limiting conductance of the individual ion. Equation
2-9 can be used to estimate the free-water diffusion coefficients of ions in infinitely diluted systems (Lide et al., 2012):

\[
D_{AB,T} = \frac{RT \lambda}{F^2 |\omega|}
\]  

(2-9)

where \(\lambda\) is the molar conductivity for common ions \(\{M^{-1}T^3A^2mol^{-1}\}\), \(F\) is the Faraday constant \((96485.3415 \text{ s A/mol})\), \(\omega\) is the ionic charge \(\{-\}\).

Both permanganate and chloride will undergo individual ionic diffusion. Figure 2.7 displays the estimates of the free-water diffusion coefficients for both \(\text{MnO}_4^-\) and \(\text{Cl}^-\). Values for molar ionic conductivity were obtained from Lide et al. (2012) at the reference temperature of 25°C. In order to adjust the diffusion coefficients for differing temperatures, an approximate correction factor of \(T/334\mu_w\) was utilized (Poling et al., 2001). Similarly, for lactate-augmented EISB, diffusion of the lactate ion \((\text{C}_3\text{H}_5\text{O}_3^-)\) must also be accounted for. The same temperature adjustment method used for \(\text{MnO}_4^-\) and \(\text{Cl}^-\) free-water diffusion coefficients was applied for \(\text{C}_3\text{H}_5\text{O}_3^-\) free-water diffusion coefficients (see Figure 2.7).
Figure 2.7: Estimation of free-water diffusion coefficients for lactate, chloride and permanganate for the temperature range of 10°C to 80°C.

2.3.4 Sorption

As temperature increases, the degree of sorption of organic contaminants typically decreases. Sorption processes are generally exothermic, in which the addition of heat should reduce the effects of sorption, in accordance with Le Châtelier’s principle (Delle Site, 2001; Petrucci et al., 2007). Past studies have described solubility and sorption to be inversely related (Gerstl, 1990; Delle Site, 2001). With the exception of some organic compounds whose solubility decreases with increasing temperature, the degree of sorption of TCE/PCE will decrease with heat addition. The solubility of both chlorinated solvents increases at elevated temperatures (see Figures 2.4 and 2.5).
Elevated temperatures will have a direct effect on the sorption isotherm. West and Kueper’s (2012) simulations utilized a linear isotherm to describe sorption of TCE/PCE ($C_{\text{sorbed}} = K_d C$) (Fetter, 1999). Estimation of the distribution coefficient ($K_d = f_{oc} K_{oc}$) is dependent on the fraction of organic carbon ($f_{oc}$) and the organic carbon partitioning coefficient ($K_{oc}$). Assuming that the fraction of organic carbon content does not vary with temperature, variation in $K_d$ is directly related to $K_{oc}$. Temperature effects on both $K_{oc}$ and $K_d$ has been studied in past literature for TCE/PCE. Heron et al. (1998a) found that the $K_d$ of TCE decreased by 15% for temperatures between 23°C to 99°C. Sleep and McClure (2001) observed that the $K_{oc}$ of PCE decreased by approximately 40% over temperatures ranging from 22°C to 92°C for a porous medium with a $f_{oc}$ of 0.0045. Gerstl (1990) examined sorption data for over 400 different compounds to determine correlations between $K_{oc}$ and solubility ($C_s$). For non-aromatic, halogenated hydrocarbons, Gerstl (1990) determined the following correlation: $\log K_{oc} = -0.346 \log C_s + 1.280$. TCE/PCE solubilities measured by Knauss et al. (2000) and Chen et al. (2012) were utilized to evaluate this empirical correlation. The temperature range used in the solubility experiments by Knauss et al. (2000) was similar to that studied by Heron et al. (1998a) and Sleep and McClure (2001). Evaluation of Gerstl’s (1990) empirical correlation, using Knauss et al’s (2000) solubility data, determined an approximate 20% and 28% decrease in $K_{oc}$ for TCE and PCE respectively, within similar temperature ranges. Comparison of $K_{oc}/K_d$ values from laboratory studies and Gerstl’s (1990) empirical expression indicates that this correlation can be utilized for illustrative calculations (Burghardt and Kueper, 2008). Figures 2.8 and 2.9 summarize the literature data on $K_{oc}/K_d$ dependence with temperature. Both experimentally measured and empirical correlation-determined $K_{oc}/K_d$ are presented.
Figure 2.8: Organic carbon partitioning coefficient versus temperature. Only Sleep and McClure (2001) experimentally measured variations in $K_{oc}$ with temperature. The remaining points were determined using the correlation determined by Gerstl (1990) using solubility measurements from Knauss et al. (2000) and Chen et al. (2012).

Figure 2.9: Distribution coefficient versus temperature (experimentally measured).
2.4 Permanganate ISCO

2.4.1 Oxidative Dechlorination

The ISCO permanganate reaction with TCE/PCE has been determined to be 2nd order overall, as depicted in Equation 2-10 (Siegrist et al., 2011). Higher temperatures will increase the rate of this reaction, in accordance with the Arrhenius expression (Equations 2-11 and 2-12):

\[
\frac{\partial [TCE]}{\partial t} = -k_{TCE} [TCE][MnO_4^-] \quad \text{or} \quad \frac{\partial [PCE]}{\partial t} = -k_{PCE} [PCE][MnO_4^-] \quad (2-10)
\]

\[
k_{rxns} = A \exp \left( -\frac{E_a}{RT} \right) \quad (2-11)
\]

\[
\ln \left( \frac{k_2}{k_1} \right) = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (2-12)
\]

where [] brackets indicate molar concentrations \( \{ \text{L}^3\text{mol}^{-1} \} \), \( k_{TCE/PCE} \) is the 2nd-order reaction rate coefficient for the reaction between TCE/PCE and MnO_4^- \( \{ \text{L}^3\text{T}^{-1}\text{mol}^{-1} \} \), \( k_{rxns} \) is a 2nd-order reaction rate coefficient for a general reaction \( \{ \text{L}^3\text{T}^{-1}\text{mol}^{-1} \} \), \( A \) is Arrhenius frequency factor \( \{-\} \), \( E_a \) is the activation energy \( \{ \text{MJ}^{-1}\text{L}^{-2}\text{T}^{-2}\text{mol}^{-1} \} \), \( k_1/k_2 \) is the 2nd-order reaction rate coefficient at reference temperature \( \{ \text{L}^3\text{T}^{-1}\text{mol}^{-1} \} \).

Activation energy for a reaction is determined by measuring reaction rate coefficients at different temperatures. Plotting \( \ln k_{rxns} \) versus \( 1/T \), the slope of the linear relationship is \( E_a/R \) (Petrucci et al., 2007). The reaction kinetics of potassium permanganate and TCE/PCE has been extensively
studied in past literature. The reaction between MnO₄⁻ and chlorinated ethenes (CEs) is composed of several steps/pathways, which are greatly dependent on the pH of the system (Yan and Schwartz, 2000; Dai and Reitsma, 2004). In trying to determine the governing reaction rate, it has been determined that the rate-limiting step for the reaction between MnO₄⁻ and CEs is the initial formation of a cyclic hypomanganate ester (CHME). In this reaction step, the carbon-carbon double bonds of CEs are attacked by MnO₄⁻, via an activated organometallic complex; unlike the proceeding steps in these oxidation reactions, the formation of the CHME is independent of the pH of the system (Yan and Schwartz, 2000). Even though greater oxidation occurs at lower pH (i.e. greater number of electrons transferred during redox reactions; less hydroxyl ion competition), MnO₄⁻/CE oxidation rates are relatively unaffected at pH ranges within common subsurface systems (Huang et al., 2002; Siegrist et al., 2011).

Temperature-dependent kinetics of MnO₄⁻/CE oxidation reactions has been studied by various authors. The activation energy of the reaction between TCE and MnO₄⁻ has been found to range from 35 to 41.5 kJ/mol (Huang et al., 1999, 2001; Yan and Schwartz, 2000). Studies conducted on the reaction between PCE and MnO₄⁻ have determined that the activation energy can range from 38.9 to 43.9 kJ/mol (Huang et al., 2002; Dai and Reitsma, 2004). Figures 2.10 and 2.11 summarize the literature data on kTCE/kPCE dependence with temperature. Both experimentally measured reaction rate coefficients and Arrhenius-determined reaction rate coefficients (some papers only reported Arrhenius Eₚ and A parameters) are presented. In comparison to TCE, the oxidation of PCE is significantly slower, which has been suggested to be a property of its additional chloride atom. Chloride atoms may induce steric effects as well as electron deficiencies
in the carbon-carbon double bond; has a greater influence in the oxidation of PCE compared to TCE (Huang et al., 2001; Dai and Reitsma, 2004).

**Figure 2.10:** Experimentally measured reaction rate coefficients versus temperature. If not noted, reaction rate coefficients were measured at near neutral pH (~7) conditions.
Figure 2.11: Arrhenius correlation-determined reaction rate coefficients versus temperature. If not noted, Arrhenius parameters ($E_a$ and $A$) were determined at near neutral pH (~7) conditions. Both data sets from Huang et al. (2001) were estimated using the linear Arrhenius correlations published by the authors (i.e. linear fits to the plot of $k_2$ vs $1/T$).

2.4.2 Natural Oxidant Demand

Reactions between MnO$_4^-$ and non-target aquifer materials will have a significant effect on the distribution of oxidant within the contaminated subsurface zone. Aquifer materials, both inorganic and organic (OAM), exert a natural oxidant demand (NOD) which must be accounted for in the ISCO design (in addition to the MnO$_4^-$ needed to degrade the contaminant source) (Siegrist et al., 2011). NOD kinetics has recently been suggested to be a kinetically controlled (rate-limited) reaction (Mumford et al., 2005; Urynowicz et al., 2008; Xu and Thomson, 2009). NOD can be represented by a continuum of different OAM reactions that occur at a continuum of
different rates (Siegrist et al., 2011). Both Urynowicz et al. (2008) and Xu and Thomson (2009) have described NOD reactions as a two part process: a fraction of NOD that undergoes fast oxidation followed by a slower reacting fraction of NOD.

West and Kueper (2012) modeled NOD kinetics as a 2nd-order overall reaction between MnO₄⁻ and reactive OAM (Mumford, 2002). Equations 2-13 and 2-14 depict the reaction stoichiometry and reaction rate expression utilized in West and Kueper’s (2012) modeling approach:

\[
3\text{CH}_2\text{O} + 4\text{MnO}_4^- \rightarrow 3\text{CO}_2 + 4\text{MnO}_2\text{(s)} + \text{H}_2\text{O} + 4\text{OH}^-
\]  
(2-13)

\[
\frac{\partial [\text{OAM}]}{\partial t} = \frac{\partial [\text{CH}_2\text{O}]}{\partial t} = -3k_{\text{OAM}} [\text{OAM}] [\text{MnO}_4^-]
\]  
(2-14)

where \(k_{\text{OAM}}\) is the 2nd-order reaction rate coefficient for the reaction between OAM and MnO₄⁻ \(\text{L}^3\text{mol}^{-1}\text{T}^{-1}\).

This expression accounts for OAM as a single reaction species (CH₂O), governed by the slow reacting fraction of NOD. A slow reaction NOD modeling approach was preferred due to its computational efficiency; however, it is limited as it does not consider the NOD kinetics (i.e. continuum of different reactions, fast/slow NOD reactions, etc.) described in recent studies (Urynowicz et al., 2008; Xu and Thomson, 2009). Over long time frames, the slow reacting fraction governs the NOD; it has been observed that the fast reacting fraction becomes depleted within short time periods (Urynowicz et al., 2008; Xu and Thomson, 2009). Mumford (2002)
observed that the fast NOD fraction made up a small portion of the NOD exerted during the column tests and a significantly small portion of the NOD\textsubscript{ultimate}.

Similar to TCE/PCE oxidation reactions, NOD reactions should also increase at greater temperatures, in accordance with the Arrhenius relationship (Petrucci et al., 2007). At this present time, NOD temperature-dependent reaction kinetics has not been strongly studied. Previous studies have analyzed the NOD and reaction rates for numerous different types of soil, but have only experimented with samples at laboratory temperatures (Cha et al., 2011). West and Kueper (2012) utilized an NOD (slow) reaction rate coefficient of $8.8 \times 10^{-8}$ L/mg/s for the ISCO simulations, which was representative of soil collected from the CFB Borden aquifer site at laboratory temperatures (Mumford, 2002). A push-pull test study conducted by Mumford et al. (2004) also analyzed the NOD of CFB Borden aquifer material, at field test conditions; past literature has indicated that the temperature of the CFB Borden aquifer ranges from about 6 to 8°C (Nicholson et al., 1983). Mathai (2011) utilized a numerical model to determine the relevant NOD kinetic parameters of CFB Borden aquifer material, obtained from field push-pull tests. Fitting of the push-pull test and model data provided an estimate of $1.03 \times 10^{-10}$ L/mg/s for the slow NOD reaction rate coefficient.

The activation energy and relevant Arrhenius parameters for the reaction between OAM and MnO$_4^-$ has not been determined by laboratory studies. The Arrhenius equations (Equations 2-11 and 2-12) cannot be applied to adjust the reaction rate coefficients for temperature. For this work, an Arrhenius-type approach (Equation 2-15) was utilized to fit the reaction rate coefficients
determined by Mumford (2002; within the temperature range of 20 to 25°C) and Mathai (2011; at approximately 7°C):

\[
k_{\text{OAM},T} = B \exp \left\{ \frac{-H}{T} \right\}
\]  

(2-15)

where \( T \) is in °K; \( B \) and \( H \) are fitting parameters.

The fitting of these two reaction rate coefficients to Equation 2-15 yielded values of 1.134 \( \times 10^{43} \) and 31328.5 for parameters \( B \) and \( H \), respectively. Figure 2.12 displays the proposed Arrhenius-type approach (Equation 2-15) for the temperature range of 5°C to 80°C. The reaction rate coefficients determined by Mumford (2002) and Mathai (2011) are also presented in this figure.

![Figure 2.12: Estimated OAM-MnO_4\(^{-}\) reaction rate coefficients determined by applying Equation 2-15 (see trendline).](image-url)
2.4.3 Manganese Dioxide Production

Solid (rind) manganese dioxide (MnO$_2$(s)) is a by-product of the oxidative dechlorination reaction between MnO$_4$$^-$ and TCE/PCE, and NOD reactions (Equation 2-13). Formation of MnO$_2$(s) rind within the free pore space has a great influence on subsurface flow processes, which ultimately affects ISCO treatment efficacy. The permeability of the porous media domain can be significantly reduced due to MnO$_2$(s) deposition. MnO$_2$(s) rind deposition contributes to flow bypassing within the porous media domain, which alters the ambient groundwater flow as well as the oxidant delivery pathways to the target contaminated zone (Siegrist et al., 2011). MnO$_2$(s) rind formation occurs at the non-aqueous–aqueous phase interface, which greatly inhibits dissolution/mass transfer. Formation of MnO$_2$(s) rind can significantly reduce the interfacial area ($a_{int}$) available for mass transfer (Crimi et al., 2009). Greater MnO$_2$(s) deposition occurs in higher saturation (i.e. higher concentration) non-wetting phase zones; if significant rind formation occurs, MnO$_2$(s) could effectively encapsulate DNAPLs resulting in incomplete treatment (West, 2009; Ward and Stroo, 2010). Additionally, MnO$_2$(s) also acts as a catalyst for the auto-decomposition of MnO$_4$$^-$ (i.e. another non-productive sink for permanganate-ISCO implementation). However, the auto-decomposition reaction has been found to be considerably slower than the dechlorination reactions and is generally not a significant concern for advection-dominated ISCO delivery systems (Siegrist et al., 2011).

West et al. (2008) utilized a linear relationship (Equation 2-16) to account for the effects of rind formation in the DNAPL3D-RX model runs for ISCO treatment simulation:
\[ k = k_0 + S_{rind} \left[ MnO_{2(s)} \right] \]  

(2-16)

where \( k_0 \) is the original intrinsic permeability \( \{L^2\} \), \( S_{rind} \) is the rind function \( \{M^{-1}L^5\} \).

This equation was calibrated to the published experimental column studies (using TCE contaminant) of Schroth et al. (2001). The phosphate-buffered column experiment from Schroth et al. (2001) was utilized for model calibration and validation (in this experimental case, the permeability reduction due to carbon dioxide (CO\(_2\)) evolution was found to be minimal). It was determined from model calibration that the value of \( S_{rind} \) was \(-5.5 \times 10^{-16} \, \text{m}^2 \, \text{L/mg}\) (West et al., 2008).

For this work, the \( S_{rind} \) value utilized by West and Kueper (2012) will be applied to the ISCO simulation scenarios. West et al. (2008) determined this parameter value from model calibration for reaction rate coefficients ranging from 0.39 to 0.80 \( \text{M}^{-1} \, \text{s}^{-1} \). Additionally, utilization of this \( S_{rind} \) value yields an ‘apparent’ maximum \( \text{MnO}_2(s) \) concentration of 1854 mg/L; DNAPL3D-RX does not set a restriction on \([\text{MnO}_2(s)]\) “but only \( \text{MnO}_2(s) \) concentrations up to 1854 mg/L contribute to reduction in permeability” (West, 2009, p.115). For this work, \( S_{rind} \) is assumed to be not temperature-dependent and will remain constant throughout the duration of the simulations. Permeability reduction will increase at increased temperature or at increased oxidant concentration due to the corresponding increases in both the dechlorination (oxidation) and NOD reaction rates. Increased \( \text{MnO}_2(s) \) concentrations will result from the increased rates of these two permanganate-consuming reactions (thereby further reducing \( k \)).
2.4.4 Oxidant Concentration/Dosage

Past MnO₄⁻ oxidation kinetics studies have looked at varying oxidant concentration (dose) and the effect on overall treatment. It has been noted that the reaction between MnO₄⁻ and TCE/PCE is a 2nd order overall process. Huang et al. (2001) observed that the 2nd order reaction rate coefficient between MnO₄⁻ and TCE/PCE did not significantly vary as potassium permanganate (KMnO₄) concentrations were increased; this behaviour is representative of a 2nd order reaction. Contaminant mass removal rates will increase as a result of increased oxidant concentrations, with reference to Equation 2-10. Woo et al. (2009) observed that 98% TCE removal efficiency was achieved after 30 minutes using a molar ratio ([MnO₄⁻]:[TCE]) of 18.4. In contrast, a molar ratio of 1.8 resulted in 58% TCE removal efficiency after 370 minutes. However, Kao et al. (2008) studied molar ratios of [oxidant]:[contaminant] to optimize TCE oxidation as well as minimize manganese dioxide production (MnO₂(s)). MnO₂(s) deposition commonly occurs near the non-aqueous–aqueous phase interface and can have significant impacts on mass transfer (Siegrist et al., 2011). Kao et al. (2008) observed that at higher TCE concentrations (100 mg/L), the optimal molar ratio required decreased (approximately 5). It was concluded that for greater TCE concentrations (i.e. source zones), the optimal ratio required would closely resemble the theoretical stoichiometric ratio (2 moles of MnO₄⁻ per mole of TCE).

Increased oxidant concentrations will also increase production of non-beneficial by-products. Both manganese dioxide (MnO₂(s)) and carbon dioxide (CO₂) production will increase with increased MnO₄⁻ concentrations. Urynowicz and Siegrist (2005) studied the effects of MnO₄⁻ concentration on the formation of MnO₂(s) interfacial film. At low MnO₄⁻ concentrations, the
formation of the interfacial film had minimal effect on mass transfer. Greater mass transfer resistance was observed at higher MnO₄⁻ concentrations as greater MnO₂(s) solids deposition occurred at the non-aqueous–aqueous interface. Petri et al. (2008) studied the effects of oxidant concentrations and groundwater velocities on TCE/PCE oxidation. Even though mass depletion rates increased at greater MnO₄⁻ concentrations, greater CO₂ concentrations were produced. Similar to MnO₂(s), CO₂ also forms intensively near the mass transfer interface, which can negatively impact dissolution rates as well as contribute to flow bypassing. Greater oxidant concentrations have also been linked to higher NOD values (Hønning et al., 2007; Siegrist et al., 2011). Urynowicz et al. (2008) observed that the NOD using low oxidant concentrations (1180 mg/L) was 2.9 g/kg compared to 6.1 g/kg for high oxidant concentrations (4721 mg/L). Increasing MnO₄⁻ concentrations can potentially negate the benefits of increased mass depletion rates since increases in NOD, MnO₂(s), and CO₂ concentrations can negatively impact oxidant supply/distribution and dissolution processes in the subsurface.

2.5 Biologically-Enhanced Reductive Dechlorination

Subsurface bioremediation of dense non-aqueous phase liquids (DNAPLs) has been extensively studied at the laboratory- and field-scales. There have been numerous microbial cultures and/or consortia that have been utilized for the reductive dechlorination of chlorinated solvents, trichloroethene (TCE) and tetrachloroethene (PCE). TCE/PCE can be degraded sequentially to less harmful/toxic daughter products (PCE→TCE→cis-dichloroethene{cDCE}→vinyl chloride{VC}→ethene{ETH}), via metabolic microbial activity, through the addition of an electron donor to mediate the biological redox reaction (Häggblom and Bossert, 2004). Equations
2-17 to 2-20 depict the reaction stoichiometry of the sequential degradation of TCE/PCE, through the utilization of the H$_2$ electron donor, which can be obtained via substrate fermentation or by direct addition of the compound (Maymo-Gatell et al., 1995; West, 2009):

$$PCE + H_2 \rightarrow TCE + Cl^- + H^+ + biomass$$ (2-17)

$$TCE + H_2 \rightarrow cDCE + Cl^- + H^+ + biomass$$ (2-18)

$$cDCE + H_2 \rightarrow VC + Cl^- + H^+ + biomass$$ (2-19)

$$VC + H_2 \rightarrow ETH + Cl^- + H^+ + biomass$$ (2-20)

where $Cl^-$ represents the chloride ion, $H^+$ represents the hydrogen ion.

Incomplete dechlorination (i.e. failure to achieve complete dechlorination to non-toxic ETH) has been observed with numerous dehalogenating microorganisms. Microbial strains such as *Dehalobacter restrictus* {PER-K23} (Holliger et al., 1993, 1998), *Desulfotobacterium* {PCE1} (Gerritse et al., 1996; Huang and Becker, 2011), and *Dehalospirillum multivorans* (Neumann et al., 1994; Scholz-Muramatsu et al., 1995; Amos et al., 2007, 2008) have been found to only dechlorinate TCE/PCE to cDCE/TCE (i.e. stalling). The extent of reductive dechlorination (i.e. the daughter end-product compound) is dependent on factors such as electron donor/acceptor availability (Huang and Becker, 2009), toxic chlorinated ethene concentrations (Yu et al., 2005), temperature (Heimann et al., 2007) and/or the metabolism of the specific microbial species (Häggblom and Bossert, 2004). The daughter products of TCE/PCE sequential dechlorination, cDCE and VC, are suspected/known carcinogens which can persist in subsurface environments if not completely dechlorinated; VC has a greater toxicity compared to its parent compounds.
Therefore, complete reductive dechlorination to ETH is crucial to the EISB treatment of contaminated subsurface environments in order to ensure the full removal and/or minimize the presence of higher chlorinated ethenes (TCE and PCE) and their equally harmful daughter by-products (cDCE and VC).

It has been generally accepted (at this point of time) that only members of the genus, *Dehalococcoides* (*Dhc*) spp., are capable of complete dechlorination of TCE/PCE to ETH (Maymo-Gatell et al., 1997; Yu and Semprini, 2004; Schaefer et al., 2009). Numerous bioremediation studies have utilized both pure *Dhc* and mixed *Dhc*-containing cultures in treating TCE/PCE contamination. *Dhc* strains such as *D. ethenogenes* strain 195 (Maymo-Gatell et al., 1995, 1997; Magnuson et al., 1998, 2000), BAV1 (He et al., 2003), VS (Cupples et al., 2004), FL2 (He et al., 2005), MB (Cheng and He, 2009), and mixed *Dhc* spp.-containing consortia such as KB-1™ (Duhamel et al., 2002; Cupples et al., 2004; Friis et al., 2007), PM (Yu and Semprini, 2004), and SDC-9 (Schaefer et al., 2009) have been shown to utilize TCE/PCE and their daughter by-products as electron acceptors for sequential dechlorination (i.e. ETH production). The KB-1™ mixed consortia consists of several microorganisms, which include: *Dhc* spp., *Geobacter* (can convert PCE to cDCE), and *Methanomethylovorans* (Friis et al., 2007). Unlike the other bacterial species mentioned in the previous paragraph, *Dhc* spp. has the ability to metabolically utilize cDCE and co-metabolically utilize VC as electron acceptors (refer to reductive dechlorination Equations 2-19 and 2-20) to produce ETH (He et al., 2003).

