INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI[®]

DEVELOPMENT AND VALIDATION OF A THREE-DIMENSIONAL MODEL FOR PREDICTING REDOX-DEPENDENT INTRINSIC REMEDIATION

By

**Grant Russell Carey
B.A.Sc.**

**A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for
the degree of Master of Engineering**

**Department of Civil and Environmental Engineering
Carleton University
Ottawa, Ontario
Canada**

January 2001

© Grant Russell Carey 2001

National Library
of Canada

Acquisitions and
Bibliographic Services

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque nationale
du Canada

Acquisitions et
services bibliographiques

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

Our file Notre référence

The author has granted a non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of this thesis in microform, paper or electronic formats.

The author retains ownership of the copyright in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de cette thèse sous la forme de microfiche/film, de reproduction sur papier ou sur format électronique.

L'auteur conserve la propriété du droit d'auteur qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

0-612-57749-X

Canada

**Thesis Acceptance Form
M.ENG. CANDIDATE**

**The undersigned recommend to the Faculty of Graduate Studies
and Research acceptance of the thesis**

**“DEVELOPMENT AND VALIDATION OF A
THREE-DIMENSIONAL MODEL FOR PREDICTING
REDOX-DEPENDENT INTRINSIC REMEDIATION”**

**Submitted by Grant Russell Carey
in partial fulfillment of the requirements
for the degree of Master of Engineering**

Thesis Supervisor

Chair, Department of Civil and Environmental Engineering

**Carleton University
January 2001**

ABSTRACT

The intrinsic bioremediation of organic pollutants in groundwater involves a complex sequence of interactions that include inorganic chemicals such as oxygen, nitrate, manganese, iron, sulfate, and methane. Reactive transport models may be important tools for evaluating the performance of integrated remedies, which include intrinsic bioremediation and active source control measures, and for evaluating remediation timeframes for natural and enhanced bioremediation alternatives.

A three-dimensional, multispecies reactive transport model (BioRedox-MT3DMS) was developed to simulate coupled oxidation-reduction reactions between multiple electron donors and electron acceptors. BioRedox-MT3DMS is also capable of simulating multiple solute biodegradation mechanisms, rates, and pathways that differ for each solute and each terminal electron accepting process (TEAP) included in the model. BioRedox-MT3DMS was designed with a flexible reaction framework to ensure its applicability for a wide range of chemicals and site conditions. The use of first-order degradation kinetics for simulating macro-scale biodegradation processes is justified by comparison to a Monod substrate utilization model.

BioRedox-MT3DMS was verified by conducting benchmark tests with proven analytical solutions and other numerical models. BioRedox-MT3DMS was validated by simulating the redox zonation observed in extensive research studies conducted at the Vejen Landfill site in Vejen, Denmark. The model simulations of aerobic, nitrate-reducing, iron(III)-reducing, sulfate-reducing, and methanogenic zones provided a reasonable approximation with conditions observed in the field.

Model simulations were conducted to evaluate the impact of ferrous iron oxidation downgradient of the iron-reducing zone on the simulated redox zones. Simulations were conducted to determine the potential influence of landfill cap permeability on the intrinsic remediation of a hypothetical TCE plume underlying an old, unlined municipal landfill. The results of these simulations demonstrate that active source control measures can have an adverse influence on downgradient intrinsic bioremediation performance.

The BioRedox-MT3DMS model appears to be an important advancement for simulating macro-scale coupling between redox zonation and biodegradation processes.

ACKNOWLEDGEMENTS

Anyone who has conducted graduate-level research, particularly those who have taken as long as I have to “evaluate” the findings, can appreciate the euphoria that sets in when the thesis has *finally* been completed.

I’m sure everyone also appreciates as much as I do the opportunity to write, in one’s own (and unedited) words, of the supporting contributions made by all those around them – the family, friends, and colleagues, who can never receive enough thanks for the invaluable contributions that they make, time and time ... and time ... again.

I’ve been waiting for this moment, so here goes...

To my very close friends, who have never given up on me and who have provided me with the strong support I needed to change my life over the years...in no particular order, Pat and Marianna, Su-Kim and Jim, Dave and Kathleen, Marissa and Nicole, JoAnne and Pete, April and Duncan, Jody and Kathy, Robin and Jen...thanks be to you!

And particularly to Viola and Don, two very dear and special friends who are always there to support me when times are rough, and to share in all that life has to offer. Special thanks be to you – I will always treasure our friendship. Please know that my renewed enthusiasm for life stems much from the inspiring spirit and courage that I see in you! Only the most special of people can keep hold of that sparkle in their eyes...