The addition of an electron donor (source) is essential to sustaining microbial dechlorinating activity. Various organic substrates have been utilized in reductive dechlorination studies using
Dhe spp., but it has been generally concluded that the primary electron donor for this species (and its associated reactions) is dihydrogen (H$_2$) (Häggblom and Bossert, 2004). However, He et al. (2002) observed reductive dechlorination of cDCE and VC, using a bacterial culture derived from the Bachman road site aquifer material, by utilizing acetate as the electron donor. H$_2$ can be obtained through the fermentation (via fermenting bacteria) of numerous organic substrates such as ethanol, pyruvate, propionate, methanol, and lactate. For West’s (2009) modeling study, a lactate substrate was utilized for the EISB model simulations since this compound provides a rapid source (and high concentration) of H$_2$ through its fermentation (He et al., 2002).

In subsurface environments, dechlorinating microorganisms will compete with other hydrogenotrophic microorganisms for the H$_2$ electron donor. Terminal electron-accepting processes (TEAPs) such as methanogenesis, acetogenesis, and sulfate/iron/nitrate reduction will utilize H$_2$ as an electron donor (He et al., 2002; Robinson et al., 2009; Malaguerra et al., 2011). However, studies have found that dechlorinating bacteria have a greater affinity for H$_2$ compared to methanogens and acetogens (Fennell and Gossett, 1998). The threshold H$_2$ concentrations and half-saturation coefficients of dechlorinating microorganisms are significantly lower in comparison to methanogens and acetogens (Smatlak et al., 1996; Ballapragada et al., 1997; Yang and McCarty, 1998). The results from these studies imply that in lower H$_2$ concentration environments, dechlorinators may out-compete methanogens and acetogens for the electron donor. These microbial properties will have a significant impact on the selection of the organic substrate source (for H$_2$ generation) as well as the electron donor injection concentration for EISB applications.
2.5.1 Temperature Effects on EISB Applications

There have been numerous studies which have looked into the effects of temperature on the microbial treatment of TCE/PCE. Incomplete reductive dechlorination of PCE was observed, within varying temperature ranges, for the following bacterial cultures: PER-K23 (Holliger et al., 1993), *D. multivorans* (Neumann et al., 1994), PCE1 (Gerritse et al., 1996), and an acetate-fed, methanogenic culture (Zhuang and Pavlostathis, 1995). More recent authors have studied the effects of temperature on the activity of *Dhc* spp.-containing mixed consortia (Aulenta et al., 2006; Friis et al., 2007; Heimann et al., 2007; Fletcher et al., 2011a). These studies support the assumption that dechlorinators are most likely mesophilic microorganisms. The maximum dechlorination (which occurs at the optimum temperature) observed in these studies occurred within the temperature range of 20 to 35°C; representative of mesophilic activity (Vaccari et al., 2006). At temperatures less/greater than the optimum temperature, dechlorination activity (i.e. dechlorinator growth) decreases.

Friis et al. (2007) studied the activity of a lactate-amended KB-1™ consortium (TCE dechlorination) for the temperature range of 4 to 60°C. The growth of KB-1™ was greatest at 30°C, and limited at 4°C and temperatures 40°C and above. Complete TCE dechlorination to ETH was observed between the temperatures 10 to 30°C, was minimal (i.e. stalling at cDCE) at 4 and 40°C, and negligible TCE transformation at temperatures 50°C and above. Heimann et al. (2007) observed similar dechlorination trends using a lactate-amended KB-1™ consortium; complete dechlorination to ETH occurred fastest at 30°C (approximately 20 days). Fletcher et al. (2011a) utilized two different *Dhc* spp.-containing consortia (for PCE dechlorination), which were both
amended with methanol substrate. After incubation between 30 to 42 days, at 30°C, complete
dechlorination to ETH was achieved by both cultures. At 35°C, ETH concentrations (73% molar
percentage) were obtained with one consortium, however, there was evidence of VC stalling in
both consortia. Greater chlorinated ethene stalling (stalling at VC, cDCE, TCE, PCE) and lower
ETH production was observed for temperatures greater than 35°C. The dechlorinating ability of
the KB-1™ culture was extremely sensitive to temperatures above 35°C. Figure 2.13 (and Figure
A.1 in Appendix A) summarizes the literature data on maximum substrate utilization rates (i.e.
related to the maximum growth rate and hence, the dechlorination rate), \( q_{\text{TCE/PCE}}^{\text{MAX}} \), of various
bacterial cultures (for TCE/PCE reductive dechlorination), at their reference temperatures. The
metabolic activity of a specific bacterial species is strongly dependent on the electron
donor/acceptor supply, redox conditions, and the reference temperature of their environment
(Häggblom and Bossert, 2004).
Figure 2.13: Maximum substrate utilization rate of TCE/PCE dechlorinators as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study. Diamond symbols represent bacteria cultures/consortia which contain (or possibly contain) \textit{Dhc} spp. The diamond symbols also refer to studies which showed evidence of ETH production from the reductive dechlorination of TCE/PCE. The growth rates determined by Zhuang and Pavlostathis (1995) were converted using a constant growth yield of 3500 mg cell/mol substrate; representative of the TCE/PCE$\rightarrow$cDCE strain \textit{D. restrictus} (Cupples et al., 2003). Growth rates determined by Friis et al. (2007), for the mixed KB-1\textsuperscript{TM} culture, were converted by assuming a constant growth yield of 5.2 x 10$^8$ cells/$\mu$mol Cl$^-$(Cupples et al., 2004).
2.5.2 Temperature Dependence of Additional EISB Processes

Elevated temperatures will affect additional processes (other than dechlorination) involved in EISB treatment. Substrate-fermenting and methanogenic microbial activity will be strongly influenced by temperature. Heimann et al. (2007) observed that lactate fermentation occurred rapidly at higher temperatures; the substrate was completely depleted after approximately 6 days at 30°C and after approximately 74 days at 4°C. This study also found that lactate fermentation did not proceed at temperatures greater than 40°C. Heimann and Jakobsen (2006) also observed that H₂ production via lactate fermentation was greater within the temperature range of 10 to 30°C. Figure 2.14 (and Figure A.2 in Appendix A) summarizes the literature data on $q_{\text{lactate}}^{\text{MAX}}$ dependence with temperature.

![Figure 2.14: Maximum substrate utilization rate of lactate fermenters as a function of temperature (values from various literature sources).]
Methanogenic activity will be affected by fluctuations in temperature. Heimann et al. (2007) observed greater methane (CH₄) production at higher temperatures for the range of 4 to 30°C. In contrast, Friis et al. (2006) observed lower methanogenic activity in thermally-treated soil (heated to 100°C and controlled cooling to 10°C) microcosms (amended with KB-1™ at 10°C) compared to the unheated KB-1™ amended microcosms (at 10°C). Even though the KB-1™ culture contained methanogens, methanogenesis was less active in the heated microcosms. The study suggested that “the heating process suppressed the native microbial community” (Friis et al., 2006, p.235), thereby minimizing methanogenic activity. However, Fletcher et al. (2011b) found that thermal treatment increased methanogenesis in bioaugmented microcosms. This study suggested that during cooling of a thermally treated site, methanogenic activity could dominate since the growth rate of methanogens is generally greater than that of dechlorinators. Figure 2.15 (and Figure A.3 in Appendix A) summarizes the literature data on $q_{max}$ dependence with temperature.
2.5.3 Temperature Adjustment of Monod Kinetics Coefficients

2.5.3.1 Half-Saturation Coefficient

The half-saturation coefficient ($K_n$) represents the electron donor concentration that is measured at half of the maximum specific growth rate. The temperature influence on half-saturation coefficients is not well established. Depending on the microbial species, $K_n$ values may increase or decrease at elevated temperatures (Vaccari et al., 2006). Figures A.4 to A.8 in Appendix A
summarize the literature values of half-saturation coefficients at different temperatures for TCE/PCE dechlorination, hydrogenotrophic dechlorinating, lactate fermenting, and methanogenic activity.

2.5.3.2 Decay Coefficient

In many bioremediation modeling studies, an estimated decay rate constant ($\lambda_n$) has been assumed for all biomass populations (Fennell and Gossett, 1998; Yu and Semprini, 2004; Christ and Abriola, 2007). Some literature studies have experimentally measured the decay rate of their microbial populations; Cupples et al. (2003) and Huang and Becker (2009) determined decay rates for bacterial strains VS and PCE1/BB1, respectively. Similar to half-saturation coefficients, the effect of temperature on the decay coefficient is not a clear trend; however, it has been suggested that decay rate increases at elevated temperatures due to the corresponding increase on reaction rates (Vaccari et al., 2006). Figure A.9 in Appendix A summarizes the literature values of decay coefficients utilized/determined in various bioremediation studies.

2.5.3.3 Biomass Yield Coefficients

Yield coefficients ($Y_n$) represent the ratio between the amount of biomass produced per amount of substrate utilized. Similar to half-saturation coefficients, the dependence of yield coefficients on temperature is not well established (Vaccari et al., 2006). The biomass yield of a specific microbial group may increase/decrease with elevated temperature. Figures A.10 to A.12 in Appendix A summarize the literature values of yield coefficients utilized/determined (from
numerous studies) for TCE/PCE dechlorinating, methanogenic, and lactate-fermenting microbial populations.

2.5.4 EISB Modeling Assumptions/Approach

The following list outlines the assumptions that have been utilized for the literature review plots in this chapter and in Appendix A:

- For the conversion of some of the utilization rate parameters, to the Monod kinetic parameter units utilized by West (2009), the following conversion factors were applied:
  - Volatile suspended solids (VSS) is 50% protein (Yang and McCarty, 2000).
  - 0.5 grams protein per gram cell (Duhamel et al., 2004).
  - Applying the assumption of 0.5 g protein/g cell, Duhamel et al. (2004) determined a conversion factor of $4.2 \times 10^{-15}$ g cells/gene copy. This incorporated characteristics specific to $Dhc$ strains 195 and BAV1; Duhamel et al. (2004) found that $Dhc$ was more disk shaped than spherical. The authors decided to not use the conversion factor of $1.6 \times 10^{-14}$ g cells/copy determined by Cupples et al. (2003). For calculative purposes, the conversion factor found by Duhamel et al. (2004) was utilized to convert the modeling parameters associated with $Dhc$-containing consortia.

- The main hydrogenotrophic, competing microbial population (of interest) for the $H_2$ electron donor were methanogens (Christ and Abriola, 2007; West, 2009). It is
recognized that other hydrogenotrophic microorganisms can exist within subsurface environments such as sulfate-reducers and acetogens.

2.6 Notation

\( a_{na} \) interfacial area between NAPL and aqueous phases \( \{L^{-1}\} \)

\( A \) Arrhenius frequency factor

\( B \) fitting parameter

\( C \) aqueous phase solute concentration in the bulk solution \( \{M^1L^{-3}\} \)

\( C_A \) concentration of solute A \( \{M^1L^{-3}\} \)

\( C_s \) thermodynamic equilibrium aqueous phase concentration (solubility) in which the non-aqueous phase is present \( \{M^1L^{-3}\} \)

\( D'_{AB} \) binary free-water molecular diffusion coefficient of solute A diffusing into solvent B in dilute solutions \( \{L^2T^{-1}\} \)

\( E_a \) activation energy \( \{M^1L^2T^{-2}M^{-1}\} \)

\( F \) Faraday constant = 96485.3415 s\(^1\)A\(^1\)mol\(^{-1}\)

\( f_{oc} \) organic carbon fraction \{-\}

\( g \) gravitational constant \( \{L^1T^{-2}\} \)

\( H \) fitting parameter

\( J \) solute mass flux from immiscible liquid phase to the aqueous phase \( \{M^1L^2T^{-1}\} \)

\( J_{AB} \) diffusive flux of solute A diffusing into solvent B \( \{M^1L^2T^{-1}\} \)

\( k \) intrinsic permeability \( \{L^2\} \)

\( K \) hydraulic conductivity \( \{L^1T^{-1}\} \)

\( k_1, k_2 \) 2\(^{nd}\) order reaction rate coefficient at reference temperatures 1 and 2 \( \{M^{-1}L^3T^{-1}\} \)

\( K_d \) sorption distribution coefficient \( \{M^{-1}L^3\} \)

\( k_f \) mass transfer coefficient \( \{L^1T^{-1}\} \)

\( K_f \) lumped mass transfer coefficient \( \{T^{-1}\} \)
\( K_n \)  Monod half-saturation coefficient \( \{M^1L^{-3}\} \)

\( k_o \)  original permeability \( \{L^2\} \)

\( k_{OAM,T} \)  2nd order reaction rate coefficient for reaction between OAM and MnO₄⁻ \( \{M^{-1}L^3T^{-1}\} \)

\( K_{oc} \)  organic carbon partitioning coefficient \( \{M^1L^{-3}\} \)

\( k_{PCE} \)  2nd order reaction rate coefficient for reaction between PCE and MnO₄⁻ \( \{M^1L^3T^{-1}\} \)

\( k_{rms} \)  2nd order reaction rate coefficient \( \{M^{-1}L^3T^{-1}\} \)

\( k_{TCE} \)  2nd order reaction rate coefficient for reaction between TCE and MnO₄⁻ \( \{M^1L^3T^{-1}\} \)

\( M_B \)  molecular weight of solvent B, \( \{M^1M^{-1}\} \)

\( P_A \)  parachor of solute A \( \{M^{1/4}L^3T^{-1/2}M^{-1}\} \); estimated using Table 11-3 of Poling et al., 2001

\( P_B \)  parachor of solvent B \( \{M^{1/4}L^3T^{-1/2}M^{-1}\} \); estimated using Table 11-3 of Poling et al., 2001

\( q_n^{MAX} \)  maximum utilization rate \( \{M^1M^{-1}T^{-1}\} \)

\( r_a \)  radius of spherical-shape solute A \( \{L^1\} \)

\( R \)  universal gas constant = 8.3144621 J/mol K

\( S_{rind} \)  rind function \( \{M^{-1}L^5\} \)

\( V_A \)  molar volume of solute A at its normal boiling point \( \{M^{-1}L^2\} \)

\( V_B \)  molar volume of solvent B at its normal boiling point \( \{M^{-1}L^2\} \)

\( T \)  reference temperature \( (^{°}K) \)

\( T_c \)  critical temperature of the solvent \( (^{°}K) \)

\( Y_n \)  biomass yield coefficient \( \{M^1M^{-1}\} \)

\( z \)  vertical transverse direction \{-\}

\( \lambda \)  molar conductivity for common ions \( \{M^{-1}T^3A^2M^{-1}\} \)

\( \lambda_n \)  first-order biotic decay rate coefficient \( \{T^{-1}\} \)

\( \eta \)  parameter associated with the solvent; based on heat of vaporization

\( \phi \)  association factor of solvent B; for water \( \phi = 2.6 \) (Poling et al., 2001; Bird et al., 2002)

\( \rho \)  fluid density \( \{M^1L^{-3}\} \)
\[ \mu \quad \text{fluid viscosity } \{M^1 L^{-1} T^{-1}\} \]

\[ \mu_B \quad \text{dynamic viscosity of solvent B at reference temperature } \{M^1 L^{-1} T^{-1}\} \]

\[ \mu_w \quad \text{dynamic viscosity of water solvent at reference temperature } \{M^1 L^{-1} T^{-1}\} \]

\[ \omega \quad \text{ionic charge } \{-\} \]

Notes:
Square brackets [ ] indicate molar concentrations (M^1 L^{-3}) of the specific compound or species.

Subscripts

- \( A \) solute (TCE, PCE, MnO_4^-, Cl^-, CO_2)
- \( B \) solvent (water)
- \( n \) species type

2.7 References


62


Chapter 3

Thermal Enhancement of *In Situ* Chemical Oxidation (ISCO) for Remediation of Groundwater Impacted by Chlorinated Solvents

3.1 Abstract

A numerical modelling study was conducted to assess the effects of elevated subsurface temperatures on the application of permanganate *in situ* chemical oxidation (ISCO) to remediate dense non-aqueous phase liquid source zones impacted by trichloroethene (TCE) and tetrachloroethene (PCE). DNAPL3D-RX (West et al., 2008) was utilized to simulate the impact of higher temperatures (20 to 80°C) on the reaction mechanisms associated with ISCO and subsurface fluid flow/transport processes. Both heated ISCO and abiotic dissolution (dissolution only) scenarios were modeled to evaluate the enhancement of treatment; the latter representing the case where only temperature was raised in the porous medium. Elevated groundwater temperatures were beneficial to ISCO treatment during the short-term (between 1 to 4 years) oxidant injection period. Contaminant mass removal and boundary mass flux reduction were enhanced by heated ISCO for these injection timeframes. The remedial benefits achieved from ISCO treatment were negated over the long term (for each temperature scenario) due to significant manganese dioxide rind deposition. TCE and PCE dissolution following ISCO treatment was severely inhibited by rind formation and the subsequent reduction in permeability which occurred. Dissolution tailing was observed in both heated ISCO and abiotic dissolution simulations, which lengthened the treatment times for each case. Tailing effects were more
significant in the ISCO scenarios due to the creation of lower permeability zones by rind deposition, in addition to the naturally low permeability geologic zones already present.

3.2 Introduction

The impact of dense non-aqueous phase liquids (DNAPLs) on subsurface systems due to their historical improper usage and disposal continues to persist at thousands of sites in North America. Trichloroethene (TCE) and tetrachloroethene (PCE) are chlorinated solvents, utilized in various past applications as metal degreasing agents, dry cleaning fluids, and chemical intermediates (Kueper et al., 2004). These compounds have low aqueous solubilities (approximately 200 to 1100 mg/L), however, these are significantly greater than the maximum contaminant level (MCL) of 5 μg/L that have been specified for both TCE and PCE (US EPA, 2013). After their initial release, these compounds can migrate and redistribute within the subsurface as disconnected blobs (ganglia) and/or as connected higher saturation pools above finer lenses under the water table (Kueper et al., 1993). The time frame for the abiotic (natural) dissolution of these compounds can range from decades to centuries, in which the formation and influence of the downgradient aqueous plume will perdure, thereby limiting groundwater resources.

In order to enhance the solubility of TCE and PCE, in situ chemical oxidation (ISCO) has been employed as an in situ partial mass removal technology. Numerous oxidants have been utilized for the remediation of subsurface contamination, such as ozone, persulfate, and hydrogen peroxide (Siegrist et al., 2011). Permanganate (MnO₄⁻) oxidation of TCE and PCE has been studied at both the laboratory (Yan and Schwartz, 2000; Huang et al., 2001; Dai and Reitsma,
2004) and field scales (Schnarr et al., 1998), and the kinetics of these reactions have been well-defined. In a system in which MnO\textsubscript{4}\textsuperscript{-} is in excess concentrations, TCE/PCE oxidation proceeds as a 2\textsuperscript{nd}-order overall reaction; the rate expressions for both TCE and PCE oxidation are shown in Equation 3-3 (Zhang and Schwartz, 2000; Siegrist et al., 2011):

\[
C_2Cl_3H (TCE) + 2MnO_4^- \rightarrow 2CO_2 + 2MnO_{2(s)} + 3Cl^- + H^+ \quad (3-1)
\]

\[
C_2Cl_4 (PCE) + 2MnO_4^- \rightarrow 2CO_2 + 2MnO_{2(s)} + 4Cl^- \quad (3-2)
\]

\[
\frac{\partial [TCE]}{\partial t} = -k_{TCE}[TCE][MnO_4^-] \quad \text{or} \quad \frac{\partial [PCE]}{\partial t} = -k_{PCE}[PCE][MnO_4^-] \quad (3-3)
\]

where [ ] brackets represent molar concentrations \{L\textsuperscript{-3}mol\textsuperscript{1}\}, \(k_{TCE/PCE}\) is the 2\textsuperscript{nd}-order reaction rate coefficient for the reaction between TCE/PCE and MnO\textsubscript{4}\textsuperscript{-}, \(MnO_2(s)\) represents manganese dioxide, \(CO_2\) represents carbon dioxide, \(MnO_{2(s)}\) represents manganese dioxide, \(Cl^-\) represents the chloride ion, and \(H^+\) represents the hydrogen ion.

MnO\textsubscript{4}\textsuperscript{-} ISCO treatment of TCE/PCE enhances DNAPL dissolution, which can accelerate contaminant mass removal as well as boundary mass flux reduction. It is assumed that MnO\textsubscript{4}\textsuperscript{-} only reacts (oxidizes) with the organic contaminant in its aqueous phase. As a result, the concentration gradient towards dissolution is enhanced due to lower solute concentrations within the bulk groundwater (Siegrist et al., 2011). Inhibiting factors specific to MnO\textsubscript{4}\textsuperscript{-} ISCO treatment include the formation of an insoluble precipitate (rind) and oxidant consumption by non-productive subsurface materials. MnO\textsubscript{2(s)} is produced as a result of this oxidation reaction, which can deposit within subsurface pores and significantly reduce the permeability \((k)\). Rind formation
has been found to be most intensive in regions closest to the DNAPL-water interface, where saturations/concentrations are highest. MnO_{2(s)} formation will also occur heavily in areas of high natural oxidant demand (NOD) (Heiderscheidt et al., 2008). If the degree of MnO_{2(s)} deposition becomes significant, DNAPL can also become entrapped within the rind formation. MnO_{2(s)} formation can detrimentally impact DNAPL dissolution and increase the time required to meet treatment objectives. MnO_4^- will also react with not only organic contaminants but with other organic/inorganic matter within the subsurface (Hønning et al., 2007). These organic/inorganic constituents contribute to the NOD and readily react with MnO_4^- . This presents a significant problem in implementing MnO_4^- ISCO as greater oxidant volumes are usually required to oxidize contaminants as well as satisfy the NOD of a particular site.

Thermal treatment has been a remedial method employed in numerous subsurface contaminant applications. Technologies such as thermal conductive heating (TCH), electrical resistive heating (ERH), steam injection and radio frequency (RF) heating are capable of elevating subsurface temperatures to at or above the boiling point of water, which is dependent on local pressures (USACE, 2009). The aqueous solubility, volatility, diffusivity, and desorption (Heron et al., 1998a) of TCE/PCE generally increases at higher temperatures. Thermal treatment also enhances mass transfer since fluid density and viscosity generally decrease at higher temperatures.

The focus of this study was to assess the effects/benefits of elevated, sub-boiling temperatures (20 to 80°C) on MnO_4^- ISCO treatment effectiveness for remediation of TCE and PCE. Higher temperatures will affect chemical reaction rates, reaction byproduct formation (rind formation), and the physicochemical properties of the ambient groundwater and the immiscible contaminant.
The influence of temperature on the reaction between TCE/PCE and MnO$_4^-$ has been studied at the laboratory scale (Huang et al., 2001; Dai and Reitsma, 2004) but has not yet been applied in field scale applications. This work utilizes the multi-phase flow, reactive transport numerical model DNAPL3D-RX employed by West and Kueper (2012); numerical simulations conducted by West and Kueper (2012) were for a reference subsurface temperature of 10°C. MnO$_4^-$ reactions with TCE/PCE as well as with organic aquifer material (OAM) will be affected by temperature in accordance with Arrhenius principles, as reaction rates generally increase at increased temperatures (Petrucci et al., 2007).

### 3.3 Methodology

The methodology adopted here was similar to the numerical model study conducted by West and Kueper (2012). The numerical model, DNAPL3D-RX, was utilized to simulate the processes and reactions involved with the MnO$_4^-$ treatment of TCE/PCE within a virtual subsurface environment. All of the initial boundary conditions and modeling assumptions made by West and Kueper (2012) were implemented in this work. West and Kueper (2012) modeled the effects of subsurface permeability and heterogeneity, DNAPL volume and type, hydraulic displacement, NOD and rind clogging on MnO$_4^-$ ISCO treatment. The emphasis of this study specifically looked at the effects of temperature on the flow and reactive transport processes associated with MnO$_4^-$ ISCO subsurface treatment, using the base case TCE and PCE virtual sites created by West and Kueper (2012).
3.3.1 Numerical Model

DNAPL3D-RX is a three-dimensional multi-phase flow, reactive transport numerical model developed by West et al. (2008) for the simulation of MnO$_4^-$ ISCO for DNAPL removal. For more in-depth details regarding initial model development, model calibration/validation/verification, incorporation of multi-phase flow and solute transport equations, and the inclusion of MnO$_4^-$ ISCO kinetic rate expressions, the reader is referred to Kueper and Frind (1991), Gerhard and Kueper (2003), Grant and Gerhard (2007a), and West et al. (2008). See Appendix B.1 for a list of the multi-phase flow, solute transport, and reaction kinetic equations utilized by DNAPL3D-RX.