To Ed McBean, a close friend and mentor in life, someone I know I can always turn to for important advice or for a joke on how the Scots rule the world. Thanks Ed – you don’t know how much I chuckle when I get your emails from the world over, and the security I feel knowing that you are always available to lend your wisdom!

And as well to Richard Murphy, Frank Rovers, and Earl Shannon of CRA, who opened the doors to an entirely new and exciting world for me...thanks guys!

To Paul Van Geel...a true friend and *enduring* supporter. The rest of the world will have no idea how much you had to put up with, Paul...it’s been a blast, and I appreciate so much the patience and confidence that you’ve always placed in me. I’ll let you know when I’m ready to start my Ph.D. (oops, more grey hairs...) THANK YOU!

To Mom, Dad, and Brett – the family that never stops loving, never stops supporting, and never stops asking when I’m going to be done. This one’s for you!!!

To Gwendolin, my loving wife...in a way I’m glad that my thesis has taken as long as it has, because it has provided us with our first real opportunity to work together, to begin that long and glorious journey together. I love you so much, and will always cherish the eternal bond that we share. thank you for showing me the true meaning of life.

And now, I’m going to learn from my experience over the past four years and stop here...

TABLE OF CONTENTS

	PAGE
Abstract	iii
Acknowledgements	v
List of Tables	xi
List of Figures	xii
Nomenclature	xv
CHAPTER 1 – INTRODUCTION	
1.1 BACKGROUND	1
1.2 PURPOSE AND SCOPE	5
1.3 ORGANIZATION	6
CHAPTER 2 - BIODEGRADATION PROCESS	
2.1 OVERVIEW OF MICROBIAL PROCESSES	8
2.1.1 Types of Microorganisms	8
2.1.2 Cell Structure	8
2.1.3 Energy and Carbon Sources	9
2.1.4 Concept of Gibb's Free Energy	11
2.1.5 Oxidation-Reduction Reactions	12
2.1.6 Physiology of Substrate Uptake By Microorganisms	12
2.1.7 Role of Enzymes in Catalyzing Decomposition Reactions	13
2.1.8 Energy Storage Within the Cell	16
2.1.9 Growth Phases of Individual Populations	17
2.1.10 Concept of the Microbial Consortium	18
2.1.11 General Growth Kinetics	19
2.2 MECHANISMS OF BIODEGRADATION	22
2.2.1 Oxidation	22
2.2.1.1 Oxygen-Reducing Zone	24
2.2.1.2 Nitrate-Reducing Zone	24

2.2.1.3 Manganese-Reducing Zone	26
2.2.1.4 Iron-Reducing Zone	27
2.2.1.5 Sulfate-Reducing Zone	29
2.2.1.6 Methanogenic Zone	30
2.2.1.7 Role of Hydrogen in Mediating TEAPs	31
2.2.1.8 Modeling of Multiple TEAPs	36
2.2.2 Fermentation	44
2.2.3 Cometabolism	44
2.2.4 Reductive Dehalogenation	45
2.2.5 Chlorinated Ethene Biodegradation Mechanisms	48
2.3 HALORESPIRATION MODELS	50
2.3.1 Sophisticated Monod Kinetic Models	51
2.3.2 Comparison of Monod and First-Order Kinetic Models	54
2.4 SUMMARY	62
2.4.1 Redox Zonation	63
2.4.2 Chlorinated Ethene Halorespiration	64
 CHAPTER 3 - MODEL DEVELOPMENT	
3.1 GENERAL	66
3.1.1 Code Features	66
3.1.2 Model Applications	70
3.1.3 Model Limitations	71
3.1.4 Development History	73
3.2 SOLUTE DEFINITIONS	74
3.2.1 Solute Classes	74
3.2.2 Solute Phases	75
3.3 GENERAL TRANSPORT EQUATIONS	76
3.3.1 Aqueous Solutes	76
3.3.2 Mineral Solutes	77
3.4 SORPTION ISOTHERMS	77