The initial base case $k$ and DNAPL saturation ($S_{np}$) fields employed by West and Kueper (2012) were used for every numerical simulation performed in this work, as presented in Figure 3.1. Spatially correlated random $k$ fields were generated by West and Kueper (2012) using the algorithm F-GEN (Robin et al., 1993). The base case permeability field had a mean $k$ of $3.03 \times 10^{-12}$ m$^2$ and a variance of natural logarithm $k$ ($\sigma^2_{ln(k)}$) of 1.74 (representative of a moderately heterogeneous, fine sand-to-silt porous medium). To simulate OAM, a fraction-of-organic carbon ($f_{oc}$) field was perfectly negatively cross-correlated to the $k$ field using F-GEN. The F-GEN input parameters for the OAM fields, which were utilized for all of the virtual sites created by West and Kueper (2012), were a mean $f_{oc}$ of 0.003 (0.3%) and variance of natural logarithm $f_{oc}$ ($\sigma^2_{ln(f_{oc})}$) of 0.24. TCE and PCE sorption were represented in this model porous media domain using a linear isotherm, similar to West and Kueper (2012).
The initial $S_{NW}$ fields were developed from the work by Richards et al. (2012), in which hydraulic displacement (HD) events were simulated for DNAPL source zones within porous media. For computational efficiency, the width of the model domain created by Richards et al. (2012) was reduced by half for the simulations conducted by West and Kueper (2012). The domain size ($x \times y \times z$) for all of the numerical simulations was 20 m (length) $\times$ 5 m (depth/thickness) $\times$ 10 m (width). For the base case simulations performed by West and Kueper (2012) and in this study, the initial $S_{NW}$ field was representative of a contaminant source zone below the water table in which the following sequential events have already taken place: 1) initial DNAPL release, 2) DNAPL migration, 3) DNAPL redistribution, 4) HD (which reduces pooled and maximizes residual DNAPL saturations). The initial DNAPL volume within each domain is about 2.4 m$^3$. Prior to the start of each simulation, the DNAPL field has not undergone dissolution. Table 3.1
summarizes the characteristics of the two model domains utilized in this work; these virtual sites were two of the nine domains studied by West and Kueper (2012).

Table 3.1: Virtual site characteristics of the model domains in this study.

<table>
<thead>
<tr>
<th>Virtual Site No.</th>
<th>Contaminant</th>
<th>Initial Volume (m³)</th>
<th>Initial DNAPL Mass (kg)</th>
<th>Mean k (m²)</th>
<th>( \sigma_{\ln k}^2 ) (ln(m²))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TCE</td>
<td>2.41</td>
<td>3520</td>
<td>3.03 \times 10^{-12}</td>
<td>1.74</td>
</tr>
<tr>
<td>2</td>
<td>PCE</td>
<td>2.37</td>
<td>3871</td>
<td>3.03 \times 10^{-12}</td>
<td>1.74</td>
</tr>
</tbody>
</table>

The MnO₄⁻ ISCO and abiotic dissolution simulations conducted in this study followed the template provided by West and Kueper (2012); the exception being the temperature adjustment for the model domain. Dissolution was modeled using a local equilibrium (LE) approach (\( C = C_s \)); the virtual model domain was assumed to be sufficiently complex in terms of subsurface heterogeneity and source architecture, which justified using a non-rate limited approach (Brusseau et al., 2002). Incorporating LE dissolution provided greater computational efficiency for the numerical simulation runs. It is recognized that solute concentrations observed in field studies can be lower than the solubility limit in heterogeneous subsurface environments (Rivett and Feenstra, 2005). Rate-limited (non-equilibrium) mass transfer considers both DNAPL saturation and advective-dispersive transport, while LE dissolution mostly considers the latter (Grant and Gerhard, 2007b). LE dissolution can overpredict dissolution (hence, contaminant mass removal), especially at later times when limited contaminant mass remains, as it is assumed that concentrations are at the solubility limit wherever DNAPL is present. Conversely, LE dissolution provides performance benefits in terms of the promotion of treatment technologies. An LE dissolution approach highlights greater effectiveness for treatment. West and Kueper (2012)
preliminarily tested the base case model domain using both LE and non-equilibrium dissolution techniques. Since no prior dissolution had occurred before the start of the simulation run (similar to the simulations conducted in this work), there was no initial presence of a dissolved contaminant phase. The non-equilibrium mass transfer correlation predicted faster dissolution than LE for the first two years, but both methods exhibited similar DNAPL mass removal trends from year 2 to year 10.

A LE dissolution approach was adopted in this study due to the reduction in computational run times as well as the sufficient complexity of the numerical model domain. The initial SNW fields utilized in this study were non-uniformly distributed and appropriate subsurface heterogeneity was accounted for (i.e. preferential flow paths, flow bypassing). These factors were more representative of large scale dissolution processes, which are primarily influenced by advective-transport (Sale and McWhorter, 2001). Brusseau et al. (2002) observed that for sufficiently complex distributions of immiscible contaminant, the LE assumption provided good results as long as large scale mass transfer factors were considered in the model.

Potassium permanganate (KMnO₄) was selected as the oxidant of choice in this study. Oxidant injection was modeled as a fixed-duration, constant concentration boundary (at the upgradient face) as shown in Figure 3.2.
All of the reaction kinetics for the MnO₄⁻ ISCO of TCE/PCE were incorporated into RT3D (Clement, 1997), which is the reactive transport component of DNAPL3D-RX (see Appendix B.1). To model transient permeability reduction due to rind formation from the MnO₄⁻ oxidation reactions with TCE/PCE and OAM, West et al. (2008) utilized a linear relationship:

\[ k = k_o + S_{rind} \left[ MnO_{2(e)} \right] \]  \hspace{1cm} (3-4)

where \( k \) is the transient permeability dependent on the degree of rind formation \( \{L^2\} \), \( k_o \) is the original intrinsic permeability \( \{L^2\} \), and \( S_{rind} \) is the rind function \( \{M^1L^5\} \), which was an empirically fitted parameter determined by West et al. (2008).

West et al. (2008) utilized DNAPL3D-RX to calibrate Equation 3-4 to the phosphate-buffered MnO₄⁻/TCE column studies by Schroth et al. (2001). A \( S_{rind} \) value of \(-5.5 \times 10^{-16} \text{ m}^2 \text{ L/mg}\) was
determined from model calibration for a reaction rate coefficient range of 0.39 to 0.80 M$^{-1}$s$^{-1}$. The value of $S_{rind}$ was assumed to be temperature-independent and constant for all simulations. The rate of increase in rind formation (MnO$_2(s)$ concentration) due to temperature was dependent on increased reaction rates as well as reactant concentrations.

In every numerical simulation, it was assumed that the model domain was perfectly buffered. It is recognized that the initial redox conditions and pH of subsurface environments will have an influence on MnO$_4^-$ ISCO-associated reactions and the resulting by-products (Siegrist et al., 2011). Each model domain was assumed to be isothermal ($\Delta T = 0$) and at local thermal equilibrium throughout the entire duration. Conceptually, heat input into the model domain was provided from two possible scenarios: 1) A thermal treatment application (e.g. ERH), 2) Application of heated water-MnO$_4^-$ mixed (at specified sub-boiling temperature) injection to the target treatment zone. It was assumed that the establishment of a uniform initial temperature within the domain was equivalent to pre-heating of the target treatment zone with ERH. ERH relies on electrical current flow produced from electrodes, which is conducted by subsurface flow within pore spaces. The resistance encountered by the conducted current results in uniform heating of the subsurface (USACE, 2009).

In all of the simulations conducted, non-aqueous, aqueous, and sorbed solute phases were considered. The generation and transport of a gas phase formed as a result of heating was not modeled in this work. Martin and Kueper (2011) applied ERH to a heterogeneous sand pack containing TCE DNAPL pools. A co-boiling plateau of 73.4°C was observed for the TCE-water system and gas generation was observed during and following co-boiling. In this work, only mass
transfer from DNAPL to aqueous and sorbed solute phases was accounted for. It is recognized that neglecting the generation of a gas phase for the 80°C TCE simulation may underestimate the reduction in DNAPL mass and/or mass flux as well as the impacts of the gas phase on mass transfer and fluid flow/transport. Not accounting for TCE-water co-boiling was justified by the fact that for this heterogeneous azeotropic system, the co-boiling temperature will increase to above 73.4°C within a matter of a few meters below the water table. By applying the Antoine equation and the appropriate empirical Antoine constants for TCE and water (Martin, 2009), the TCE-water co-boiling temperature increases to approximately 80°C at an estimated depth of 2.74 meters below the water table.

3.3.2 Numerical Simulations

In total, 16 simulations were performed: 8 TCE simulations (4 MnO₄⁻ ISCO, 4 abiotic dissolution) and 8 PCE simulations (4 MnO₄⁻ ISCO, 4 abiotic dissolution). Four temperatures were studied in this work: 20, 40, 60, and 80°C. In all of the ISCO simulations, KMnO₄ was injected at a concentration of 10,000 mg/L; KMnO₄ injection was terminated once the stoichiometric oxidant amount was reached that was theoretically capable of dechlorinating the entire DNAPL mass as well as satisfying the full NOD within the model domain. All of the TCE scenarios were simulated until all of the DNAPL mass was removed. PCE scenarios were simulated for a timeframe of 50 years as the lower solubility of this compound significantly increased remediation and model run times. Table 3.2 outlines the schedule of each ISCO simulation conducted.
### Table 3.2: Schedule of ISCO treatment simulations.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>ISCO Simulation No.</th>
<th>Temperature (°C)</th>
<th>KMnO₄ Injection Concentration (g/L)</th>
<th>Injection Duration (days)</th>
<th>Injection Duration (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>1</td>
<td>20</td>
<td>10</td>
<td>1442</td>
<td>3.95</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>40</td>
<td>937</td>
<td>666</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>60</td>
<td>666</td>
<td>504</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>80</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCE</td>
<td>5</td>
<td>20</td>
<td>1423</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>40</td>
<td>927</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>60</td>
<td>662</td>
<td>1.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>80</td>
<td>502</td>
<td>1.38</td>
<td></td>
</tr>
</tbody>
</table>

Note(s): The mass of oxidant injected was calculated as the theoretical stoichiometric equivalent to satisfy both contaminant and natural oxidant demands. For every ISCO simulation mentioned in the table, a corresponding “dissolution only” simulation was also performed at the same reference temperature for the same DNAPL (16 simulations were performed in total).

The specified oxidant concentration was four times greater than the concentration utilized by West and Kueper (2012). It is recognized that higher KMnO₄ concentrations can have detrimental effects on remediation; MnO₂(s) and CO₂(g) generation can be increased at higher oxidant concentrations, especially within low velocity systems (Heiderscheidt et al., 2008; Petri et al., 2008). The assumption made in this numerical model study was that the domain was perfectly buffered and fluctuations in pH were negligible. Phosphate and additional carbonate have been utilized in laboratory ISCO studies as external buffers (Schroth et al., 2001; Dai and Reitsma, 2004; Kao et al., 2008). Depending on the geology, subsurface environments can also have a
wide range of natural buffering capacity. In neutral pH environments, the dominant species in the carbonate system is dissolved bicarbonate (HCO$_3^-$) (Snoeyink and Jenkins, 1980). In all of the ISCO simulations, it was assumed that aqueous CO$_2$ concentrations generated from MnO$_4^-$ reactions were not significant enough to reach super-saturation and subsequent CO$_2$(g) production due to the adequate buffering of the system domain. The representation of $k$ reduction in this study is therefore only partial since the actual flow bypassing and pore clogging would be more significant if CO$_2$(g) generation was considered.

3.3.3 Temperature-Dependent Properties

Model parameters for each simulation were adjusted for temperature and are presented in Table 3.3. Higher temperatures provide greater kinetic energy, which reduces the strength of intermolecular forces within fluids. The density and viscosity of fluids tend to decrease at higher temperatures as intermolecular bond structure decreases (Petrucci et al., 2007). From 20°C to 80°C, the viscosity of PCE was found to decrease by approximately 30%; within this same temperature range, PCE density was reduced by about 4.3% (Sleep and Ma, 1997). In order to comparatively evaluate the transient mass removal of each simulation, TCE/PCE density was assumed to be constant over the range of temperatures used in this work (temperature had a negligible effect on density compared to viscosity). For each TCE/PCE simulation, the initial DNAPL mass within each model domain was the same.

The interfacial tension that exists between TCE/PCE and water was assumed to be constant throughout each temperature simulation. Studies by Imhoff et al. (1997) and Sleep and Ma (1997)
found that temperature did not significantly affect PCE interfacial tension. Even though interfacial tension will likely decrease somewhat with temperature, it was assumed that this effect was negligible for the TCE/PCE simulations performed in this study. Increases in temperature will have an impact on mass transfer (dissolution) processes. Dissolution can be represented as either an equilibrium \((C = C_x)\) or rate-limited process; a common representation of the rate-limited approach utilizes the steady-state approximation of the thin stagnant film model, as depicted in Equation 3-5 (Miller et al., 1990):

\[
J = k_i a_{ma} \left( C_s - C \right) = K_i \left( C_s - C \right)
\]  

(3-5)

where \(J\) is the solute mass flux from the immiscible liquid phase to the aqueous phase \(\{M^1 L^{-2} T^{-1}\}\), \(k_i\) is the mass transfer coefficient \(\{L^1 T^{-1}\}\), \(a_{ma}\) is the interfacial area between NAPL and aqueous phases \(\{L^{-1}\}\), \(C_s\) is the thermodynamic equilibrium phase concentration (aqueous solubility) in which the non-aqueous phase is present \(\{M^1 L^{-3}\}\), \(C\) is the bulk-solution aqueous phase solute concentration \(\{M^1 L^{-3}\}\), and \(K_i\) is the lumped mass transfer rate coefficient \(\{T^{-1}\}\).

Elevated temperatures will enhance the rate of dissolution from the non-aqueous to aqueous phase. Past studies have related the lumped mass transfer coefficient \((K_i)\) to experimentally-determined dimensionless parameters: Reynolds (Re), Schmidt (Sc), and modified Sherwood (Sh) numbers (Miller et al., 1990). These dimensionless parameters are temperature-dependent as they are a function of fluid properties; physicochemical properties such as diffusivity, density, viscosity, and interfacial tension (all of which vary with temperature) are used in order to calculate these parameters. Imhoff et al. (1997) observed that the \(K_i\) of a PCE-water system
increased by a factor of approximately 2 from 5 to 40°C. The experimental results suggested that mass transfer enhancement was more attributed to the PCE viscosity reduction at higher temperature rather than the decrease in PCE-water interfacial tension (approximate decrease of 7% from 5 to 40°C). The combined effect of the increase in diffusivity and decreases in viscosity, and interfacial tension (which is inversely proportional to the interfacial area for mass transfer) at higher temperatures should result in greater mass transfer.

Dissolution of TCE/PCE will also be enhanced at higher temperatures as the aqueous solubility ($C_s$) of these compounds tends to increase. Increase in $C_s$ will increase the concentration gradient between non-aqueous and aqueous phases. Past laboratory studies have characterized the $C_s$ of TCE/PCE at higher temperatures (Stephenson, 1992; Pankow and Cherry, 1996; Imhoff et al., 1997; Sleep and Ma, 1997; Heron et al., 1998b; Knauss et al., 2000; Chen et al., 2012), as presented in Figures 3.3 and 3.4. Most of these studies have observed an apparent solubility minimum for both compounds within sub-boiling temperature ranges (approximately 20 to 35°C). Past this minimum solubility, higher temperatures increase $C_s$ of both TCE and PCE. For this modeling study, temperature adjustment of $C_s$ for TCE/PCE followed the laboratory work and empirical correlations determined by Knauss et al. (2000). Knauss et al. (2000) recorded higher $C_s$ values than the other referenced studies due to the experimental technique used (pressurized gold bag reactors). It is recognized that the use of this experimental correlation may result in a higher estimation for TCE/PCE solubility. For this work, the Knauss et al. (2000) solubility correlations for TCE and PCE were preferred over other literature correlations since it showed greater variability in $C_s$ with temperature. Because one of the goals of this study was to highlight
some of the potential benefits of heating the subsurface for remediation purposes, a wider range of TCE/PCE solubility values was adopted.

Figure 3.3: TCE aqueous solubility versus temperature. Data points represent laboratory measured solubilities.
Temperature will affect the degree of sorption of the aqueous phase contaminant to soil grains; many studies quantify sorption by measuring organic carbon partitioning ($K_{oc}$) and/or distribution ($K_d = K_{oc}f_{oc}$) coefficients. Assuming that $f_{oc}$ does not vary significantly with temperature (minimal organic carbon release due to higher temperatures; Friis et al., 2005), changes in $K_d$ are directly related to $K_{oc}$. Heron et al. (1998a) found that the $K_d$ of TCE decreased by approximately 15% for temperatures between 23 and 99°C. Sleep and McClure (2001) observed that the $K_{oc}$ of PCE decreased by approximately 40% for temperatures ranging from 22 to 92°C in a porous medium with a $f_{oc}$ of 0.0045. $K_{oc}$ of both TCE and PCE were adjusted for temperature by utilizing similar trends as observed in these two studies.
3.3.4 MnO$_4^-$ ISCO Reactions

MnO$_4^-$ reactions with both aqueous TCE/PCE and OAM (2$^{nd}$-order reactions) will increase at higher temperatures in accordance with Arrhenius principles (Petrucci et al., 2007). Equations 3-6 and 3-7 represent Arrhenius equations for 2$^{nd}$-order reactions:

\[ k_{rnx} = A \exp \left\{ -\frac{E_a}{RT} \right\} \]  (3-6)

\[ \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]  (3-7)

where $k_{rnx}$ is a 2$^{nd}$-order reaction rate coefficient for a specific reaction {L$^3$T$^{-1}$mol$^{-1}$}, $A$ is the Arrhenius frequency factor with units for 2$^{nd}$-order reactions {L$^3$T$^{-1}$mol$^{-1}$}, $E_a$ is the activation energy {M$^1$L$^2$T$^{-2}$mol$^{-1}$}, $k_1/k_2$ is the 2$^{nd}$-order reaction rate coefficient at reference temperature {L$^3$T$^{-1}$mol$^{-1}$}.

The temperature-dependent reaction kinetics between MnO$_4^-$ and TCE/PCE has been studied by various authors. The $E_a$ of the reaction between TCE and MnO$_4^-$ has been found to range from 35 to 41.5 kJ/mol (Huang et al., 1999, 2001; Yan and Schwartz, 2000). Studies conducted with MnO$_4^-$ and PCE have found that the $E_a$ can range from 38.9 to 43.9 kJ/mol (Huang et al., 2002; Dai and Reitsma, 2004). MnO$_4^-$ reactions with PCE, compared to TCE, are significantly slower, which has been suggested to be attributed to its additional chlorine atom. The Arrhenius
correlations determined by Huang et al. (2001) for TCE and PCE reactions with MnO$_4^-$ were utilized for temperature adjustment of $k_{TCE}$ and $k_{PCE}$.

Reactions between MnO$_4^-$ and non-target aquifer materials (OAM) will have an effect on the distribution of oxidant within the contaminated subsurface zone. Both inorganic and organic aquifer materials will exert a natural oxidant demand (NOD), which must be accounted for in the ISCO design (more oxidant may be required in addition to the MnO$_4^-$ required for contaminant source degradation) (Siegrist et al., 2011). NOD kinetics has recently been depicted as a kinetically controlled (rate-limited) reaction (Mumford et al., 2005; Urynowicz et al., 2008; Xu and Thomson, 2009). NOD can involve a number of different reactions that occur at a variety of different rates. Both Urynowicz et al. (2008) and Xu and Thomson (2009) have described NOD reactions as a two part process: a fraction of NOD that undergoes fast oxidation followed by a slower reacting fraction of NOD. West and Kueper (2012) modeled NOD kinetics as a 2$^{nd}$-order overall reaction between MnO$_4^-$ and reactive OAM (as a single carbon species; Mumford, 2002), governed by the slow reacting fraction of NOD:

$$3CH_2O + 4MnO_4^- \rightarrow 3CO_2 + 4MnO_2(s) + H_2O + 4OH^- \quad (3-8)$$

$$\frac{\partial [OAM]}{\partial t} = \frac{\partial [CH_2O]}{\partial t} = -3k_{OAM} [OAM][MnO_4^-] \quad (3-9)$$

where $k_{OAM}$ is the 2$^{nd}$-order reaction rate coefficient for the reaction between OAM and MnO$_4^-$ ($L^3T^{-1}mol^{-1}$), $CH_2O$ is a single carbon species which is representative of an OAM species, $OH^-$ represents the hydroxide ion.

85
A single reaction (slow NOD) representation between \( \text{MnO}_4^- \) and OAM was adopted because the slow reacting fraction will govern NOD over long time frames. It has been observed that the fast reacting fraction becomes depleted within short time periods (Hønning et al., 2007; Urynowicz et al., 2008). Mumford (2002) observed that the fast NOD fraction made up a small portion of the NOD exerted during column tests and a significantly small portion of the NOD_{ultimate}.

Similar to TCE/PCE oxidation reactions, NOD reactions should increase at greater temperatures in accordance with the Arrhenius relationship (Petrucci et al., 2007). At this present time, NOD temperature-dependent reaction kinetics has not been extensively studied. Previous studies have analyzed the NOD and reaction rates for different types of soil, but only experimented with samples at laboratory temperatures (Cha et al., 2011). West and Kueper (2012) utilized a NOD (slow) reaction rate coefficient of \( 8.8 \times 10^{-8} \text{ L/mg/s} \) for ISCO simulations, which was representative of soil collected from the CFB Borden aquifer site at laboratory temperatures (Mumford, 2002). A push-pull test study conducted by Mumford et al. (2004) also analyzed the NOD of CFB Borden aquifer material, at field test conditions; past literature has indicated that the temperature of the CFB Borden aquifer ranges from about 6 to 8 °C (Nicholson et al., 1983). Mathai (2011) utilized a numerical model to determine the NOD kinetic parameters of CFB Borden aquifer material, obtained from field push-pull tests. Fitting of the push-pull test and model data provided an estimate of \( 1.03 \times 10^{-10} \text{ L/mg/s} \) for the slow NOD reaction rate coefficient.

The activation energy and relevant Arrhenius parameters for the reaction between OAM and \( \text{MnO}_4^- \) has not been determined by laboratory studies. The Arrhenius equation cannot be applied
to adjust the reaction rate coefficients for temperature. For this work, an Arrhenius-type approach (Equation 3-10) was utilized to fit the reaction rate coefficients determined by Mumford (2002; \( \approx 20 \) to \( 25^\circ C \)) and Mathai (2011; at approximately \( 7^\circ C \)):

\[
k_{OAM,T} = B \exp \left\{ \frac{-H}{T} \right\}
\]

where \( T \) is in °K; \( B \) and \( H \) are fitting parameters. The fitting of the two reaction rate coefficients from Mumford (2002) and Mathai (2011) yielded values of \( B = 1.134 \times 10^{13} \) and \( H = 31328.5 \).

The authors recognize that this Arrhenius-type approach may yield reaction rate coefficients that are significantly higher in absolute value. Laboratory study of the temperature dependency of NOD-related reactions is recommended in order to accurately depict the activity between \( \text{MnO}_4^- \) and OAM under heated conditions. The reaction rate coefficients used in this study should only serve as “what if” scenarios; increases in \( k_{OAM} \) will have an increased effect on the rate of \( \text{MnO}_2(s) \) formation as well as act as a greater non-productive sink for \( \text{MnO}_4^- \) consumption.
Table 3.3: ISCO simulation input parameters.

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>TCE</th>
<th>PCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Parameter</td>
<td>SI Units</td>
<td></td>
</tr>
<tr>
<td>$\rho_{w}^{(1)}$</td>
<td>kg/m$^3$</td>
<td>998.2</td>
</tr>
<tr>
<td>$\rho_{nw}^{(2)}$</td>
<td>kg/m$^3$</td>
<td>1460</td>
</tr>
<tr>
<td>$\mu_{w}^{(1)}$</td>
<td>Pa*s</td>
<td>1.00E-03</td>
</tr>
<tr>
<td>$\mu_{nw}^{(3,4)}$</td>
<td>Pa*s</td>
<td>0.00058</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Pa$^{-1}$</td>
<td>0</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Pa$^{-1}$</td>
<td>0</td>
</tr>
<tr>
<td>$K_{oc}^{(5)}$</td>
<td>mL/g</td>
<td>126</td>
</tr>
<tr>
<td>$d_{50}$</td>
<td>m</td>
<td>0.0005</td>
</tr>
<tr>
<td>$\theta$</td>
<td>-</td>
<td>0.30</td>
</tr>
<tr>
<td>$\alpha_x$</td>
<td>m</td>
<td>0.1</td>
</tr>
<tr>
<td>$\alpha_x : \alpha_z$</td>
<td>m</td>
<td>10:1</td>
</tr>
<tr>
<td>$\alpha_x : \alpha_y$</td>
<td>m</td>
<td>100:1</td>
</tr>
<tr>
<td>$\tau$</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>$k_{TCE/PCE}^{(6)}$</td>
<td>M$^{-1}$ s$^{-1}$</td>
<td>0.94</td>
</tr>
<tr>
<td>$k_{OAM}^{(7)}$</td>
<td>L/mg/s</td>
<td>1.46E-08</td>
</tr>
<tr>
<td>$S_{r,nd}^{(8)}$</td>
<td>m$^2$ L mg$^{-1}$</td>
<td>-5.50E-16</td>
</tr>
<tr>
<td>$C_s^{(9)}$</td>
<td>mg/L</td>
<td>1427</td>
</tr>
<tr>
<td>$C_{KMnO_4}^{(10)}$</td>
<td>mg/L</td>
<td>10000</td>
</tr>
<tr>
<td>$D_{TCE/PCE}^{(11)}$</td>
<td>m$^2$/s</td>
<td>7.65E-10</td>
</tr>
<tr>
<td>$D_{MnO_4}^{(12)}$</td>
<td>m$^2$/s</td>
<td>1.43E-09</td>
</tr>
<tr>
<td>$D_{CT}^{(12)}$</td>
<td>m$^2$/s</td>
<td>1.78E-09</td>
</tr>
<tr>
<td>$\nabla h^{(k)}$</td>
<td>-</td>
<td>0.05</td>
</tr>
<tr>
<td>----------------</td>
<td>---</td>
<td>-------</td>
</tr>
<tr>
<td>$X$ (longitudinal)</td>
<td>m</td>
<td>20</td>
</tr>
<tr>
<td>$Y$ (vertical)</td>
<td>m</td>
<td>5</td>
</tr>
<tr>
<td>$Z$ (width)</td>
<td>m</td>
<td>10</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>m</td>
<td>0.4</td>
</tr>
<tr>
<td>$\Delta y$</td>
<td>m</td>
<td>0.05</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>m</td>
<td>0.4</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>-</td>
<td>125000</td>
</tr>
</tbody>
</table>


### 3.3.5 Metrics of Evaluation

Each model simulation was evaluated for DNAPL mass removal and boundary mass flux ($M_f$) $\{M^1L^{-2}T^{-1}\}$ reduction (see Equation 3-11). DNAPL mass removal rate $\{M^1T^{-1}\}$ was calculated for
each simulation using a central finite difference approximation for the first order derivative, for a
selected time step ($\Delta t$) of 0.25 years (for graphical clarity):

$$M_j^n = \sum_{i=1}^{N} C_i^n q_i \tag{3-11}$$

$$\frac{\partial M_{DNAPL}(t)}{\partial t} = \frac{M_{DNAPL(t+\Delta t)} - M_{DNAPL(t-\Delta t)}}{2\Delta t} \tag{3-12}$$

where $i$ represents individual boundary nodes, $n$ represents the mobile aqueous species of interest,
$q$ is the nodal wetting phase Darcy flux {L$^1$T$^{-1}$}, $C$ is the nodal concentration {M$^1$L$^{-3}$}, and $t$ is
time {T$^1$}.

DNAPL mass was defined with regards to the non-aqueous phase and this mass does not consider
aqueous or sorbed solute phases. Enhancement factors were also calculated at certain points of
time in order to compare the performance of heated ISCO and heated abiotic dissolution in terms
of DNAPL mass removal ($E_m$) and boundary mass flux ($E_j$) reduction (West and Kueper, 2012):

$$E_m = \frac{M_{DNAPL}^0 - M_{DISCO, DNAPL}^0(t)}{M_{DNAPL}^0 - M_{DISCO, DNAPL}^0(t)} \tag{3-13}$$

$$E_j = \frac{M_{f, DISCO}^0(t)}{M_{f, ISCO}^0(t)} \tag{3-14}$$
where $M_{DNAPL}^0$ is the initial DNAPL mass in the domain ($t = 0$), $M_{DNAPL}^{ISCO} / M_{DNAPL}^{Diss}$ is the DNAPL mass remaining in the ISCO/dissolution model domain at a specific time $t$, $M_{f}^{ISCO} / M_{f}^{Diss}$ is the boundary mass flux for the ISCO/dissolution simulation at a specific time $t$.

$E_m$ and $E_f$ values greater than 1 indicate remedial enhancement due to ISCO operation. A mathematical approach by Falta et al. (2005) was utilized to compare DNAPL mass removal to boundary mass flux reduction and mean concentration. This metric elucidates the influence of subsurface heterogeneity and DNAPL source zone architecture on both heated ISCO and heated dissolution treatment efficacy:

\[
\frac{C(t)}{C(t_0)} = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right)^\Gamma \quad \text{or} \quad C_n = (M_n)^\Gamma
\]  \hspace{1cm} (3-15)

\[
\frac{M_f(t)}{M_f(t_0)} = \left(\frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)}\right)^\Gamma \quad \text{or} \quad F_n = (M_n)^\Gamma
\]  \hspace{1cm} (3-16)

where $t_0$ is the initial time of reference $\{T^1\}$, $t$ is the current time ($t \geq t_0$) $\{T^1\}$, $\Gamma$ is an empirical fitting parameter and graphical boundary which is dependent on domain characteristics such as subsurface heterogeneity and local-scale DNAPL distribution, $C$ is the aqueous phase solute concentration in the bulk solution $\{M^1L^{-3}\}$ at times $t$ and $t_0$, $C_n$ is the normalized mean concentration $\{-\}$, $F_n$ is the normalized downgradient boundary mass flux $\{-\}$, $M_{DNAPL}$ is the DNAPL mass within the model domain $\{M^1\}$, and $M_n$ is the normalized DNAPL mass remaining $\{-\}$. 

91
3.4 Results & Discussion

All of the heated ISCO and abiotic dissolution simulations were evaluated using the metrics described in section 3.3.5. The abiotic dissolution simulations represent scenarios in which the target treatment zone was only heated (no further treatment). The treatment enhancement achieved for the ISCO scenarios was analyzed by comparing these simulations to the corresponding-temperature “dissolution only” simulations.

3.4.1 DNAPL Source Zone Mass Removal

The DNAPL mass removal versus time plots for the heated TCE ISCO/dissolution and heated PCE ISCO/dissolution simulations are displayed in Figures 3.5 and 3.6, respectively. Enhancement factors for the TCE and PCE ISCO simulations were calculated using Equation 3-13, and are shown in Tables 3.4 and 3.5, respectively. For all of the ISCO simulations, the mass removal observed was greater during MnO$_4^-$ injection (active treatment duration) when compared to the same timeframe for the corresponding-temperature abiotic dissolution scenario. Mass removal enhancement from ISCO treatment was greater for PCE compared to TCE due to its lower aqueous solubility; see $E_m$ values displayed in Tables 3.4 and 3.5.
Figure 3.5: DNAPL source zone mass removal versus time for TCE ISCO and TCE abiotic dissolution simulations after 50 years. Inflection points represent the termination of oxidant injection.
Figure 3.6: DNAPL source zone mass removal versus time for PCE ISCO and PCE abiotic dissolution simulations after 50 years. Inflection points represent the termination of oxidant injection.
Figure 3.7: Total DNAPL mass removed at the end of the MnO$_4^-$ injection period for both TCE (♦) and PCE (●) ISCO scenarios (refer to Table 3.2). The DNAPL mass removed at this same timepoint was also plotted for the corresponding-temperature heated abiotic dissolution of TCE (◊) and PCE (○).

Table 3.4: Mass removal enhancement factors for TCE ISCO simulations.

<table>
<thead>
<tr>
<th>Temperature Scenario (˚C)</th>
<th>$E_m$</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End of treatment</td>
<td>5 years</td>
<td>10 years</td>
<td>20 years</td>
<td>40 years</td>
<td>60 years</td>
<td>80 years</td>
</tr>
<tr>
<td>20</td>
<td>1.13</td>
<td>1.08</td>
<td>1.00</td>
<td>0.97</td>
<td>0.96</td>
<td>0.97</td>
<td>*-</td>
</tr>
<tr>
<td>40</td>
<td>1.19</td>
<td>1.06</td>
<td>1.02</td>
<td>1.00</td>
<td>0.99</td>
<td>*-</td>
<td>*-</td>
</tr>
<tr>
<td>60</td>
<td>1.15</td>
<td>1.03</td>
<td>1.01</td>
<td>0.99</td>
<td>*-</td>
<td>*-</td>
<td>*-</td>
</tr>
<tr>
<td>80</td>
<td>1.09</td>
<td>1.01</td>
<td>0.98</td>
<td>*-</td>
<td>*-</td>
<td>*-</td>
<td>*-</td>
</tr>
</tbody>
</table>

*All of the DNAPL mass within the heated abiotic dissolution domain was completely removed.
Table 3.5: Mass removal enhancement factors for PCE ISCO simulations.

<table>
<thead>
<tr>
<th>Temperature Scenario (°C)</th>
<th>$E_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End of treatment 5 years</td>
</tr>
<tr>
<td>20</td>
<td>6.75</td>
</tr>
<tr>
<td>40</td>
<td>5.88</td>
</tr>
<tr>
<td>60</td>
<td>4.59</td>
</tr>
<tr>
<td>80</td>
<td>3.48</td>
</tr>
</tbody>
</table>

Figure 3.7 shows that enhancement in contaminant mass removal was achieved in every ISCO scenario up to the time where oxidant injection concluded. Once treatment was terminated, the enhanced removal achieved during oxidant injection progressively decreased over time for each ISCO simulation. In all of the TCE simulations, complete DNAPL mass removal within the virtual domain required less time for heated abiotic dissolution compared to heated ISCO scenarios. From Table 3.4, values of $E_m$ for the heated ISCO simulations steadily decreased to values of 1 or below (minimal to no enhancement) at later times. Eventually, $E_m$ values were not calculated since all of the DNAPL mass within the TCE abiotic dissolution domains was removed. As a reference for comparison, the 20°C TCE ISCO case required a timeframe of 419 years for complete source zone mass removal in comparison to 74 years for 20°C TCE abiotic dissolution. Declining values of $E_m$ were also observed for the heated PCE ISCO scenarios but mass removal enhancement ($E_m > 1$) was found in all of these simulations at the 50 year time point. From a temperature consideration, heating of the subsurface virtual domain generally resulted in enhancement when comparing ISCO and abiotic dissolution cases separately. As temperature increased, the amount of DNAPL mass removed in the abiotic dissolution scenarios
increased. When comparing all of the ISCO scenarios, increasing the temperature generally resulted in more enhanced mass removal, with the exception being the 60°C and 80°C TCE ISCO simulations.

As calculated using Equation 3-12 and presented in Figures 3.8 and 3.9, the rate of mass removal declines for each heated ISCO and abiotic dissolution simulation. Over time, as the DNAPL mass dissolves (both enhanced by ISCO and abiotically), the rate of removal decreases as the DNAPL mass available becomes depleted. This observation coincides with the decrease in downgradient concentrations, as later depicted in Figures 3.12 to 3.15. The mass removal rate for every ISCO simulation rapidly dropped up to the time where MnO₄⁻ injection was terminated (enhanced mass removal and dissolution). This effect was more pronounced in the PCE ISCO simulations as these scenarios experienced greater mass removal enhancement (in comparison to TCE ISCO) due to the lower solubility of this compound. At later times, the ISCO mass removal rates more gradually declined, which was representative of MnO₂(s)-inhibited, abiotic dissolution (slower dissolution). In the “dissolution only” scenarios, the mass removal rate decreased more significantly at early times (greater mass removal) and more moderately at later times (less mass within the domain). Abiotic dissolution within these virtual domains was not hindered by reaction by-product formation, and the timeframes required for DNAPL mass removal in these cases were greatly controlled by the dissolution occurring within natural lower k geological features.
Figure 3.8: DNAPL mass removal rate versus time for TCE ISCO and TCE abiotic dissolution simulations after 50 years.
Figure 3.9: DNAPL mass removal rate versus time for PCE ISCO and PCE abiotic dissolution simulations after 50 years.

The mass removal enhancement obtained from ISCO treatment was negated over time due to severe dissolution tailing effects caused by MnO\(_2(s)\) formation and the subsequent \(k\) reduction which occurred. The dissolution of the DNAPL source zone mass was greatly inhibited by MnO\(_2(s)\) formation as this precipitate most readily formed around the higher saturation regions closest to the DNAPL-water interface (Siegrist et al., 2011). Significant flow bypassing occurred within the ISCO virtual domains, resulting in groundwater flow around these low \(k\) features and reducing flow contact with DNAPL mass. Rind formation ultimately acted as the primary barrier to mass transfer, inhibited advective transport, and increased the remedial time required following ISCO treatment.
MnO$_4^-$ consumption by OAM was the secondary inhibitor to ISCO treatment. For the ISCO simulations, NOD had a significant impact on the MnO$_4^-$ contact with contaminant zones. From the observation of the cumulative Cl$^-\$ mass produced (results not shown), it was determined that only 10 to 18% of the oxidant reacted with aqueous TCE/PCE. Most of the MnO$_4^-$ injected was consumed by OAM and the majority of MnO$_2$(s) rind was contributed by the NOD. In addition to zones of high saturation (at the DNAPL-water interface), reduction in $k$ can also be severe in areas of high NOD (Heiderscheidt et al., 2008). Additional simulations were performed for the 80°C TCE ISCO scenario (highest solubility used in this study) to assess the impacts of rind formation and NOD on ISCO treatment. For the cases where (a) NOD, (b) rind formation, (c) NOD and rind formation were omitted, mass removal at the 5 year time point was 92%, 98%, and 99%, respectively. The combined effect of NOD and rind formation negated the benefits achieved from the application of ISCO treatment.

The values of $k_{OAM}$ used in this study ranged from $k_{TCE/PCE} > k_{OAM} \to k_{OAM} >>> k_{TCE/PCE}$, which showed a wide variation in the magnitude of the NOD non-productive sink. In the case of 80°C TCE ISCO, greater time (118 years) was required for complete DNAPL mass removal in comparison to the 60°C TCE ISCO (87 years) scenario due to the higher $k_{OAM} / k_{TCE}$ ratio. After review of MnO$_2$(s) concentration and $k$ field data (see time shots in Appendix B.2), there were a greater number of reduced $k$ nodes in the 80°C compared to the 60°C TCE ISCO case. The values of $k_{TCE}$ and $k_{OAM}$ (highest reaction rates used in this study) combined with the higher solubility of TCE (higher initial concentrations) could have also contributed to the more severe pore-clogging observed at 80°C.
3.4.2 Boundary Mass Flux

The mass flux at the downgradient (x-direction) boundary for all of the heated ISCO and abiotic dissolution simulations was calculated using Equation 3-11 for the same time duration as presented in Figures 3.5 and 3.6. Figures 3.10 and 3.11 display the mass flux versus time for the TCE and PCE simulations carried out in this study. Enhancement factors for mass flux reduction were calculated using Equation 3-14 and were organized in Tables 3.6 (TCE) and 3.7 (PCE). Similar to the findings by West and Kueper (2012), the enhancement in mass flux reduction was greater in comparison to the mass removal enhancement by ISCO. This was attributed to the fact that MnO₄⁻ oxidant preferentially migrated through the higher k zones within the porous media domain (Borden et al., 2010); see Figure B.5 in Appendix B for the preferential MnO₄⁻ migration pathways within the 40°C TCE ISCO case during the injection period. The mass flux reduction enhancement for the PCE ISCO cases was greater than for the TCE ISCO scenarios because of the compound’s lower solubility.
Figure 3.10: Downgradient boundary mass flux versus time for TCE ISCO and TCE abiotic dissolution simulations after 50 years.
Figure 3.11: Downgradient boundary mass flux versus time for PCE ISCO and PCE abiotic dissolution simulations after 50 years.

Table 3.6: Mass flux reduction enhancement factors for TCE ISCO simulations.

<table>
<thead>
<tr>
<th>Temperature Scenario (°C)</th>
<th>$E_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End of treatment</td>
</tr>
<tr>
<td>20</td>
<td>7.62</td>
</tr>
<tr>
<td>40</td>
<td>6.86</td>
</tr>
<tr>
<td>60</td>
<td>5.77</td>
</tr>
<tr>
<td>80</td>
<td>4.04</td>
</tr>
</tbody>
</table>

*All of the DNAPL mass within the heated abiotic dissolution domain was completely removed.
Mass flux rebound was observed in every ISCO simulation after MnO$_4^-$ injection was terminated. At the time where oxidant delivery was shut off, untreated DNAPL mass remained in each ISCO virtual domain. Mass flux and/or concentration rebound is associated with the slow dissolution of contaminants, which is influenced by DNAPL dissolution through rind formation, slow desorption processes, slow advective transport as well as back-diffusion from low $k$ materials (Huling and Pivetz, 2006). In the heated abiotic dissolution simulations, the mass flux reduction was not as rapid compared to the ISCO scenarios during oxidant delivery. However, due to the MnO$_2(s)$ formation in the ISCO cases, the inhibition of DNAPL dissolution contributed to mass flux persisting over greater time periods for ISCO compared to abiotic dissolution.

Rind formation affected the mass flux leaving the domain for the ISCO simulations. As depicted in Figure 3.10 (for TCE ISCO), the creation of low $k$ zones due to MnO$_2(s)$ deposition resulted in lower mass flux reduction at early times after MnO$_4^-$ injection and plateau effects at later times. The plateau trends in flux reduction were attributed to the inhibited dissolution of the remaining DNAPL mass within the domain. For the PCE ISCO simulations (Figure 3.11), the mass flux

### Table 3.7: Mass flux reduction enhancement factors for PCE ISCO simulations.

<table>
<thead>
<tr>
<th>Temperature Scenario (°C)</th>
<th>$E_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End of treatment</td>
</tr>
<tr>
<td>20</td>
<td>22.18</td>
</tr>
<tr>
<td>40</td>
<td>20.81</td>
</tr>
<tr>
<td>60</td>
<td>20.52</td>
</tr>
<tr>
<td>80</td>
<td>20.35</td>
</tr>
</tbody>
</table>
gradually/mildly declined at times right after rebound was observed. At later times, the PCE mass flux showed a somewhat singular plateau trend, indicative of significantly slow (low solubility and \( \text{MnO}_2(\text{s}) \)-inhibited) DNAPL dissolution. The low \( k \) zones created from \( \text{MnO}_2(\text{s}) \) deposition lengthened the time required for DNAPL dissolution following ISCO treatment.

### 3.4.3 Mass Flux vs Mass Removal

An analytical source zone metric developed by Falta et al. (2005) was utilized to assess the influence of subsurface heterogeneity and DNAPL source zone architecture on the relationship between contaminant mass removal and the mass flux leaving the target treatment zone. Results presented in sections 3.4.1 and 3.4.2 and Equations 3-15 and 3-16 were applied to produce the normalized mass (\( M_n \)) versus normalized mass flux (\( F_n \)) and normalized concentration (\( C_n \)) plots, as shown in Figures 3.12 to 3.15. Prior to the start of each model run, dissolution had not taken place within the domain; the peaks in the mass flux and concentration, and the time point (\( t_0 \)) in which they occurred were adjusted accordingly in these figures.
Figure 3.12: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.
Figure 3.13: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the ISCO treatment simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.
Figure 3.14: Normalized PCE mass flux ($F_n$) and PCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.
Figure 3.15: Normalized PCE mass flux ($F_n$) and PCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the ISCO treatment simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.

For TCE (Figure 3.12) and PCE (Figure 3.14) abiotic dissolution, the $C_n$ and $F_n$ curves follow similar non-linear trends for each of these individual compounds. The effects of temperature on the mass removal versus mass flux (concentration) trends for abiotic dissolution were minimal. Each TCE and PCE virtual domain had the same initial $S_{NW}$ and $k$ fields; the combination of these two factors had the greatest influence on this source zone metric. For TCE dissolution (Figure 3.12), $C_n$ lied between $0.5 \leq \Gamma \leq 1.25$ and $F_n$ lied between $0.5 \leq \Gamma \leq 2$. In comparison, for PCE dissolution (Figure 3.14), $C_n$ was located within $1 \leq \Gamma \leq 2$ and $F_n$ was located within $1 \leq \Gamma \leq 3$. Values of $\Gamma > 1$ represent remedial treatments capable of significantly reducing source strength in
the short term, contributing to greater decreases in concentration compared to mass removal. In the long term for $\Gamma > 1$, DNAPL source zone mass will continue to persist (i.e. mass remaining after treatment), resulting in considerable dissolution (concentration) tailing effects which can ultimately negate the benefits achieved in the short term.

$C_n$ and $F_n$ for the ISCO simulations (Figures 3.13 and 3.15) showed greater divergence from $\Gamma = 1$ (mass discharge linearly proportional to mass reduction) towards $\Gamma > 1$, in comparison to the abiotic dissolution scenarios. ISCO greatly enhanced the reduction in mass flux compared to the enhancement in DNAPL mass removal, due to the preferential migration of $\text{MnO}_4^-$ through higher $k$ zones (Borden et al., 2010). For TCE ISCO (Figure 3.13), $C_n$ and $F_n$ lied between $0.5 \leq \Gamma \leq 2$ and $0.5 \leq \Gamma \leq 3$, respectively. $C_n$ and $F_n$ were located within the ranges of $0.5 \leq \Gamma \leq 2.5$ and $1 \leq \Gamma \leq 4$, respectively for PCE ISCO (Figure 3.15). As temperature increased, higher $\text{MnO}_4^-$ reaction rates resulted in greater DNAPL masses removed (shifts the curves slightly left on the plot; lower $M_n$) up to the time where oxidant injection was terminated (the point in the curve just before rebound). Concentration and mass flux rebound were observed in each ISCO simulation after treatment was terminated, which had a detrimental effect on reducing concentrations and downgradient mass fluxes in the long term.

A comparison of the values of $\Gamma$ for both heated abiotic dissolution and heated ISCO scenarios does show an agreement in terms of both treatment options. Overall, the values of $\Gamma$ for ISCO were relatively greater than for abiotic dissolution, depicting that ISCO did provide an enhancement in mass flux (concentration) reduction and DNAPL mass removal in the short term, while $\text{MnO}_4^-$ was continuously injected. Over the long term, both heated abiotic dissolution and
heated ISCO experienced dissolution tailing effects. Abiotic dissolution treatment times were ultimately governed by the DNAPL mass dissolving within natural lower $k$ geologic zones. In terms of ISCO, more significant long-term tailing effects (higher $I'$ values compared to abiotic dissolution) were observed due to rind formation. The timeframes required for ISCO were significantly longer (as clearly shown in the TCE simulations) due to the DNAPL mass dissolving within naturally (non-rind clogged) low $k$ geologic zones as well as areas impacted by rind formation.

3.5 Conclusions

Temperature provided an enhancement for heated ISCO compared to heated abiotic dissolution scenarios. With the exception of the 80°C TCE ISCO simulation, elevated temperatures provided greater benefits in both DNAPL mass removal and mass flux reduction when implementing ISCO. ISCO provided greater mass removal and mass flux reduction enhancement in the PCE simulations due to the compound’s lower solubility. The ratio of $k_{OAM}/k_{TCE}$ for the 80°C TCE ISCO scenario was significantly greater than the ratio for 60°C TCE ISCO; a longer timeframe was required for contaminant mass removal in this higher temperature case due to the more intense MnO$_2$(s) rind formation (greater $k$ reduction). Elevated temperatures for the heated abiotic dissolution scenarios also accelerated both DNAPL mass removal and mass flux reduction over the 50 year timeframe. Complete DNAPL mass removal was observed in the 40°C, 60°C, and 80°C TCE abiotic dissolution cases before 50 years had passed. Even though the mass removal and mass flux reduction in the heated abiotic dissolution scenarios was not as significant compared to the heated ISCO cases during the same timeframe for MnO$_4^-$ injection, the short-
term enhancement achieved using partial mass removal ISCO were negated over time due to the rind formation. MnO$_2(s)$ was the primary inhibitor of DNAPL dissolution within the ISCO domains and contributed to considerable flow bypassing around contaminated zones, which increased remedial durations. Minimizing the influence of rind formation is the key factor in trying to implement MnO$_4^-$ ISCO successfully for contaminant remediation. Appropriate site characterization (i.e. subsurface velocity, level of NOD at a site) as well as the management of oxidant concentrations are some of the key design factors to consider in trying to reduce the impacts of rind formation (Petri et al., 2008; Siegrist et al., 2011).

Downgradient boundary mass flux and mean concentration reduction were compared to the mass removed for all of the heated ISCO and abiotic dissolution simulations. Both $C_n$ and $F_n$ showed similar trends for both heated TCE and PCE abiotic dissolution. Each simulation had the same geological ($k$) and contaminant field ($S_{nm}$) characteristics prior to the start of ISCO or abiotic dissolution. The results from the heated abiotic dissolution scenarios showed that $C_n / F_n$ versus $M_n$ was primarily influenced by the initial subsurface heterogeneity and DNAPL source zone architecture; the $C_n / F_n$ vs $M_n$ trends for all of the TCE/PCE abiotic dissolution simulations were similar. In terms of the ISCO scenarios, greater initial reduction in $C_n$ and $F_n$ were observed during MnO$_4^-$ injection in comparison to “dissolution only”. Mass flux and concentration rebound was observed in each ISCO simulation once injection was terminated. Dissolution tailing was evident in both ISCO and abiotic dissolution simulations. Tailing effects in the “dissolution only” scenarios were primarily governed by DNAPL dissolution within natural low $k$ geologic zones. More severe dissolution tailing was observed in the ISCO cases due to significant $k$ reduction by rind formation. Long term DNAPL dissolution within the ISCO domains was significantly
inhibited since dissolution needed to occur within naturally (non-rind clogged) low $k$ geologic zones as well as areas impacted by rind formation.

The results from this study highlight some of the potential drawbacks of utilizing MnO$_4^-$ ISCO as a partial mass removal remedial technology. The contaminant mass remaining after MnO$_4^-$ injection exerted a significant influence on long term downgradient concentrations and mass flux, which reduced the benefits achieved during ISCO operation. MnO$_{2(s)}$ rind formation contributed to significant flow bypassing within the porous media domain and ultimately limited DNAPL dissolution in the long term. Consumption of MnO$_4^-$ by OAM was the secondary inhibiting factor to ISCO treatment as it prevented the majority of injected oxidant from contacting TCE/PCE. The MnO$_{2(s)}$ produced from the oxidant reactions with OAM had a substantial effect on the overall $k$ reduction due to ISCO. Elevated subsurface temperatures did provide enhancement during ISCO operation but overall treatment efficacy was ultimately influenced by these MnO$_4^-$ ISCO-specific detrimental after-effects.

### 3.6 Acknowledgements

Funding for this work was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada through Strategic Project Grant SPG-396730-10, scholarship funding from Queen’s University, and scholarship funding from the Ontario Graduate Scholarship Program (OGS). The contributions of Golder Associates Ltd, McMillan-McGee Corp, the Ontario Ministry of the Environment, and The Johnson Company as industrial partners to the Strategic Project Grant are acknowledged.
3.7 Notation

\( a_{na} \) interfacial area between NAPL and aqueous phases \( \{L^{-1}\} \)

\( A \) Arrhenius frequency factor

\( B \) fitting parameter

\( C \) aqueous phase solute concentration in the bulk solution \( \{M^1L^{-3}\} \)

\( C_A \) concentration of solute A \( \{M^1L^{-3}\} \)

\( C_n \) normalized mean concentration \( \{-\} \)

\( C_s \) thermodynamic equilibrium aqueous phase concentration (solubility) in which the non-aqueous phase is present \( \{M^1L^{-3}\} \)

\( d_{so} \) mean grain size diameter \( \{L^1\} \)

\( D \) hydrodynamic dispersion tensor \( \{L^2T^{-1}\} \)

\( D^o \) free-water diffusion coefficient \( \{L^2T^{-1}\} \)

\( D_{AB}^o \) binary free-water molecular diffusion coefficient of solute A diffusing into solvent B in dilute solutions \( \{L^2T^{-1}\} \)

\( E_a \) activation energy \( \{M^1L^2T^{-2}M^{-1}\} \)

\( E_f \) boundary mass flux reduction enhancement factor \( \{-\} \)

\( E_m \) DNAPL mass removal enhancement factor \( \{-\} \)

\( F \) Faraday constant = 96485.3415 s\(^1\)A\(^1\)mol\(^{-1}\)

\( F_n \) normalized downgradient boundary mass flux \( \{-\} \)

\( f_{oc} \) organic carbon fraction \( \{-\} \)

\( g \) gravitational constant \( \{L^1T^{-2}\} \)

\( H \) fitting parameter

\( \nabla h \) hydraulic gradient \( \{-\} \)

\( J \) solute mass flux from immiscible liquid phase to the aqueous phase \( \{M^1L^{-2}T^{-1}\} \)

\( J_{AB} \) diffusive flux of solute A diffusing into solvent B \( \{M^1L^{-2}T^{-1}\} \)

\( k \) intrinsic permeability \( \{L^2\} \)
$k_1, k_2$  2nd order reaction rate coefficient at reference temperatures 1 and 2 \{M^{-1}L^{3}T^{-1}\}

$K_d$  sorption distribution coefficient \{M^{-1}L^{3}\}

$k_y$  intrinsic permeability tensor \{L^2\}

$k_l$  mass transfer coefficient \{L^1T^{-1}\}

$K_f$  lumped mass transfer coefficient \{T^{-1}\}

$k_o$  original permeability \{L^2\}

$k_{OAM,T}$  2nd order reaction rate coefficient for reaction between OAM and MnO$_4^-$ \{M$^{-1}$L$^{3}$T$^{-1}$\}

$K_{oc}$  organic carbon partitioning coefficient \{M$^{-1}$L$^{3}$\}

$k_{PCE}$  2nd order reaction rate coefficient for reaction between PCE and MnO$_4^-$ \{M$^{-1}$L$^{3}$T$^{-1}$\}

$k_r$  relative permeability \{-\}

$k_{rms}$  2nd order reaction rate coefficient \{M$^{-1}$L$^{3}$T$^{-1}$\}

$k_{TCE}$  2nd order reaction rate coefficient for reaction between TCE and MnO$_4^-$ \{M$^{-1}$L$^{3}$T$^{-1}$\}

$M_B$  molecular weight of solvent B, \{M$^1$M$^{-1}$\}

$M_{DNAPL}$  DNAPL mass within the model domain \{M$^1$\}

$M_f$  boundary mass flux \{M$^1$L$^{-2}$T$^{-1}$\}

$M_n$  normalized DNAPL mass remaining \{-\}

$P$  pressure \{M$^1$L$^{-1}$T$^{-2}$\}

$P_A$  parachor of solute A \{M$^{1/4}$L$^{3}$T$^{-1/2}$M$^{-1}$\}; estimated using Table 11-3 of Poling et al., 2001

$P_B$  parachor of solvent B \{M$^{1/4}$L$^{3}$T$^{-1/2}$M$^{-1}$\}; estimated using Table 11-3 of Poling et al., 2001

$P_C$  capillary pressure \{M$^1$L$^{-1}$T$^{-2}$\}

$q$  volumetric (Darcy) flux \{L$^3$L$^{-2}$T$^{-1}$\}

$q_s$  source/sink term represented as a volumetric flux \{T$^{-1}$\}

$r_a$  radius of spherical-shape solute A \{L$^1$\}

$R_n$  retardation factor \{-\}
$S$  phase saturation \{-\}

$S_{\text{rind}}$  rind function \{M^{-1}L^5\}

$S_w$  wetting phase saturation \{-\}

$V_A$  molar volume of solute A at its normal boiling point \{M^{-1}L^2\}

$V_B$  molar volume of solvent B at its normal boiling point \{M^{-1}L^2\}

$t$  time \{T\}

$T$  reference temperature (°K or °C)

$T_c$  critical temperature of the solvent (°K)

$v$  average linear groundwater velocity \{L^1T^{-1}\}

$x$  horizontal longitudinal direction

$X$  domain length along $x$ \{L\}

$y$  vertical direction

$Y$  domain length along $y$ \{L\}

$z$  horizontal transverse direction

$Z$  domain length along $z$ \{L\}

$\Delta x$  nodal discretization along the $x$-direction \{L\}

$\Delta y$  nodal discretization along the $y$-direction \{L\}

$\Delta z$  nodal discretization along the $z$-direction \{L\}

$\alpha$  compressibility of the porous medium \{M^{-1}L^1T^2\}

$\alpha_{x,y,z}$  dispersivity \{L\}

$\beta$  compressibility of the wetting fluid \{M^{-1}L^1T^2\}

$\Gamma$  fitting parameter

$\lambda$  molar conductivity for common ions \{M^{-1}T^3A^2M^{-1}\}

$\eta$  parameter associated with the solvent; based on heat of vaporization

$\phi$  association factor of solvent B; for water $\phi = 2.6$ (Poling et al., 2001; Bird et al., 2002)

$\rho$  fluid density \{M^1L^{-3}\}

$\mu$  fluid dynamic viscosity \{M^1L^{-1}T^{-1}\}
\( \mu_B \) dynamic viscosity of solvent B at reference temperature \( \{M^1L^{-1}T^{-1}\} \)

\( \mu_{\text{lnk}} \) mean of ln \( k \) \( \{\ln (L^2)\} \)

\( \sigma_{\text{lnk}}^2 \) variance of ln \( k \) \( \{[\ln (L^2)]^2\} \)

\( \tau \) tortuosity \{-\}

\( \theta \) porosity \{-\}

Notes
Square brackets [ ] indicate molar concentrations \( \{M^1L^{-3}\} \) of the specific compound or species.

Common Subscripts

0 initial condition

A solute (TCE, PCE, MnO_4^-, Cl^-, CO_2)

B solvent (water)

n species type

NW non-wetting phase (DNAPL)

W wetting phase (water)

3.8 References


Heron, G., Van Zutphen, M., Christensen, T. H., & Enfield, C. G. (1998a). Soil heating for enhanced remediation of chlorinated solvents: A laboratory study on resistive heating and vapor


Kueper, B. H., Redman, D., Starr, R. C., Reitsma, S., Mah, M. (1993). A Field Experiment to Study the Behavior of Tetrachloroethylene Below the Water Table: Spatial Distribution of


Chapter 4

Thermal Enhancement of Enhanced In Situ Bioremediation (EISB) for Remediation of Groundwater Impacted by Chlorinated Solvents

4.1 Abstract

A numerical model was utilized to simulate the effects of temperature (10 to 40°C) on the factors pertaining to the EISB of trichloroethene (TCE) and subsurface fluid flow/transport processes. Heated EISB and abiotic dissolution scenarios were modeled to assess the enhancement of treatment. The bacterial groups associated with EISB were modeled as mesophilic species, with a hypothetical optimum temperature of 30°C. It was found that temperatures at or below the optimum temperature did provide benefits to EISB treatment during the substrate injection period. An enhancement in TCE mass removal and mass flux reduction was achieved in the 10 to 30°C EISB simulations. Dechlorination of TCE was found to be most effective at 20°C, compared to 30°C, due to the reduced methanogenesis (biocompetition for the H\textsubscript{2} electron donor) at the lower temperature. At 40°C, dechlorinator growth was minimal and methanogens were the main consumer of H\textsubscript{2}. In the long term, after substrate injection was terminated, the remedial benefits achieved from 10 to 30°C EISB steadily declined due to the reduced electron donor availability and bioclogging. Substrate fermentation was the only source of electron donor for dechlorinators; dechlorination was minimal at times past the end of substrate injection. Bioclogging due to biomass growth resulted in the formation of lower permeability zones and contributed to greater dissolution tailing effects in all simulations. The treatment times were lengthened for the EISB
scenarios due to the long term tailing effects. Over time, these tailing effects were partially reduced due to the partial recovery of permeability from biomass decay.

4.2 Introduction

Dense non-aqueous phase liquids (DNAPLs) are one of the most common types of contaminants that continue to negatively impact subsurface systems throughout North America. Chlorinated solvents, such as trichloroethene (TCE) and tetrachloroethene (PCE), were utilized in the past for commercial/industrial applications such as metal degreasing, dry-cleaning, as well as chemical intermediates. The improper usage and disposal of these fluids resulted in the release of these compounds to subsurface systems (Kueper et al., 2004). After initial release, these compounds can migrate and redistribute within the subsurface as disconnected blobs (ganglia) and/or as connected, higher saturation pools above finer grained materials (Kueper et al., 1993). The aqueous solubilities of both compounds are low ($\approx 200–1100$ mg/L), but these concentrations are considerably greater than the maximum contaminant level (MCL) of 5 ppb (US EPA, 2013). The time frame for the abiotic dissolution of TCE and PCE can range from decades to centuries (from initial release) for full mass depletion.

In order to enhance the solubility of TCE and PCE, enhanced in situ bioremediation (EISB) has been applied as an in situ partial mass removal technology. Subsurface bioremediation of DNAPLs has been studied at the laboratory scale (Maymó-Gatell et al., 1997; Yang and McCarty, 2000) and the field scale (Hood et al., 2008). Numerous bacterial cultures and/or consortia have been utilized for the reductive dechlorination (RD) of chlorinated solvents (Holliger et al., 1993;
Scholz-Muramatsu et al., 1995; Gerritte et al., 1996). TCE and PCE can be sequentially degraded (or biotransformed), via metabolic microbial activity, to less harmful/toxic daughter by-products: cis-dichloroethene (cDCE), vinyl chloride (VC), ethene (ETH) (Maymó-Gatell et al., 1997). Within each of these sequential reaction steps, an electron donor is required to mediate the biological redox reaction (Häggblom and Bossert, 2004). Equations 4-1 to 4-4 depict a general reaction stoichiometry for the sequential degradation of TCE/PCE (Maymó-Gatell et al., 1995), through the utilization of the hydrogen (H₂) electron donor, which can be obtained via organic substrate fermentation (Fennell and Gossett, 1998):

\[
\begin{align*}
PCE + H_2 & \rightarrow TCE + Cl^- + H^+ + biomass \\
TCE + H_2 & \rightarrow cDCE + Cl^- + H^+ + biomass \\
cDCE + H_2 & \rightarrow VC + Cl^- + H^+ + biomass \\
VC + H_2 & \rightarrow ETH + Cl^- + H^+ + biomass
\end{align*}
\]  

where Cl\(^-\) represents the chloride ion and H\(^+\) represents the hydrogen ion.

EISB treatment of TCE/PCE enhances DNAPL dissolution which can accelerate the removal of contaminant mass as well as reduce boundary mass flux. Similar to other partial mass removal technologies (e.g. \textit{in situ} chemical oxidation (ISCO)), it is assumed that bacteria/consortia primarily utilize (dechlorinates) the aqueous phase of the contaminant (Ward and Stroo, 2010). The concentration gradient towards dissolution is enhanced as aqueous phase concentrations are reduced due to biodegradation. Inhibiting factors to EISB can include competitive biological processes, substrate/nutrient availability, redox conditions, and bioclogging. Competitive hydrogenotrophic microbial reactions such as acetogenesis, methanogenesis, sulfate/iron/nitrate
reduction can be additional consumers of the electron donor, H₂ (He et al., 2002; Robinson et al., 2009; Malaguerra et al., 2011). Depending on the H₂ concentration available, these aforementioned terminal electron accepting processes (TEAPs) can out-compete dechlorinating microbial populations. Past studies have shown that dechlorinating bacteria can out-compete TEAPs at lower H₂ concentrations due to their higher H₂ affinity (Smatlak et al., 1996; Ballapragada et al., 1997; Fennell and Gossett, 1998; Yang and McCarty, 1998). The ability to augment/stimulate dechlorinating cultures with the necessary concentration of organic substrate (which can be fermented to H₂) will be significantly impacted by competitive TEAPs.

Substrate/nutrient availability is another key issue involved with EISB treatment efficacy, which will ultimately govern the selection of the organic substrate and distribution technique. It has generally been accepted that only members of the genus *Dehalococcoides* (*Dhc*) spp. are capable of complete dechlorination of TCE/PCE to non-toxic ETH (Maymó-Gatell et al., 1997; Yu and Semprini, 2004; Schaefer et al., 2009). Other bioremediation studies have utilized other microbial strains such as *Dehalobacter restrictus* {PER-K23} (Holliger et al., 1993, 1998), *Desulfitobacterium* {PCE1} (Gerritse et al., 1996; Huang and Becker, 2011), and *Dehalospirillum multivorans* (Neumann et al., 1994; Scholz-Muramatsu et al., 1995; Amos et al., 2007, 2008), but these authors observed incomplete dechlorination (i.e. stalling) of TCE/PCE, as these cultures could not dechlorinate past cDCE/TCE. Incomplete dechlorination creates daughter products which present additional risks to human health; cDCE and VC are suspected/known carcinogens. VC has a greater toxicity compared to its parent compounds (Malaguerra et al., 2011). Incomplete dechlorination can also arise due to limiting electron donor/acceptor conditions. It has been generally accepted that *Dhc* spp. (and other dechlorinating cultures)
primarily utilize the electron donor \( \text{H}_2 \) for RD; the selection of a fermentable organic substrate must consider electron donor biocompetition as well as the necessary \( \text{H}_2 \) concentration to promote complete RD.

Distribution and supply of the electron donor to the microbial community will also impact subsurface processes. Considerable costs (both monetary and performance-wise) can be incurred during EISB due to the oversupply of substrate (electron donor) in order to account for the competing biological processes. Enhanced microbial activity can cause excessive biomass production, especially in subsurface regions where electron donor concentrations are greatest. As a result, well/aquifer biofouling can occur resulting in the reduction of subsurface permeability \((k)\) due to bioclogging (Häggbloom and Bossert, 2004). \( k \) can also be reduced, at high \( \text{H}_2 \) concentrations, as methane \((\text{CH}_4)\) produced from methanogenesis can form gas bubbles within pore spaces (Yang and McCarty, 2002).

Thermal treatment has been a common remedial technology employed in numerous subsurface remediation applications. Thermal conductive heating (TCH), electrical resistive heating (ERH), steam injection and radio frequency (RF) heating are thermal treatment technologies capable of elevating subsurface temperatures to at or above the boiling point of water, which is strongly dependent on local pressures (USACE, 2009). Higher temperatures generally correspond to an increase in the aqueous solubility (dissolution), volatility, diffusivity, and desorption (Heron et al., 1998a) of TCE/PCE. Mass transfer enhancement can also be attained from thermal treatment since fluid density and viscosity generally decrease at higher temperatures.
The focus of this study was to assess the effects of elevated, sub-boiling temperatures (10 to 40°C) on EISB operations for the remediation of TCE. This work utilizes the multi-phase flow, reactive transport numerical model DNAPL3D-RX employed in West’s (2009) study, in which numerical simulations were conducted for a subsurface reference temperature of 10°C. West (2009) applied DNAPL3D-RX to model the effects of different subsurface properties, DNAPL volume and type, hydraulic displacement, and inhibitory processes specific to EISB. The emphasis of this study specifically looked at the effects of temperature on the flow and reactive transport processes associated with lactate-amended EISB subsurface treatment, using the base case TCE virtual site created by West (2009). Temperature was the main property of interest in this study; TCE dechlorination reactions, biomass production/decay, as well as fermentative and competitive inhibitory processes (e.g. methanogenesis) will be affected by temperature (Vaccari et al., 2006). The physicochemical properties of the ambient groundwater and the contaminant are also sensitive to temperature, which will have an effect on subsurface flow and transport processes.

4.3 Methodology

The methodology adopted in this work was similar to the numerical model study conducted by West (2009). The numerical model, DNAPL3D-RX, was applied to simulate the processes and reactions involved with the EISB treatment of TCE. All of the initial boundary conditions and modeling assumptions made by West (2009) were implemented in this work.
4.3.1 Numerical Model

DNAPL3D-RX is a 3-D multi-phase flow, reactive transport numerical model developed by West (2009) for the simulation of lactate-amended EISB for DNAPL removal. For more in-depth details with regards to initial model development, model calibration/validation/verification, incorporation of multi-phase flow and solute transport equations, and the inclusion of Monod kinetic expressions, the reader is referred to Kueper and Frind (1991), Gerhard and Kueper (2003), Grant and Gerhard (2007a) and West (2009). See Appendix C.1 for a list of the multiphase flow, solute transport, and Monod kinetic equations utilized by DNAPL3D-RX.

The initial base case $k$ and DNAPL saturation ($S_{NW}$) fields employed by West (2009) were used for the numerical simulations performed in this study, as shown in Figure 4.1. Spatially correlated random $k$ fields were generated by West (2009) using the algorithm F-GEN (Robin et al., 1993). The base case permeability field had a mean $k$ of $3.03 \times 10^{-12}$ m$^2$ and a variance of natural logarithm $k$ ($\sigma_{lnk}^2$) of 1.74 (representative of a moderately heterogeneous, fine sand-to-silt porous medium). To simulate the impact of organic carbon (sorption), a fraction-of-organic carbon ($f_{oc}$) field was perfectly negatively cross-correlated to the $k$ field using F-GEN. The F-GEN input parameters were a mean $f_{oc}$ of 0.003 (0.3%) and variance of natural logarithm $f_{oc}$ ($\sigma_{lnf_{oc}}^2$) of 0.24. TCE and cDCE sorption were represented in these model porous media domains using a linear isotherm, similar to West (2009).
Figure 4.1: Base case DNAPL saturation ($S_{NW}$) and permeability ($k$) fields (West, 2009).

The initial $S_{NW}$ fields were developed from the work by Richards et al. (2012), in which hydraulic displacement (HD) events were simulated for DNAPL source zones within porous media. For computational efficiency, the width of the model domain created by Richards et al. (2012) was reduced by half. The domain size ($x \times y \times z$) for all of the numerical simulations was 20 m (length) $\times$ 5 m (depth/thickness) $\times$ 10 m (width). The initial $S_{NW}$ field was representative of a contaminant source zone, below the water table, in which the following sequential events have already occurred: 1) initial TCE DNAPL release, 2) DNAPL migration, 3) DNAPL redistribution, and 4) HD (which reduces pooled and maximizes residual DNAPL saturations). The initial DNAPL volume within each domain was approximately 2.41 m$^3$. Prior to the start of each simulation, the DNAPL field has not undergone dissolution; there is no initial plume development.

Upon implementation of EISB, dissolution was modeled using a local equilibrium (LE) approach ($C = C_x$); the virtual model domain was assumed to be sufficiently complex in terms of subsurface heterogeneity and source architecture, which justified the use of a non-rate limited
Incorporating LE dissolution provided greater computational efficiency for the numerical simulation runs. It is recognized that solute concentrations observed in field studies can be lower than the solubility limit in heterogeneous subsurface environments (Rivett and Feenstra, 2005). Rate-limited (non-equilibrium) mass transfer considers both DNAPL saturation and advective-dispersive transport, while LE dissolution mostly considers the latter (Grant and Gerhard, 2007b). LE dissolution can overpredict dissolution (hence, contaminant mass removal), especially at later times when limited contaminant mass remains, as it is assumed that concentrations are at the solubility limit wherever DNAPL is present. Conversely, LE dissolution provides performance benefits in terms of the promotion of treatment technologies. An LE dissolution approach highlights greater effectiveness for treatment. West and Kueper (2012) preliminarily tested the base case model domain using both LE and non-equilibrium dissolution techniques. Since no prior dissolution had occurred before the start of the simulation run (similar to the simulations conducted in this work), there was no initial presence of a dissolved contaminant phase. The non-equilibrium mass transfer correlation predicted faster dissolution than LE for the first two years, but both methods exhibited similar DNAPL mass removal trends from year 2 to year 10.

A LE dissolution approach was adopted in this study due to the reduction in computational run times as well as the sufficient complexity of the numerical model domain. The initial $S_{NW}$ fields utilized in this study were non-uniformly distributed and appropriate subsurface heterogeneity was accounted for (i.e. preferential flow paths, flow bypassing and dilution effects). These factors were more representative of large scale dissolution processes, which are primarily influenced by advective-transport (Sale and McWhorter, 2001). Brusseau et al. (2002) observed that for
sufficiently complex distributions of immiscible contaminant, the LE assumption provided good results as long as large scale mass transfer factors were considered in the model.

Lactate was selected as the fermentable organic substrate since this compound provides a rapid source (and high concentration) of H₂ (He et al., 2002). It is recognized that a slower fermentable organic substrate may be preferred for RD. The degree of competition between methanogens and dechlorinators is dependent on the concentration of electron donor available; at higher H₂ concentrations, methanogenesis becomes more rapid and dominant (Heimann et al., 2007). At lower H₂ concentrations, dechlorinators can out-compete methanogens, based on kinetics and/or threshold concentrations (Ballapragada et al., 1997; Yang and McCarty, 1998). However, the rapid fermentation of lactate may still be preferred (in some cases) as the generation of high H₂ concentrations reduces the time for complete dechlorination. Heimann et al. (2007) observed that the lag phase leading up to VC production was more prevalent in the propionate-amended (slowly fermentable) compared to the lactate-amended cultures. The time required for complete RD (at the applicable temperatures studied) was greater for the propionate-fed cultures. The selection of any individual fermentable organic substrate used for TCE dechlorination will have its advantages and drawbacks; the decision will be strongly based on the consideration of both electron donor availability and the degree of biocompetition.

Bacterial and biomass populations (dechlorinating, fermentative, methanogenic) were assumed to be in situ immobile species adhered to soil grains within the subsurface domain. Lactate substrate was supplied to the target treatment zone using a pulse injection strategy of 1 day per week, over the duration of 2.5 years. Substrate injection was simulated in this particular domain as an up-
gradient, pulsed constant concentration boundary (Figure 4.2), which was representative of a network of closely spaced injection wells or injection trench.

Figure 4.2: Cross-section cut-out of the model domain at A-A' (see Figure 4.1; at $z = 5\text{m}$) displaying the permeability ($k$) field with the overlying DNAPL saturation ($S_{NW}$) field at this slice (West, 2009).

All of the specific Monod kinetic equations for the RD of TCE to cDCE, lactate fermentation, and methanogenesis were incorporated into RT3D (Clement et al., 1997), which was the reactive transport component of DNAPL3D-RX. Only the dechlorination of TCE to cDCE was modeled; this was a simplified assumption based on the cDCE stalling observed in numerous studies (Holliger et al., 1993; Gerritse et al., 1996) and significantly improved simulation run-times. Two inhibiting factors to EISB treatment are incorporated into the model (West, 2009): 1) hydrogenotrophic, methanogenic competition, and 2) bioclogging. Methanogenic activity can detrimentally impact EISB treatment efficacy as it is a major consumer (and competitor) for the $H_2$ electron donor (Fennell and Gossett, 1998). Bioclogging and subsequent $k$ reduction was modeled by utilizing the following approaches: a hydraulic conductivity reduction expression
(Clement et al., 1996) and a relative porosity term (Chu et al., 2003). It was assumed that 20% of the biomass produced was recalcitrant, contributing to a permanent reduction in $k$. The following expression was used to simulate $k$ reduction due to bioclogging (West, 2009):

$$
k = \begin{cases} 
  k_o \left[ 1 - \left( \frac{\sum_{i=1}^{N} X_i}{X_{\text{MAX}}} \right)^{19/6} \right] & \text{if } \sum_{i=1}^{N} X_i \leq X_{\text{MAX}} \\
  k_{\text{min}} & \text{if } \sum_{i=1}^{N} X_i > X_{\text{MAX}} 
\end{cases} \left[ 1 - \left( \frac{1}{2000} \right)^{19/6} \right]$$

(4-5)

where $k_o$ is the original intrinsic permeability \(\{L^2\}\), $X_i$ is the nodal biomass concentration \(\{M^1L^{-3}\}\), $X_{\text{MAX}}$ is the maximum nodal biomass concentration \(\{M^1L^{-3}\}\), and $k_{\text{min}}$ is the minimum intrinsic permeability \(\{L^2\}\) that can occur due to bioclogging. $k_{\text{min}}$ is approximately equal to $k_o/2000$, with reference to the work by Taylor and Jaffe (1990) and Chu et al. (2004). Based on sensitivity analyses conducted by West (2009), $X_{\text{MAX}}$ was assumed to be equal to 20,000 mg/L.

In every numerical simulation in this study, it was assumed that the model domain was perfectly buffered. It is recognized that acidic conditions can be generated as a result of the microbial reactions with TCE and PCE (see Equations 4-1 to 4-4). The redox conditions and pH of subsurface environments will have a significant influence on microbial reactions (Zhuang and Pavlostathis, 1995; Robinson et al., 2009). Each model domain was also assumed to be isothermal and at local thermal equilibrium throughout the entire duration. Conceptually, heat input into the model domain is thought to be provided from two possible scenarios: 1) A thermal treatment application (e.g. ERH), 2) Heated water-lactate (at specified sub-boiling temperature) mixture
injection amendment; EISB biostimulation application. It is recognized that the constant
temperature assumption for each model domain was non-conservative; cooler temperatures will
exist in the domain regions downgradient of the heat source (non-uniform temperature
distribution). It was assumed that the establishment of a uniform initial temperature within the
domain was equivalent to pre-heating of the target treatment zone with ERH. ERH relies on
electrical current flow produced from electrodes, which is conducted by subsurface flow within
pore spaces. The resistance encountered by the conducted current results in uniform heating of
the subsurface (USACE, 2009).

For this numerical model study, non-aqueous, aqueous, and sorbed solute phases were
considered. Contaminant vapour phase and CH₄ gas (due to methanogenesis) generation and
transport were not accounted for. The temperature range of 10 to 40°C is lower than the co-
boiling points for TCE-water (Martin and Kueper, 2011) and cDCE-water (Davis, 2007). It is
recognized that the incorporation of CH₄ gas production would contribute to further k reduction
within the porous media domain (Yang and McCarty, 2002). The representation of k reduction in
this work is therefore only partial since the actual flow bypassing and pore clogging would be
more significant if CH₄ gas generation was considered.

4.3.2 Numerical Simulations

In total, 8 numerical simulations were performed: 4 lactate-amended EISB and 4 abiotic
dissolution TCE simulations. Four temperatures were studied in this work: 10, 20, 30, and 40°C.
In all of the EISB simulations, lactate was injected as pulses (1 day/week) for a period of 2.5
years. Past this point, supply of the substrate (source of electron donor H₂) to the microbial communities was terminated. All of the simulations were run for a virtual time period of 50 years. Table 4.1 outlines the schedule of each EISB simulation conducted:

Table 4.1: Schedule of EISB treatment simulations.

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Simulation No.</th>
<th>Temperature (°C)</th>
<th>Lactate Injection Concentration (mg/L)</th>
<th>Pulse Injection Duration (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCE</td>
<td>1</td>
<td>10</td>
<td>39130</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

West (2009) utilized a safety factor of 5 for calculating the required lactate pulse concentrations for the virtual TCE contaminant source zones. The premise of this decision was to account for the uncertainties associated with EISB (Yang and McCarty, 2002) as well as subsurface heterogeneity. For this work, even though solubility will change with temperature, consistent lactate pulse concentrations were used for comparative purposes. For the TCE EISB simulations conducted in this study (and the respective temperature-dependent solubility values used), the safety factor varied from 3.5 – 4.

4.3.3 Temperature-Dependent Properties

DNAPL3D-RX parameters for each simulation were adjusted for temperature. Higher temperatures provide greater kinetic energy, which reduces the strength of intermolecular forces within fluids. The density and viscosity of fluids tend to decrease at higher temperatures as
intermolecular bond structure decreases (Petrucci et al., 2007). From 10°C to 40°C, the viscosity of PCE was found to decrease by approximately 16%; within this same temperature range, PCE density was reduced by about 1.7% (Sleep and Ma, 1997). The density and viscosity of TCE also decreases at higher temperatures, the latter property having greater temperature sensitivity (NOAA, 1999). In order to comparatively evaluate the transient mass removal in each simulation, TCE density was assumed to be constant over the range of temperatures used in this work (temperature had a negligible effect on density compared to viscosity). For each TCE simulation, the initial DNAPL mass within the model domain was the same.

The interfacial tension that exists between TCE and water was assumed to remain constant throughout each simulation. Studies by Imhoff et al. (1997) and Sleep and Ma (1997) found that temperature did not have a significant effect on PCE interfacial tension. Dissolution will be enhanced at higher temperatures as the aqueous solubility ($C_s$) of TCE generally increases. Increases in $C_s$ will increase the concentration gradient between non-aqueous and aqueous phases. Past laboratory studies have characterized the $C_s$ of TCE at higher temperatures (Imhoff et al., 1997; Heron et al., 1998b; Knauss et al., 2000; Chen et al., 2012), as shown in Figure 4.3. Most of these studies have found an apparent solubility minimum for TCE within sub-boiling temperature ranges (within 20 to 35°C). Past this minimum solubility point, greater temperatures increase the $C_s$ of TCE. Knauss et al. (2000) recorded higher solubility values than the other referenced studies likely due to the experimental technique used (pressurized gold bag reactors). For this work, the Knauss et al. (2000) solubility correlation for TCE was preferred over other literature correlations since it showed greater variability in $C_s$ with temperature.
Temperature will affect the degree of sorption of the contaminant to soil grains; many studies quantify sorption by measuring organic carbon partitioning ($K_{oc}$) and/or distribution ($K_d = K_{oc}f_{oc}$) coefficients. Assuming that $f_{oc}$ does not vary significantly with temperature (minimal organic carbon release due to higher temperatures; Friis et al., 2005), changes in $K_d$ are directly related to $K_{oc}$. Heron et al. (1998a) found that the $K_d$ of TCE decreased by approximately 15% for temperatures between 23 and 99°C. Sleep and McClure (2001) observed that the $K_{oc}$ of PCE decreased by approximately 40% over temperatures ranging from 22 to 92°C, for a porous medium with a $f_{oc}$ of 0.0045. $K_{oc}$ of TCE was adjusted for temperature by utilizing the similar trend observed in the study by Heron et al. (1998a). cDCE sorption was assumed to remain constant throughout all of the heated EISB simulations. Gerstl (1990) correlated $K_{oc}$ to aqueous solubility.

Figure 4.3: TCE aqueous solubility versus temperature. Data points represent laboratory measured solubilities.
solubility after examining sorption data from over 400 different compounds, including non-aromatic, halogenated hydrocarbons. The solubility of cDCE did not vary significantly within the temperature range of 8 to 75°C (Chen et al., 2012); for this work, it was assumed that $K_{oc(cDCE)}$ did not vary significantly for the temperature range of 10 to 40°C. Table 4.2 displays the temperature-adjusted general parameters utilized in this numerical model study:

Table 4.2: General simulation parameters.

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>10</td>
</tr>
<tr>
<td>Parameter</td>
<td>SI Units</td>
</tr>
<tr>
<td>$\rho_{w}^{(1)}$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{nw}^{(2)}$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\mu_{w}^{(1)}$</td>
<td>Pa•s</td>
</tr>
<tr>
<td>$\mu_{nw}^{(3)}$</td>
<td>Pa•s</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Pa$^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Pa$^{-1}$</td>
</tr>
<tr>
<td>$K_{oc(TCE)}^{(4)}$</td>
<td>mL/g</td>
</tr>
<tr>
<td>$d_{50}$</td>
<td>m</td>
</tr>
<tr>
<td>$\theta$</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha_{x}$</td>
<td>m</td>
</tr>
<tr>
<td>$\alpha_{x} : \alpha_{y}$</td>
<td>m</td>
</tr>
<tr>
<td>$\alpha_{x} : \alpha_{z}$</td>
<td>m</td>
</tr>
<tr>
<td>$\tau$</td>
<td>-</td>
</tr>
<tr>
<td>$K_{oc(cDCE)}^{(5)}$</td>
<td>mL/g</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>$C_s^{(6)}$</td>
<td>mg/L</td>
</tr>
<tr>
<td>$C_{inj}^{lactate , (7)}$</td>
<td>mg/L</td>
</tr>
<tr>
<td>$D_{TCE/PCE}^{o , (8)}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{cDCE}^{o , (8)}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{lactate}^{o , (9)}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$D_{H_2}^{o , (10)}$</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$\nabla H^{(7)}$</td>
<td>-</td>
</tr>
<tr>
<td>$X$ (longitudinal)</td>
<td>m</td>
</tr>
<tr>
<td>$Y$ (vertical)</td>
<td>m</td>
</tr>
<tr>
<td>$Z$ (width)</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta y$</td>
<td>m</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>m</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>-</td>
</tr>
</tbody>
</table>

(4) Value for 20°C from Pankow and Cherry (1996). Values were scaled for temperature by utilizing the experimental trend observed by Heron et al. (1998a). (5) Organic-carbon partitioning coefficients for cDCE from Pankow and Cherry (1996). The value of this coefficient was assumed to be constant for each temperature scenario. (6) Knauss et al. (2000). (7) West (2009).
4.3.4 Temperature Considerations for EISB Microbial Reactions

All of the Monod kinetic parameters utilized by DNAPL3D-RX were adjusted for the temperatures of 10, 20, 30, and 40°C. A catalogue of Monod kinetic parameters (data sets) was compiled from scientific literature, from both experimental and numerical model studies (see Appendix A). Non-linear trends were visually fit to these data sets in order to estimate the effects of temperature on EISB treatment (see Appendix D). The non-linear data fits provide a hypothesized interpretation of biological activity to account for changes in temperature.

The microbial activity of each species (dechlorinating, fermenting, and methanogenic) will be sensitive to temperature. Numerous studies have looked at temperature effects on the microbial treatment of TCE/PCE. Incomplete RD of TCE/PCE has been observed within varying temperature ranges for PER-K23 (Holliger et al., 1993), D. multivorans (Neumann et al., 1994), and PCE1 (Gerritse et al., 1996) cultures. Temperature studies conducted on the activity of Dhc spp.-containing mixed consortia (Aulenta et al., 2006; Friis et al., 2007; Heimann et al., 2007, Fletcher et al., 2011a) also present evidence that dechlorinators are most likely mesophilic microorganisms. The maximum dechlorination and/or least chlorinated daughter by-product (which occurs at the optimum temperature) was achieved in these aforementioned studies within the temperature range of 20 to 35°C, which is representative of mesophilic activity (Vaccari et al., 2006). At temperatures below/higher than the optimum temperature, the rate and extent (dechlorination end by-product) of dechlorination decreased.
Elevated temperatures will also impact the additional biological processes associated with EISB. Substrate-fermenting and methanogenic microbial activity will be strongly influenced by temperature. Heimann et al. (2007) observed that lactate fermentation occurred more rapidly at higher temperatures from 4 to 30°C; however, fermentation did not proceed at temperatures greater than 40°C. Fletcher et al. (2011b) found that thermal treatment increased methanogenesis in bioaugmented microcosms. At temperatures greater than 35°C, RD of TCE/PCE was inhibited and methanogenesis was the dominating biological activity. This study suggested that during cooling of a thermal treated site, methanogenic activity could dominate since the growth rate of methanogens is generally greater than that of dechlorinators.

**4.3.4.1 EISB Modeling Assumptions**

It was assumed that all of the microbial species modeled in this work were mesophilic. The three microbial species modeled in this work were dechlorinators (conversion of TCE to cDCE), lactate-fermenters, and methanogens (biocompetitor for H₂). The optimum temperature of mesophiles is commonly located within the temperature range of 20 to 35°C (Vaccari et al., 2006); for this work, the optimum temperature was specified at 30°C. The growth rate (utilization rate), activity, and substrate affinity were assumed to be greatest for each species at 30°C. The temperature-adjusted Monod kinetic parameters (from the non-linear graphical fits shown in Appendix D) utilized in this numerical model study was organized in Table 4.3:
Table 4.3: TCE EISB specific input parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Temperature (°C)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{TCE}^{(1)}$</td>
<td>M</td>
<td>1.7E-05</td>
<td>7.1E-06</td>
<td>1.1E-06</td>
<td>2.1E-05</td>
</tr>
<tr>
<td>$q_{TCE}^{MAX(2)}$</td>
<td>mol / mg VSS s</td>
<td>8.5E-11</td>
<td>3.4E-10</td>
<td>5.2E-10</td>
<td>6.3E-11</td>
</tr>
<tr>
<td>$q_{lactate}^{MAX(1)}$</td>
<td>mol / mg VSS s</td>
<td>2.06E-10</td>
<td>6.95E-10</td>
<td>1.58E-09</td>
<td>3.48E-10</td>
</tr>
<tr>
<td>$q_{meth}^{MAX(1)}$</td>
<td>mol / mg VSS s</td>
<td>3.74E-10</td>
<td>2.60E-09</td>
<td>4.34E-09</td>
<td>6.13E-10</td>
</tr>
<tr>
<td>$\lambda_{biomass}^{(1)}$</td>
<td>s$^{-1}$</td>
<td>2.89E-07</td>
<td>5.79E-07</td>
<td>1.16E-06</td>
<td>2.31E-06</td>
</tr>
<tr>
<td>$C_{toxicity}^{(3)}$</td>
<td>mg/L</td>
<td>530</td>
<td>530</td>
<td>530</td>
<td>530</td>
</tr>
<tr>
<td>$Y_{MAX}^{(4)}$</td>
<td>mg/L</td>
<td>20000</td>
<td>20000</td>
<td>20000</td>
<td>20000</td>
</tr>
<tr>
<td>$X_{ferm}^{o(4)}$</td>
<td>mg/L</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$X_{CE}^{o(4)}$</td>
<td>mg/L</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>$X_{meth}^{o(4)}$</td>
<td>mg/L</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$H^{*^{(4)}}$</td>
<td>nM</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$Y_{TCE}^{(5)}$</td>
<td>mg cell / mol substrate</td>
<td>4.1E+03</td>
<td>4.1E+03</td>
<td>4.1E+03</td>
<td>4.1E+03</td>
</tr>
<tr>
<td>$Y_{lactate}^{(5)}$</td>
<td>mg cell / mol substrate</td>
<td>3.5E+03</td>
<td>3.5E+03</td>
<td>3.5E+03</td>
<td>3.5E+03</td>
</tr>
<tr>
<td>$Y_{meth}^{(5)}$</td>
<td>mg cell / mol substrate</td>
<td>8.8E+02</td>
<td>8.8E+02</td>
<td>8.8E+02</td>
<td>8.8E+02</td>
</tr>
<tr>
<td>$F_{TCE}^{(6)}$</td>
<td>mol H$_2$ / mol substrate</td>
<td>1.22</td>
<td>1.22</td>
<td>1.22</td>
<td>1.22</td>
</tr>
<tr>
<td>$F_{lactate}^{(6)}$</td>
<td>mol H$_2$ / mol substrate</td>
<td>1.90</td>
<td>1.90</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td>$F_{meth}^{(6)}$</td>
<td>mol H$_2$ / mol substrate</td>
<td>4.08</td>
<td>4.08</td>
<td>4.08</td>
<td>4.08</td>
</tr>
<tr>
<td>$K_{H^2}^{(1)}$</td>
<td>M</td>
<td>3.9E-08</td>
<td>1.4E-08</td>
<td>6.5E-09</td>
<td>4.9E-08</td>
</tr>
<tr>
<td>$K_{lactate}^{(1)}$</td>
<td>M</td>
<td>8.6E-05</td>
<td>3.2E-05</td>
<td>9.9E-06</td>
<td>1.4E-04</td>
</tr>
<tr>
<td>$K_{meth}^{(1)}$</td>
<td>M</td>
<td>6.8E-06</td>
<td>5.6E-06</td>
<td>5.5E-06</td>
<td>9.1E-06</td>
</tr>
</tbody>
</table>

(1) Graphically fitted/determined from literature data. (2) Graphically fitted/determined from literature data. Reduced by an order of magnitude as per the assumptions stated by Christ and Abriola (2007). (3) Inhibitory TCE concentrations to RD used in this work were similar to the

Monod half-saturation coefficients ($K_a$) were adjusted for temperature by fitting a mesophilic-type trend. $K_a$ is inversely related to the substrate affinity for the enzyme (Rittmann and McCarty, 2001); for this work, the minimum $K_a$ (maximum substrate affinity) for all microbial species was assumed to occur at 30°C, increasing at temperatures lower/higher than this optimum temperature (Reay et al., 1999). Similar to other bioremediation modeling studies (Fennell and Gossett, 1998; Yu and Semprini, 2004; Christ and Abriola, 2007), a single decay rate coefficient ($\lambda_{\text{biomass}}$) was specified for all biomass populations. It was assumed that $\lambda_{\text{biomass}}$ continually increased with temperature, which corresponded with the increase in reaction rates (Banik et al., 1998; Vaccari et al., 2006). Even though maximum utilization rates ($q_{\text{MAX}}$, $M_{\text{AX}}$) were reduced for all species in the 40°C EISB case, the greatest biomass decay was modeled in this case to account for the denaturation of proteins due to the stresses applied by this higher temperature (Vaccari et al., 2006).

Dechlorinator maximum utilization rate ($q_{\text{TCE}}^{\text{MAX}}$) values determined from literature studies varied with temperature and microbial species type. For this work, reported utilization rates for both TCE and PCE were utilized for the non-linear temperature-fitting trend for $q_{\text{TCE}}^{\text{MAX}}$; the parameter value range for both compounds were similar (Clapp et al., 2004). In some studies, dechlorinator growth rate (instead of utilization rate) and biomass yields ($Y_n$) were measured. Depending on the
units of these reported parameters, conversion factors were applied to convert these values to utilization rates. The following assumptions were applied in this work when parameter conversion was required: 1) Volatile suspended solids (VSS) was 50% protein (Yang and McCarty, 2000), 2) 0.5 g protein was equivalent to 1 g cell (Duhamel et al., 2004). In addition, for Dhc-containing consortia, a conversion factor of 4.2 x 10^{-15} g cells/gene copy was assumed. This value was characteristic of Dhc strains 195 and BAV1, which were found to be better represented as a disk shape rather than spherical (Duhamel et al., 2004).

Christ and Abriola (2007) reduced PCE utilization rates by an order of magnitude to account for the following EISB effects: back partitioning of dechlorination daughter products, reduced $k$ due to CH$_4$ production and the assumption of a uniform biomass distribution within the domain. The fitted $q_{TCE}^{MAX}$ non-linear trend for this work (Figure D.1) was reduced by an order of magnitude in accordance with the study by Christ and Abriola (2007). $Y_n$ for all three microbial species were assumed to remain relatively constant over the mesophilic temperature range modeled in this study. The dependence of $Y_n$ on temperature is not well established (Vaccari et al., 2006); the biomass yield of a specific microbial group may increase/decrease with elevated temperature. For this work, mean $Y_n$ values were calculated from literature data.

**4.3.5 Metrics of Evaluation**

Each model simulation was evaluated for DNAPL mass removal ($M_{DNAPL}$) \{M$^1$\} and boundary mass flux ($M_{f}$) \{M$^1$L$^{-2}$T$^{-1}$\} reduction (see Equation 4-7). DNAPL mass removal rate \{M$^1$T$^{-1}$\} was
calculated for each simulation using a central finite difference approximation for the first order derivative, for a selected time step (Δt) of 0.25 years (for graphical clarity):

\[ M_f^n = \sum_{i=1}^{N} C_i^n q_i \]  \hspace{1cm} (4-7)

\[ \frac{\partial M_{\text{DNAPL}}(t)}{\partial t} = \frac{M_{\text{DNAPL}}(t + \Delta t) - M_{\text{DNAPL}}(t - \Delta t)}{2 \Delta t} \]  \hspace{1cm} (4-8)

where \( i \) represents individual boundary nodes, \( n \) represents the mobile aqueous species of interest, \( q \) is the nodal wetting phase Darcy flux \( \{L^1T^{-1}\} \), \( C \) is the nodal concentration \( \{M^1L^{-3}\} \), and \( t \) is time \( \{T^1\} \).

DNAPL mass was defined with regards to the non-aqueous phase and does not include aqueous or sorbed solute phases. Enhancement factors were also calculated at certain points of time in order to compare the performance of heated EISB and heated abiotic dissolution in terms of DNAPL mass removal (\( E_m \)) and boundary mass flux (\( E_f \)) reduction (West, 2009):

\[ E_m = \frac{M_{\text{DNAPL}}^0 - M_{\text{DNAPL}}^{\text{EISB}}(t)}{M_{\text{DNAPL}}^0 - M_{\text{DNAPL}}^{\text{DISS}}(t)} \]  \hspace{1cm} (4-9)

\[ E_f = \frac{M_f^{\text{DISS}}(t)}{M_f^{\text{EISB}}(t)} \]  \hspace{1cm} (4-10)
where $M_{DNAPL}^0$ is the initial DNAPL mass in the domain ($t = 0$), $M_{DNAPL}^{EISB} / M_{DNAPL}^{Diss}$ is the DNAPL mass remaining in the EISB/dissolution model domain at a specific time $t$, $M_f^{EISB} / M_f^{Diss}$ is the boundary mass flux for the EISB/dissolution simulation at a specific time $t$.

$E_m$ and $E_f$ values greater than 1 indicate remedial enhancement due to EISB operation. A mathematical approach by Falta et al. (2005) was utilized to compare DNAPL mass removal to boundary mass flux reduction and mean concentration. This metric was used to elucidate the influence of subsurface heterogeneity and DNAPL source zone architecture on both heated EISB and heated dissolution treatment efficacy:

\[
\frac{C(t)}{C(t_0)} = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right)^\Gamma \quad \text{or} \quad C_n = (M_n)^\Gamma
\]

\[
\frac{M_f(t)}{M_f(t_0)} = \left( \frac{M_{DNAPL}(t)}{M_{DNAPL}(t_0)} \right)^\Gamma \quad \text{or} \quad F_n = (M_n)^\Gamma
\]

where $t_0$ is the time of reference \{T\}, $t$ is a time point past $t_0$ (i.e. $t \geq t_0$) \{T\}, $\Gamma$ is an empirical fitting parameter and graphical boundary which is dependent on domain characteristics such as subsurface heterogeneity and local-scale DNAPL distribution, $C$ is the aqueous phase solute concentration in the bulk solution \{M^{1}L^{-3}\} at times $t$ and $t_0$, $C_n$ is the normalized mean concentration \{\cdot\}, $F_n$ is the normalized downgradient boundary mass flux \{\cdot\}, $M_{DNAPL}$ is the DNAPL mass within the model domain \{M\}, $M_n$ is the normalized DNAPL mass remaining \{\cdot\}.  

147
4.4 Results & Discussion

All of the heated EISB and abiotic dissolution simulations were evaluated using the metrics described in section 4.3.5. The abiotic dissolution (‘dissolution only”) simulations were representative of scenarios in which the target treatment zone was only heated (no EISB treatment). Enhancement factors achieved through the implementation of EISB were determined by comparing these simulations to their temperature-corresponding abiotic dissolution scenarios.

4.4.1 DNAPL Source Zone Mass Removal

The DNAPL mass removal versus time plot for the heated TCE EISB and abiotic dissolution simulations is shown in Figure 4.4. Enhancement factors for mass removal ($E_m$) were calculated using Equation 4-9, and displayed in Table 4.4. The EISB simulations for the temperature range of 10 to 30°C resulted in greater mass removal compared to their temperature-corresponding abiotic dissolution scenarios during the time period of lactate pulse injection, as depicted in Figure 4.5. At 40°C, where dechlorinating activity was significantly reduced and considerably less than methanogenic activity (which was also reduced), EISB treatment was non-beneficial ($E_m \leq 1$). Methanogenic growth dominated in this temperature scenario, which contributed to the majority of the bioclogging observed in this domain. The $k$ reduction caused by the methanogenic biomass growth resulted in flow bypassing within regions of the subsurface domain and proved to be a slight inhibitor of DNAPL dissolution.
Figure 4.4: DNAPL source zone mass removal versus time for TCE EISB and TCE abiotic dissolution simulations after 50 years. Inflection points represent the termination of substrate injection.
Figure 4.5: Total DNAPL mass removed at the end of the 2.5 year pulse lactate injection period for the TCE EISB scenarios. The DNAPL mass removed at this same timepoint was also plotted for the temperature-corresponding heated TCE abiotic dissolution simulations.

Table 4.4: Mass removal enhancement factors for the TCE EISB simulations.

<table>
<thead>
<tr>
<th>Temperature Scenario (°C)</th>
<th>$E_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>End of treatment</td>
</tr>
<tr>
<td>10</td>
<td>1.34</td>
</tr>
<tr>
<td>20</td>
<td>1.49</td>
</tr>
<tr>
<td>30</td>
<td>1.34</td>
</tr>
<tr>
<td>40</td>
<td>0.98</td>
</tr>
</tbody>
</table>

*At 50 years, all of the DNAPL mass within the 40°C abiotic dissolution domain was completely removed.
From Figure 4.5, the greatest TCE mass removal at the 2.5 year point was achieved in the 20°C EISB case. Even though the highest dechlorination rate \( q_{TCE}^{\text{MAX}} \) was modeled for 30°C EISB, the greatest biocompetitive rate \( q_{\text{meth}}^{\text{MAX}} \) was also used in this domain. At the end of the 2.5 year injection period (active treatment), the ratio of methanogenic to dechlorinating biomass \( R_{\text{biomass}} \) for 20°C and 30°C was 4.37 and 11.8, respectively. The competition for the H\(_2\) electron donor between methanogens and dechlorinators was the main factor in comparing these two EISB temperature scenarios. Even though \( q_{\text{meth}}^{\text{MAX}} \) and \( q_{TCE}^{\text{MAX}} \) were greatest at 30°C, the 20°C case showed that dechlorinators exhibited better relative growth when the biocompetitive rate was lower. 20°C conditions were preferred over 10°C even though the \( R_{\text{biomass}} \) for 10°C at the termination of injection was 2.19. The difference between these two ratios was not as considerable compared to the 20°C and 30°C \( R_{\text{biomass}} \) difference. The least TCE mass removed at the end of active treatment was observed in the 40°C EISB case, which represented conditions where dechlorinating activity was greatly inhibited due to temperatures greater than the optimum. Biomass growth within this domain was mostly comprised of methanogens and minimal to non-existent dechlorinator populations.

Even though enhanced DNAPL mass removal was achieved for the 10°C to 30°C EISB scenarios at the 2.5 year point, once active treatment was terminated, the \( E_m \)'s steadily declined over the 50 year timeframe. At 50 years, the EISB and natural abiotic dissolution scenarios achieved similar results \( E_m \approx 1 \). Electron donor availability and bioclogging were the main factors in the reduction of \( E_m \) at later times. The termination of lactate injection had a profound effect on bacterial growth; the H\(_2\) electron donor was only produced via lactate fermentation. As a result, dechlorinating biomass populations drastically decreased at early times following the end of
active treatment for all of the EISB cases. The degree of bioclogging was different for each EISB case, which was based on biomass growth. Biomass growth was most pronounced in the 10 to 30°C EISB scenarios and less prominent in the 40°C case. \( k \) reduction due to bioclogging was significant for the 10 to 30°C EISB simulations, which caused considerable dissolution tailing effects at later times following the termination of lactate injection. Bioclogging was also observed in the 40°C EISB case (mostly methanogenic biomass growth) but not to the same extent as the other bioremediation cases. Flow bypassing occurred within each EISB domain, which resulted in groundwater flow around these biologically-created lower \( k \) zones and reduced flow contact with the remaining DNAPL mass. The combination of substrate (electron donor) starvation and bioclogging ultimately negated the mass removal benefits achieved during the active treatment period for the EISB simulations. Termination of the lactate injection stunted dechlorinator growth and bioclogging acted as a barrier to DNAPL dissolution. The 40°C EISB case was the exception as no enhancement was achieved during the 50 year period.

As calculated using Equation 4-8 and presented in Figure 4.6, the rate of mass removal declines for both heated EISB and abiotic dissolution simulations. Over time, as DNAPL dissolution proceeds (both enhanced by EISB and abiotically), the removal rate decreases significantly as the available DNAPL for mass transfer becomes depleted. This observation coincides with the decrease in downgradient concentrations, as later shown in Figures 4.8 and 4.9. For the 10 to 30°C EISB cases (enhanced mass removal), the rate of mass removal drastically dropped during the lactate injection period (accelerated mass removal and dissolution). Once active treatment was terminated, mass removal rates steadily declined as a result of \( \text{H}_2 \) starvation and the bioclogging that occurred during active treatment (inhibited DNAPL dissolution). The mass removal rate for
the heated abiotic dissolution scenarios decreased more considerably at early times (greater mass removal) and more moderately at later times due to the less available DNAPL for mass transfer within these domains. These simulations were not hindered by bioclogging and subsequent $k$ reduction; the timeframes required for DNAPL mass removal in the “dissolution only” cases were strongly governed by the dissolution occurring within natural low $k$ geological regions.

![Figure 4.6: DNAPL mass removal rate versus time for TCE EISB and TCE abiotic dissolution simulations after 50 years.](image)

4.4.2 Boundary Mass Flux

The mass flux at the down-gradient boundary for all of the heated EISB and abiotic dissolution simulations was calculated using Equation 4-7 over the 50 year time period and is shown in
Figure 4.7. Enhancement factors for mass flux reduction ($E_f$) were calculated using Equation 4-10 and were tabulated in Table 4.5. The enhancement in mass flux reduction was greater in comparison to the mass removal enhancement due to the preferential migration of lactate within higher $k$ zones of the porous media domain (Borden et al., 2012).

Figure 4.7: Downgradient boundary mass flux versus time for TCE EISB and TCE abiotic dissolution simulations after 50 years.
Table 4.5: Mass flux reduction enhancement factors for TCE EISB simulations

<table>
<thead>
<tr>
<th>Temperature Scenario (°C)</th>
<th>End of treatment</th>
<th>5 years</th>
<th>10 years</th>
<th>25 years</th>
<th>50 years</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>5.73</td>
<td>1.97</td>
<td>1.22</td>
<td>1.07</td>
<td>1.34</td>
</tr>
<tr>
<td>20</td>
<td>17.79</td>
<td>2.82</td>
<td>1.40</td>
<td>1.65</td>
<td>1.00</td>
</tr>
<tr>
<td>30</td>
<td>11.92</td>
<td>2.09</td>
<td>1.34</td>
<td>1.62</td>
<td>0.81</td>
</tr>
<tr>
<td>40</td>
<td>0.97</td>
<td>0.91</td>
<td>0.95</td>
<td>1.07</td>
<td>-*</td>
</tr>
</tbody>
</table>

*At 50 years, all of the DNAPL mass within the 40°C abiotic dissolution domain was completely removed.

At the end of the lactate injection period, mass flux rebound was observed in the 10 to 30°C EISB cases. There was minimal rebound observed for 40°C EISB; no enhancement in mass removal and mass flux reduction was achieved in this scenario. Bioclogging due to methanogenic biomass growth during the 40°C EISB injection period inhibited DNAPL dissolution; abiotic dissolution was more effective at this temperature. Rebound in the mass flux/concentration is related to slow contaminant dissolution caused by factors such as slow desorption, slow advective transport, as well as dissolution through and back-diffusion from low $k$ materials (Huling and Pivetz, 2006). For the temperature range of 10 to 30°C, mass flux reduction in the abiotic dissolution cases was not as rapid compared to EISB during the substrate injection period. Over the 50 year timeframe, the enhancements achieved from 10 to 30°C EISB were reduced due to the inhibition of DNAPL dissolution from bioclogging.
From Table 4.5, it was observed in each EISB case that $E_f$ declines after active treatment but then recovers at later times within the 50 year period. Even though lactate was not injected at times past the 2.5 year point, biomass populations still existed within the porous media domain. Fluctuations in the flux at the downgradient boundary were influenced by the degree of biomass decay and subsequent recovery in $k$ (Kim and Fogler, 2000; Brovelli et al., 2009) over the long term. In this study, biomass decay was assumed to increase with temperature, which corresponded with the increase in reaction rates (Banik et al., 1998; Vaccari et al., 2006). At lower temperatures (10°C EISB), these flux fluctuations occurred later compared to at higher temperatures (40°C EISB). Greater biomass decay was modeled at higher temperatures, which contributed to earlier $k$ recovery in these cases (reduced bioclogging) and an earlier fluctuating increase in $E_f$. Based on the initial modeling assumptions, however, only 80% of the total biomass was naturally degradable. When this point was reached for each simulation, 20% of the biomass contributed to permanent $k$ reduction within the domain. It was observed in all of the EISB cases that the $E_f$ steadily declined (after the fluctual increase) once all of degradable biomass had decayed and the permanent reduction in $k$ was established. For the 10°C EISB scenario (lowest biomass decay), $E_f$ after active treatment reached a maximum (1.67) at about 45 years and steadily declined afterwards. The decay rate was slowest in this domain and required a greater time for the partial recovery of the $k$ field (only 80%).

4.4.3 Mass Flux vs Mass Removal

The data results from sections 4.4.1 and 4.4.2 and Equations 4-11 and 4-12 were applied to produce the normalized mass ($M_n$) versus normalized mass flux ($F_n$) and normalized
concentration ($C_n$) plots for both heated EISB and abiotic dissolution scenarios (Figures 4.8 and 4.9). No prior dissolution occurred within each simulation domain before the initialization of the model runs; peaks in the mass flux and concentration, and the reference time point ($t_0$) for each were adjusted accordingly.

Figure 4.8: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the abiotic dissolution simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.
Figure 4.9: Normalized TCE mass flux ($F_n$) and TCE solute concentration ($C_n$) versus normalized DNAPL source zone mass ($M_n$) for the EISB treatment simulations. Since there is no prior dissolution before the model was initiated, the flux and concentration results were adjusted accordingly.

For abiotic dissolution (Figure 4.8), the $C_n$ and $F_n$ curves showed similar non-linear trends at all four temperatures. Temperature had a minimal effect on the mass removal versus mass flux (concentration) behaviour for abiotic dissolution. Each model domain had the same initial $S_{NW}$ and $k$ fields, which had the greatest influence on this source zone metric. For abiotic dissolution, $C_n$ was located between $0.5 \leq \Gamma \leq 1.25$ and $F_n$ lied between $0.75 \leq \Gamma \leq 2$. $\Gamma > 1$ is representative of remedial scenarios in which there is significant reduction in source strength in the short term, which contributes to a greater decrease in concentration compared to contaminant mass removal. In the long term for $\Gamma > 1$, as DNAPL source zone mass continues to persist (contaminant mass
still remaining within the domain), significant dissolution (concentration) tailing effects can ultimately reduce the treatment benefits achieved in the short term.

$C_n$ and $F_n$ for the EISB simulations (Figure 4.9) showed greater divergence from $\Gamma = 1$ towards $\Gamma > 1$, in comparison to the abiotic dissolution scenarios. EISB had a greater influence on the mass flux reduction enhancement, in comparison to the mass removal enhancement due to the preferential migration of lactate within higher $k$ zones. $C_n$ and $F_n$ were located within the ranges of $0.25 \leq \Gamma \leq 2$ and $0.5 \leq \Gamma \leq 4$, respectively for the EISB treatment scenarios. During the lactate injection period for the 10 to 30°C EISB simulations, there was a significant reduction in mass flux and concentration. After the injection period was terminated, concentration and mass flux rebound was observed in every EISB scenario, which had a detrimental impact on the reduction of concentrations and downgradient mass fluxes at later times.

$\Gamma$ values for EISB (10 to 30°C) were generally greater than for abiotic dissolution during the short term indicating that EISB provided enhancement in mass flux (concentration) reduction and contaminant mass removal during the lactate injection. In the long term, the heated EISB scenarios experienced greater dissolution tailing effects due to bioclogging and the subsequent reduction in $k$. Concentration tailing effects in the EISB simulations were slightly reduced over time due to biomass decay and the partial recovery of $k$ within the porous media domain. For the heated abiotic dissolution scenarios, natural low $k$ zones governed the treatment times required for DNAPL dissolution. DNAPL located within these low $k$ geologic zones contributed to the tailing effects within the abiotic dissolution cases.
4.5 Conclusions

Temperature enhancement of TCE EISB (in comparison to abiotic dissolution) was observed in this work during the period of active treatment (lactate injection) for 10 to 30°C. The optimum temperature of 30°C specified in this study did not provide the greatest benefit during EISB treatment. 20°C was preferred over 30°C for EISB due to the reduced relative presence ($R_{biomass}$) of the H$_2$-competing methanogens within the domain. Even though increased temperatures had a positive effect on “dissolution only” simulations (10 to 40°C), EISB enhancement was still governed by the impact of biocompetition. Minimizing biocompetition is still the key factor in improving the efficacy of EISB treatment. Heating past the optimum temperature during active treatment resulted in minimal dechlorinating activity and ultimately inhibited DNAPL dissolution in comparison to 40°C abiotic dissolution. Mass removal ($E_m$) and mass flux reduction ($E_f$) enhancement was achieved during substrate injection for 10 to 30°C TCE EISB. $E_f$ was greater than $E_m$ due to the preferential migration of lactate within higher $k$ zones within these porous media domains.

The enhancements achieved in DNAPL mass removal and mass flux reduction during lactate injection for the 10 to 30°C EISB cases declined over the long term. Bioclogging and substrate starvation were the main factors behind the decrease in enhancement over time. H$_2$ electron donor was generated only by the fermentation of lactate within the EISB domains, resulting in a sharp decrease in dechlorinating activity. Subsurface clogging due to biomass growth led to a reduction in $k$ within the EISB domains, contributing to flow bypassing around the remaining zones containing DNAPL. DNAPL dissolution after active treatment in the EISB domains was
significantly inhibited by $k$ reduction. Over the timeframe of 50 years, a recovery in the $E_f$ was observed in each EISB domain due to the transient change in the bioclogged zones. Biomass decay aided in the partial recovery of $k$ (to a maximum of 80%) resulting in a slight decrease in the mass flux reduction at later times. However, once partial recovery of $k$ was achieved, $E_f$ steadily decreased; the overall $k$ within the EISB domains after partial recovery was still less than for their temperature-corresponding abiotic dissolution scenarios.

Mass flux (concentration rebound) was observed in every heated EISB simulation at the end of the lactate injection period. An analysis of the downgradient boundary mass flux ($F_n$) and mean concentration ($C_n$) reduction versus mass removal ($M_n$) was conducted for both heated EISB and abiotic dissolution scenarios. All of the heated abiotic dissolution simulations exhibited similar $C_n/F_n$ versus $M_n$ profiles. The initial $k$ and $S_{NW}$ fields were the same for every simulation conducted in this study. In the case of heated abiotic dissolution, temperature had a minimal effect on this metric, and was primarily influenced by the initial geological conditions and DNAPL source zone architecture. In the heated EISB simulations, greater initial reduction in the mass flux and concentration was observed during active treatment. After lactate injection was terminated, followed by mass flux and concentration rebound, greater dissolution tailing effects were found for heated EISB compared to abiotic dissolution. Tailing effects in the “dissolution only” scenarios were governed by DNAPL dissolution that was occurring within naturally low $k$ regions of the domain. More detrimental tailing effects were observed for the EISB simulations due to bioclogging and the subsequent reduction in $k$. Over time, the tailing effects in the EISB domains were slightly reduced due to biomass decay and the partial recovery of $k$ which followed.
Methanogenic biocompetition, bioclogging, and substrate availability were the main factors which ultimately impacted EISB treatment efficacy. Temperature had a significant effect on dechlorinating as well as methanogenic activity, the latter process considerably inhibiting dechlorination at the optimum temperature of 30°C. Biomass growth reduced the permeability within the EISB domains resulting in flow bypassing around the remaining DNAPL masses. The partial recovery of $k$ over the long term within the 50 year time period had a slight effect on the mass flux. The application of EISB as a partial mass removal technology was not able to remove all of the TCE mass within 50 years at any of the four temperatures studied. Out of all the simulations performed in this study, only 40°C abiotic dissolution was capable of full DNAPL mass removal by the end of the 50 year timeframe. Lactate was injected at a pulse schedule of 1 day/week for 2.5 years but once terminated, the EISB domains experienced considerable dissolution tailing effects which lengthened the treatment time period and reduced treatment enhancement.

4.6 Acknowledgements

Funding for this work was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada through Strategic Project Grant SPG-396730-10, scholarship funding from Queen’s University, and scholarship funding from the Ontario Graduate Scholarship Program (OGS). The contributions of Golder Associates Ltd, McMillan-McGee Corp, the Ontario Ministry of the Environment, and The Johnson Company as industrial partners to the Strategic Project Grant are acknowledged. The author acknowledges the help and assistance provided by Dr.
Juliana Ramsay (Queen’s University), Dr. Brent Sleep (University of Toronto), and Dr. David Major (Geosyntec Consultants, Inc.).

### 4.7 Notation

- $a_{na}$: interfacial area between NAPL and aqueous phases $\{L^{-1}\}$
- $C$: aqueous phase solute concentration in the bulk solution $\{M^1L^{-3}\}$
- $C_A$: concentration of solute A $\{M^1L^{-3}\}$
- $C_n$: normalized mean concentration $\{-\}$
- $C_s$: thermodynamic equilibrium aqueous phase concentration (solubility) in which the non-aqueous phase is present $\{M^1L^{-3}\}$
- $C_{toxicity}$: maximum tolerable solute concentration $\{M^1L^{-3}\}$; can also be depicted as $[TCE]_{max}$
- $d_s$: mean grain size diameter $\{L^1\}$
- $D$: hydrodynamic dispersion tensor $\{L^2T^{-1}\}$
- $D^o$: free-water diffusion coefficient $\{L^2T^{-1}\}$
- $D_{AB}^o$: binary free-water molecular diffusion coefficient of solute A diffusing into solvent B in dilute solutions $\{L^2T^{-1}\}$
- $E_a$: activation energy $\{M^1L^2T^{-2}M^{-1}\}$
- $E_f$: boundary mass flux reduction enhancement factor $\{-\}$
- $E_m$: DNAPL mass removal enhancement factor $\{-\}$
- $F$: Faraday constant = 96485.3415 s$^1$A$^1$mol$^{-1}$
- $F_n$: normalized downgradient boundary mass flux $\{-\}$
- $F_{species}$: stoichiometric production/consumption coefficient $\{M^1M^{-1}\}$
- $f_{oc}$: organic carbon fraction $\{-\}$
- $g$: gravitational constant $\{L^1T^{-2}\}$
- $\nabla h$: hydraulic gradient $\{-\}$
\( I_{\text{toxic}} \) inhibition coefficient to account for solute toxicity {\( \text{\text{-}} \) \\
\( J \) solute mass flux from immiscible liquid phase to the aqueous phase \{M^1L^{-2}T^{-1}\} \\
\( J_{AB} \) diffusive flux of solute A diffusing into solvent B \{M^1L^{-2}T^{-1}\} \\
k \text{ intrinsic permeability } \{L^2\} \\
\( K_d \) sorption distribution coefficient \{M^1L^3\} \\
k_g \text{ intrinsic permeability tensor } \{L^2\} \\
k_{f} \text{ mass transfer coefficient } \{L^1T^{-1}\} \\
\( K_f \) lumped mass transfer coefficient \{T^{-1}\} \\
\( K_n \) Monod half-saturation coefficient \{M^1L^{-3}\} \\
k_o \text{ original permeability } \{L^2\} \\
\( K_{oc} \) organic carbon partitioning coefficient \{M^1L^3\} \\
k_r \text{ relative permeability } \{\text{-}\} \\
M_B \text{ molecular weight of solvent B, } \{M^1M^{-1}\} \\
M_{\text{DNAPL}} \text{ DNAPL mass within the model domain } \{M^1\} \\
M_f \text{ boundary mass flux } \{M^1L^2T^{-1}\} \\
M_n \text{ normalized DNAPL mass remaining } \{\text{-}\} \\
P \text{ pressure } \{M^1L^{-1}T^{-2}\} \\
\( P_A \) parachor of solute A \{M^{1/4}L^3T^{-1/2}M^{-1}\}; estimated using Table 11-3 of Poling et al., 2001 \\
\( P_B \) parachor of solvent B \{M^{1/4}L^3T^{-1/2}M^{-1}\}; estimated using Table 11-3 of Poling et al., 2001 \\
P_C \text{ capillary pressure } \{M^1L^{-1}T^{-2}\} \\
q \text{ volumetric (Darcy) flux } \{L^3L^{-2}T^{-1}\} \\
q_{\text{MAX}} \text{ maximum utilization rate } \{M^1M^{-1}T^{-1}\} \\
q_s \text{ source/sink term represented as a volumetric flux } \{T^{-1}\} \\
r_a \text{ radius of spherical-shape solute A } \{L^1\} \\
R_a \text{ retardation factor } \{\text{-}\}
$S$ phase saturation \{ - \}
$S_E$ effective saturation \{ - \}
$t$ time \{ T^{-1} \}
$T$ reference temperature \(^\circ\)K
$T_c$ critical temperature of the solvent \(^\circ\)K
$v$ average linear groundwater velocity \{ L^1 T^{-1} \}
$V_A$ molar volume of solute A at its normal boiling point \{ M^{-1} L^2 \}
$V_B$ molar volume of solvent B at its normal boiling point \{ M^{-1} L^2 \}
$x$ horizontal longitudinal direction
$X$ domain length along $x$ \{ L^1 \}
$X_n$ biomass concentration \{ M^1 L^{-3} \}
$X_{max}$ maximum biomass concentration \{ M^1 L^{-3} \}
$y$ vertical direction
$Y$ domain length along $y$ \{ L^1 \}
$Y_n$ biomass yield coefficient \{ M^1 M^{-1} \}
$z$ horizontal transverse direction
$Z$ domain length along $z$ \{ L^1 \}
$\Delta x$ nodal discretization along the $x$-direction \{ L^1 \}
$\Delta y$ nodal discretization along the $y$-direction \{ L^1 \}
$\Delta z$ nodal discretization along the $z$-direction \{ L^1 \}
$\alpha$ compressibility of the porous medium \{ M^{-1} L^1 T^2 \}
$\alpha_{x,y,z}$ dispersivity \{ L^1 \}
$\beta$ compressibility of the wetting fluid \{ M^{-1} L^1 T^2 \}
$\Gamma$ fitting parameter
$\lambda$ molar conductivity for common ions \{ M^{-1} T^3 A^2 M^{-1} \}
$\lambda_n$ first-order biotic decay rate coefficient \{ T^{-1} \}
$\eta$ parameter associated with the solvent; based on heat of vaporization
$\phi$ association factor of solvent B; for water $\phi = 2.6$ (Poling et al., 2001; Bird et al., 2002)
\[ \rho \quad \text{fluid density} \{ \text{M}^{1} \text{L}^{-3} \} \]
\[ \mu \quad \text{fluid dynamic viscosity} \{ \text{M}^{1} \text{L}^{-1} \text{T}^{-1} \} \]
\[ \mu_{B} \quad \text{dynamic viscosity of solvent B at reference temperature} \{ \text{M}^{1} \text{L}^{-1} \text{T}^{-1} \} \]
\[ \mu_{mk} \quad \text{mean of } \ln k \{ \ln (L^{2}) \} \]
\[ \sigma_{mk}^{2} \quad \text{variance of } \ln k \{ [\ln (L^{2})]^{2} \} \]
\[ \tau \quad \text{tortuosity} \{-\} \]
\[ \theta \quad \text{porosity} \{-\} \]
\[ \mathbb{R} \quad \text{rate of all reactions} \{ \text{M}^{1} \text{L}^{-3} \text{T}^{-1} \} \]

**Notes**

Square brackets [ ] indicate molar concentrations (M\(^{1}\)L\(^{-3}\)) of the specific compound or species.

**Common Subscripts**

- \(0\) initial condition
- \(A\) solute
- \(B\) solvent (water)
- \(i, j\) coordinate indices for \(x, y, z\)
- \(n\) species type (\textit{meth} – methanogenic, \textit{ferm/lactate} – lactate fermenting, \textit{TCE/CE} – TCE dechlorinating)
- \(NW\) non-wetting phase (DNAPL)
- \(W\) wetting phase (water)

### 4.8 References


166


Kueper, B. H., Redman, D., Starr, R. C., Reitsma, S., Mah, M. (1993). A Field Experiment to Study the Behavior of Tetrachloroethylene Below the Water Table: Spatial Distribution of


Chapter 5
Conclusions

The numerical model DNAPL3D-RX was utilized to simulate the impact of elevated temperature on the application of permanganate (MnO$_4^-$) in situ chemical oxidation (ISCO) and lactate-amended enhanced in situ bioremediation (EISB) for the subsurface remediation of trichloroethene (TCE) and tetrachloroethene (PCE). The temperature ranges of 20 to 80°C and 10 to 40°C were studied for ISCO and EISB, respectively. The physicochemical properties of the contaminant and the chemical/biological reactions associated with ISCO and EISB were adjusted for temperature. The reaction rates pertaining to MnO$_4^-$ ISCO were increased at higher temperatures in accordance with Arrhenius principles. The microbial groups associated with EISB were modeled as mesophilic species, with a hypothetical optimum growth temperature of 30°C. Both ISCO and EISB were simulated as partial mass removal treatments; active treatment (oxidant/substrate injection period) occurred over a finite timeframe. At later times following ISCO/EISB termination, only dissolution within the subsurface domain was modeled. In order to determine the benefits of higher temperatures on ISCO and EISB treatment, temperature-corresponding abiotic dissolution scenarios (“dissolution only”) were simulated.

The results of this study indicated that temperature did provide an enhancement to ISCO and EISB treatment during the short-term oxidant/substrate injection period. DNAPL mass removal and mass flux reduction were enhanced during these timeframes for 20–80°C ISCO and 10–30°C EISB. EISB treatment was found to be more effective at 20°C compared to the optimum 30°C temperature due to the reduced methanogenic activity (biocompetition). At 40°C, there was no
enhancement in EISB since dechlorinator growth was minimal and methanogenesis was the main 
$H_2$-consuming microbial process at this higher temperature. In the heated ISCO scenarios, greater 
contaminant mass removal was achieved at higher temperatures during the $\text{MnO}_4^-$ injection 
period.

After active treatment, the remedial benefits achieved from ISCO and EISB treatment were 
negated over the long term. Permeability ($k$) reduction due to rind formation from $\text{MnO}_4^-$ ISCO 
reactions and bioclogging from EISB contributed to more significant later-time dissolution tailing 
effects. Mass flux and concentration rebound was observed after oxidant/substrate injection was 
terminated. DNAPL dissolution was inhibited in both ISCO and EISB scenarios but to varying 
degrees. Rind formation contributed to a permanent $k$ reduction; $k$ reduction from bioclogging 
was partially reduced over time due to biomass decay. As a result, dissolution tailing effects were 
more severe in the ISCO cases, which significantly increased treatment times. In conclusion, even 
though elevated temperatures were beneficial to ISCO and EISB during the active treatment 
period, the overall treatment efficacy was ultimately influenced by the detrimental after-effects 
generated by the associative chemical/biological reactions.
Appendix A

Literature Review Figures
Figure A.1: Maximum utilization rate of TCE/PCE dechlorinators as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study. Diamond symbols represent bacteria cultures/consortia which contain (or possibly contain) *Dhc* spp. The diamond symbols also refer to studies which showed evidence of ETH production from the reductive dechlorination of TCE/PCE. The growth rates determined by Zhuang and Pavlostathis (1995) were converted using a constant growth yield of 3500 mg cell/mol substrate; representative of the TCE/PCE→cDCE strain *D. restrictus* (Cupples et al., 2003).

Growth rates determined by Friis et al. (2007), for the mixed KB-1™ culture, were converted by assuming a constant growth yield of 5.2 x 10^8 cells/µmol Cl⁻ (Cupples et al., 2004).
Figure A.2: Maximum utilization rate of lactate fermenters as a function of temperature (values from various literature sources).
Figure A.3: Maximum utilization rate of methanogens as a function of temperature (values from various literature sources).
Figure A.4: PCE reductive dechlorination half-saturation coefficients as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study.
Figure A.5: TCE reductive dechlorination half-saturation coefficients as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study.
Figure A.6: H₂ utilization half-saturation coefficients as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study.
Figure A.7: Lactate fermentation half-saturation coefficients as a function of temperature (values from various literature sources).

Figure A.8: Methanogenic half-saturation coefficients as a function of temperature (values from various literature sources).
Figure A.9: Biomass decay coefficients as a function of temperature (values used by various literature studies).
Figure A.10: Dechlorinator biomass yield coefficients as a function of temperature (values from various literature sources). Brackets beside references (see legend right of the plot) indicate the bacterial species utilized in the literature study.
Figure A.11: Methanogenic biomass yield coefficients as a function of temperature (values from various literature sources).

Figure A.12: Lactate-fermentative biomass yield coefficients as a function of temperature (values from various literature sources).
Appendix B

Additional Material for Chapter 3
B.1 DNAPL3D-RX Model Equations (West et al., 2008; West and Kueper, 2012)

**Multiphase Flow Equations (Kueper and Frind, 1991; Gerhard and Kueper, 2003; Grant and Gerhard, 2007):**

\[
\frac{\partial}{\partial x_i} \left[ k_{ij} \frac{\partial P_w}{\partial x_j} + \rho_w g \frac{\partial z}{\partial x_j} \right] + S_w (\alpha + \theta \beta) \frac{\partial P_w}{\partial t} = 0, \quad i,j = x,y,z \tag{B-1}
\]

\[
\frac{\partial}{\partial x_i} \left[ k_{ij} \frac{\partial (P_w + P_c)}{\partial x_j} + \rho_{NW} g \frac{\partial z}{\partial x_j} \right] + \left( 1 - S_w \right) (\alpha) \frac{\partial P_w}{\partial t} + \theta \frac{\partial S_w}{\partial t} = -J_{NW} \quad \tag{B-2}
\]

where \( P \) is pressure \( \{M^1L^{-1}T^{-2}\} \), \( P_c \) is capillary pressure \( \{M^1L^{-1}T^{-2}\} \), \( k_{ij} \) is the intrinsic permeability tensor \( \{L^2\} \), \( k_r \) is the relative permeability \( \{-\} \), \( \mu \) is dynamic viscosity \( \{M^1L^{-1}T^{-1}\} \), \( \rho \) is fluid density \( \{M^1L^{-3}\} \), \( \Theta \) is porosity \( \{-\} \), \( S \) is phase saturation \( \{-\} \), \( g \) is gravitational acceleration \( \{L^1T^{-2}\} \), \( \alpha \) is porous medium compressibility \( \{M^{-1}L^1T^2\} \), \( \beta \) is wetting phase compressibility \( \{M^1L^{-1}T^2\} \), \( t \) is time \( \{T^1\} \), \( J \) is the solute mass flux from the immiscible liquid phase to the aqueous phase \( \{M^1L^{-3}T^{-1}\} \). \( x,y,z \) represent spatial coordinates \( \{L^1\} \), and subscripts W and NW represent both wetting and non-wetting phases, respectively.

**Solute Transport Equations (Clement, 1997; Clement et al., 1998):**

\[
\frac{\partial (\Theta C_m^n)}{\partial t} = \frac{\partial}{\partial x_i} \left[ \Theta D_{ij} \frac{\partial C_m^n}{\partial x_j} \right] - \frac{\partial}{\partial x_i} \left[ \Theta v_i C_m^n \right] + q_i C_m^n + \sum \mathbb{R}_m + J \quad i,j = x,y,z \tag{B-3}
\]

\[
\frac{\partial (\Theta C_{im}^n)}{\partial t} = \sum \mathbb{R}_{im} \quad \tag{B-4}
\]
where $D_{ij}$ is the hydrodynamic dispersion tensor (L²T⁻¹), $v_i$ is the average linear groundwater velocity (L¹T⁻¹) obtained from the multiphase flow model component, $q_s$ is the source/sink term represented as a volumetric flux (T⁻¹), $R$ is the rate of all reactions (M¹L⁻³T⁻¹), $t$ is time (T¹).

Superscript $n$ represents species number, and subscripts $m$ and $im$ represent mobile and immobile species, respectively.

Reaction Equations (West et al., 2008; West and Kueper, 2012):

For the ISCO reactions in which trichloroethene (TCE) was the main contaminant (equations were adjusted for the different stoichiometry for the PCE simulations), the following reaction rate equations were used. The reactants and products of these reactions also include permanganate ($MnO_4^-$), sorbed TCE ($TCE_{sorbed}$), organic aquifer materials ($OAM$), chloride ($Cl^-$), carbon dioxide ($CO_2$), and manganese dioxide ($MnO_2(s)$).

\[
\frac{\partial [TCE]}{\partial t} = -k_{TCE} [TCE][MnO_4^-] \quad \text{(B-5)}
\]

\[
\frac{\partial [TCE_{sorbed}]}{\partial t} = -k_{TCE} [TCE_{sorbed}][MnO_4^-] \quad \text{(B-6)}
\]

\[
\frac{\partial [MnO_4^-]}{\partial t} = -2k_{TCE} ([TCE] + [TCE_{sorbed}])[MnO_4^-] - 4k_{OAM} [OAM][MnO_4^-] \quad \text{(B-7)}
\]

\[
\frac{\partial [OAM]}{\partial t} = -3k_{OAM} [OAM][MnO_4^-] \quad \text{(B-8)}
\]

\[
\frac{\partial [Cl^-]}{\partial t} = 3k_{TCE} [TCE][MnO_4^-] \quad \text{(B-9)}
\]

\[
\frac{\partial [CO_2]}{\partial t} = 2k_{TCE} [TCE][MnO_4^-] + 3k_{OAM} [OAM][MnO_4^-] \quad \text{(B-10)}
\]
\[
\frac{\partial}{\partial t} \left[ MnO_{2(s)} \right] = 2k_{TCE} [TCE][MnO_4^-] + 4k_{OAM} [OAM][MnO_4^-]
\]  

(B-11)

where square brackets [ ] represent molar concentrations, \( k_{TCE} \) is the reaction rate coefficient for the reaction between \( TCE \) and \( MnO_4^- \) \( \{M^{-1}L^{3}T^{-1}\} \), \( k_{OAM} \) is the reaction rate coefficient for the reaction between \( OAM \) and \( MnO_4^- \) \( \{M^{-1}L^{3}T^{-1}\} \), \( R_{TCE} \) is the retardation factor for \( TCE \).

B.2 Additional Chapter Figures

Figure B.1: Saturation (\( S_{SNW} \)) and TCE/MnO\(_{2(s)}\) concentration fields for 20°C TCE ISCO and abiotic dissolution at 10 years at \( z = 5\) m.
Figure B.2: Saturation ($S_{NH}$) and TCE/MnO$_2(s)$ concentration fields for 40°C TCE ISCO and abiotic dissolution at 10 years at $z = 5$m.
Figure B.3: Saturation ($S_{SW}$) and TCE/MnO$_2$(s) concentration fields for 60°C TCE ISCO and abiotic dissolution at 10 years at $z = 5$m.
Figure B.4: Saturation ($S_{NW}$) and TCE/MnO$_2$(s) concentration fields for 80°C TCE ISCO and abiotic dissolution at 5 years at $z = 5m$. 
Figure B.5: Permanganate (MnO$_4^-$) oxidant preferential migration pathways at a) 1 month, b) 1 year, and c) end of the injection period for the 40°C TCE ISCO scenario at z = 5m.
Appendix C

Additional Material for Chapter 4
C.1 DNAPL3D-RX Model Equations (West, 2009)

**Multiphase Flow Equations (Kueper and Frind, 1991; Gerhard and Kueper, 2003; Grant and Gerhard, 2007):**

\[
\frac{\partial}{\partial x_i} \left[ k_{ij} \frac{k_{nw}}{\mu_W} \left( \frac{\partial P_W}{\partial x_j} + \rho_W g g \frac{\partial z}{\partial x_j} \right) \right] + \rho_W g g \frac{\partial}{\partial t} \left( \alpha + \theta \beta \right) \frac{\partial P_W}{\partial t} = 0, \quad i,j = x,y,z \quad (C-1)
\]

\[
\frac{\partial}{\partial x_i} \left[ k_{ij} \frac{k_{nw}}{\mu_{NW}} \left( \frac{\partial (P_W + P_c)}{\partial x_j} + \rho_{NW} g g \frac{\partial z}{\partial x_j} \right) \right] + \frac{\partial}{\partial t} \left( 1 - S_w \right) \left( \alpha \right) \frac{\partial P_W}{\partial t} + \theta \frac{\partial S_W}{\partial t} = -J_{NW} \quad (C-2)
\]

where \( P \) is pressure \{M^{1}L^{-1}T^{-2}\}, \( P_c \) is capillary pressure \{M^{1}L^{-1}T^{-2}\}, \( k_{ij} \) is the intrinsic permeability tensor \{L^{2}\}, \( k \) is the relative permeability \{-\}, \( \mu \) is dynamic viscosity \{M^{1}L^{-1}T^{-1}\}, \( \rho \) is fluid density \{M^{1}L^{-3}\}, \( \theta \) is porosity \{-\}, \( S \) is phase saturation \{-\}, \( g \) is gravitational acceleration \{L^{1}T^{-2}\}, \( \alpha \) is porous medium compressibility \{M^{-1}L^{1}T^{2}\}, \( \beta \) is wetting phase compressibility \{M^{1}L^{1}T^{2}\}, \( t \) is time \{T^{1}\}, \( J \) is the solute mass flux from the immiscible liquid phase to the aqueous phase \{M^{1}L^{-3}T^{-1}\}. \( x,y,z \) represent spatial coordinates \{L^{1}\}, and subscripts W and NW represent both wetting and non-wetting phases, respectively.

**Solute Transport Equations (Clement, 1997; Clement et al., 1998):**

\[
\frac{\partial \left( \theta C^n_m \right)}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta D^n_{ij} \frac{\partial C^n_m}{\partial x_j} \right) - \frac{\partial}{\partial x_i} \left( \theta v_i C^n_m \right) + q_s C^n_s + \sum R_m + J \quad i,j = x,y,z \quad (C-3)
\]

\[
\frac{\partial \left( \theta C^n_{im} \right)}{\partial t} = \sum R_{im} \quad (C-4)
\]
where $D_{ij}$ is the hydrodynamic dispersion tensor \{L$^2$T$^{-1}$\}, $v_i$ is the average linear groundwater velocity \{L$^1$T$^{-1}$\} obtained from the multiphase flow model component, $q_s$ is the source/sink term represented as a volumetric flux \{T$^{-1}$\}, \( \mathbb{R} \) is the rate of all reactions \{M$^1$L$^{-3}$T$^{-1}$\}, $t$ is time \{T$^1$\}. Superscript $n$ represents species number, and subscripts $m$ and $im$ represent mobile and immobile species, respectively.

**Reaction Equations (West, 2009):**

For the EISB reactions in which trichloroethene (TCE) was the contaminant, the following Monod kinetic equations were used. The reactants and products of these reactions include the hydrogen electron donor ($H_2$), lactate, cis-dichloroethene (cDCE), dechlorinating bacteria (subscript TCE/CE), methanogenic bacteria (subscript meth), and lactate fermenting bacteria (subscript lactate).

\[
\frac{\partial [\text{TCE}]}{\partial t} = -\frac{q_{\text{TCE}}^{\text{MAX}} [X_{\text{CE}}]}{R_{\text{TCE}}} \left( \frac{[\text{TCE}]}{K_{\text{TCE}} + [\text{TCE}]} \left( \frac{[H_2] - H^*}{K_{H_2} + ([H_2] - H^*)} \right) \right) I_{\text{toxic}} \tag{C-5}
\]

\[
\frac{\partial [\text{cDCE}]}{\partial t} = \frac{R_{\text{TCE}}}{R_{\text{cDCE}}} \left( \frac{\partial [\text{TCE}]}{\partial t} \right)
\]

\[
\frac{\partial [\text{lactate}]}{\partial t} = -q_{\text{lactate}}^{\text{MAX}} [X_{\text{lactate}}] \left( \frac{[\text{lactate}]}{K_{\text{lactate}} + [\text{lactate}]} \right)
\]

\[
\frac{\partial [H_2^{\text{meth}}]}{\partial t} = -q_{\text{meth}}^{\text{MAX}} [X_{\text{meth}}] \left( \frac{[H_2]}{K_{H_2}^{\text{meth}} + ([H_2] - H^*_\text{meth})} \right) I_{\text{toxic}}
\]

\[
\frac{\partial [H_2]}{\partial t} = F_{\text{lactate}} \frac{\partial [\text{lactate}]}{\partial t} - \left( F_{\text{TCE}} \frac{\partial [\text{TCE}]}{\partial t} + F_{\text{meth}} \frac{\partial [H_2^{\text{meth}}]}{\partial t} \right)
\]

201
\[
\frac{d[X_{lactate}]}{d\tau} = -Y_{lactate} \frac{d[lactate]}{d\tau} - \lambda_{lactate} [X_{lactate}]
\]  
(C-10)

\[
\frac{d[X_{meth}]}{d\tau} = -Y_{meth} \frac{d[H_2^{meth}]}{d\tau} - \lambda_{meth} [X_{meth}]
\]  
(C-11)

\[
\frac{d[X_{CE}]}{d\tau} = -Y_{TCE} \frac{d[TCE]}{d\tau} - \lambda_{CE} [X_{CE}]
\]  
(C-12)

\[
I_{toxic} = \begin{cases} 
1 - \frac{[TCE]}{[TCE]_{max}} & \text{if } [TCE] \leq [TCE]_{max} \\
0 & \text{if } [TCE] > [TCE]_{max}
\end{cases}
\]  
(C-13)

where square brackets [ ] represent molar concentrations, \( q_{n,MAX} \) is the maximum utilization rate for species \( n \) \{M'L'T'\}, \( I_{toxic} \) is the TCE inhibition coefficient to account for toxicity on dechlorinating (Haest et al., 2010) and methanogenic (Oldenhuis et al., 1991) activity, \( K_n \) is the half-saturation coefficient for species \( n \) \{M'L'\}, \( X_n \) is the biomass concentration of species \( n \) \{M'L'\}, \( H^* \) is the threshold electron donor concentration for the dechlorinator species \{M'L'\}, \( H_{meth}^* \) is the threshold electron donor concentration for the methanogenic species \{M'L'\}, \( F_{species} \) is the stoichiometric production/consumption coefficient for each species \{M'L'\}, \( Y_n \) is the biomass yield coefficient for species \( n \) \{M'L'\}, \( \lambda_n \) is the first-order biomass decay rate coefficient \{T'\}, \([TCE]_{max}\) is the maximum tolerable TCE concentration in which dechlorinating and methanogenic activity is inhibited \{M'L'\}, \( R_{TCE} \) is the retardation factor for TCE, \( R_{cDCE} \) is the retardation factor for cDCE.
Appendix D

EISB/Monod Parameter Estimation Fitting
Figure D.1: Fitting of maximum utilization (for TCE reductive dechlorination) rate data from literature. The dotted line plot displays the “initial” visual fit to the literature data set; the “final” fit represents the “initial” fit reduced by one order of magnitude, incorporating the modeling assumptions used by Christ and Abriola (2007).
Figure D.2: Fitting of maximum utilization (for lactate fermentation) rate data from literature.

\[
q_{\text{lactate}} = -1.024E-14T^4 + 6.054E-13T^3 - 8.740E-12T^2 + 4.092E-11T + 1.677E-10
\]
Figure D.3: Fitting of maximum utilization (for methanogenesis) rate data from literature.
Figure D.4: Fitting of TCE reductive dechlorination half-saturation coefficient data from literature.

Figure D.5: Fitting of methanogenic half-saturation coefficient data from literature.
Figure D.6: Fitting of H$_2$ utilization half-saturation coefficient data from literature.

\[ K_{H2} = 5.462 \times 10^{-12} T^3 - 2.409 \times 10^{-10} T^2 + 8.993 \times 10^{-10} T + 4.882 \times 10^{-8} \]

Figure D.7: Fitting of lactate fermentation half-saturation coefficient data from literature.

\[ K_{lactate} = 2.008 \times 10^{-8} T^3 - 1.048 \times 10^{-6} T^2 + 1.200 \times 10^{-5} T + 5.058 \times 10^{-5} \]
Figure D.8: Dechlorinator biomass yield coefficient data from literature.
Figure D.9: Methanogenic biomass yield coefficient data from literature.

![Methanogenic biomass yield coefficient data](image)

Figure D.10: Lactate-fermentative biomass yield coefficient data from literature.

![Lactate-fermentative biomass yield coefficient data](image)
Figure D.11: Biomass decay coefficient data from literature. An Arrhenius-type relationship was applied (using the value determined by Cupples et al. (2003) as the reference point) to show a $Q_{10}$-like relationship (Vaccari et al., 2006); the decay rate doubles per 10$^\circ$C increase in temperature.