3.4.1	Linear Isotherm	78
3.4.2	Freundlich Isotherm	78
3.4.3	Langmuir Isotherm	78
3.5	TRANSFORMATION REACTIONS	79
3.5.1	Electron Donors	79
3.5.1.1	Instantaneous Reaction Model	80
3.5.1.2	First-Order Reaction Model	81
3.5.2	Electron Acceptors	82
3.5.3	General Solutes	85
3.5.4.	Halogens	85
3.6	BOUNDARY AND INITIAL CONDITIONS	85
3.6.1	NAPL Dissolution Source Model	86
3.6.2	Landfill Source Model	87
3.7	NUMERICAL IMPLEMENTATION	88
3.7.1	Grid and Time Step Discretization	88
3.7.2	General Solution	89
3.7.3	Evaluation of the Reaction Term	91
3.7.4	Stability and Accuracy Criterion	93
3.7.4.1	Stability Criterion	94
3.7.4.2	Accuracy Criterion	95
3.7.5	Boundary and Initial Conditions	96
3.7.6	Mass Budget	96
 CHAPTER 4 – VERIFICATION		
4.1	VERIFICATION STRATEGY	98
4.2	LEVEL I TEST	102
4.3	LEVEL II TESTS	105
4.3.1	Test II.A - 3D MT3D Comparison	105
4.3.2	Test II.B - 2D NAPL Model Verification	112
4.3.3	Test II.C - 2D RT3D Comparison	114

CHAPTER 5 - MODEL VALIDATION

5.1 SITE CHARACTERIZATION	117
5.1.1 Landfill History	119
5.1.2 Hydrogeologic Setting	122
5.1.3 Groundwater Chemistry Distribution	124
5.1.3.1 Chloride	126
5.1.3.2 NVOC	127
5.1.3.3 Electron Acceptors and Metabolic By-Products	129
5.1.4 Observed Redox Zonation	135
5.1.4.1 Assessment of Dissolved Redox Indicator Concentrations	135
5.1.4.2 Assessment of Mineral-Phase Iron Speciation	137
5.2 SIMULATION MODEL DEVELOPMENT	145
5.2.1 Groundwater Flow Model (MODFLOW)	147
5.2.2 Landfill Leachate Composition Model	148
5.2.3 Solute Transport Model (BioRedox)	149
5.3 SIMULATED REDOX ZONATION	152
5.3.1 Redox Zone Visualization Approach	152
5.3.2 Discussion of Simulated Redox Zonation	159
5.3.2.1 Redox Zonation at 15 years	159
5.3.2.2 TOC Mass Budget	162
5.3.2.3 Discrepancy in Vertical Extent of Redox Zonation Below Landfill	163
5.3.2.4 Transient Redox Zone Development	164
5.3.2.5 Effect of Model Dimensionality	166
5.3.3 Validation of BioRedox TEAP Representation	168
5.3.4 Sensitivity to Iron(II) Mobilization and Transport	169
5.4 HYPOTHETICAL SOURCE CONTROL SIMULATIONS	171

CHAPTER 6 - CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS	178
6.2 RECOMMENDATIONS	180
REFERENCES	181

LIST OF TABLES

		PAGE
Table 2.1	Microorganism Population Sizes in Soil and Groundwater.	9
Table 2.2	Reduction half-reactions for organic and inorganic electron acceptors.	46
Table 2.3	Free energy for reduction reactions coupled to hydrogen oxidation.	47
Table 4.1	BIOREDOX Functionality.	101
Table 5.1	Range and average concentrations of NVOC and geochemical parameters measured in each redox zone.	125
Table 5.2	Redox zone criteria for evaluating dominant TEAPs at sampling locations.	135
Table 5.3	Model solutes, oxidation-reduction half-reactions, and reaction threshold concentrations.	150
Table 5.4	Solute molecular weights, and boundary and initial concentrations.	151
Table 5.5	Simulation model criteria for preferential utilization of TEAPs during TOC oxidation.	157
Table 5.6	Summary of TEAP-specific TOC mass degradation for Base Case.	162

LIST OF FIGURES

		PAGE
Figure 2.1	Energy relationship for the burning of metabolic respiration of a carbohydrate such as glucose (CH_2O). <i>Source: Kimball (1983)</i>	14
Figure 2.2	Conceptual process of substrate binding to enzyme, undergoing a chemical transformation, and the subsequent release of new products from the enzyme. <i>Source: Kimball (1983)</i>	15
Figure 2.3	General phases of population growth. <i>Source: Metcalf and Eddy (1979)</i>	17
Figure 2.4	Chlorinated ethene equivalent half-life values for Monod kinetics.	59
Figure 2.5	PCE utilization rate versus concentration: comparison between Monod and first-order relationships.	60
Figure 2.6	TCE utilization rate versus concentration: comparison between Monod and first-order relationships.	61
Figure 2.7	DCE utilization rate versus concentration: comparison between Monod and first-order relationships.	62
Figure 2.8	Vinyl chloride utilization rate versus concentration: comparison between Monod and first-order relationships.	63
Figure 4.1a	Sequential Decay ($t = 50$ hours)	104
Figure 4.1b	Sequential Decay ($t = 100$ hours)	104
Figure 4.1c	Sequential Decay ($t = 200$ hours)	104
Figure 4.2	Model Dimensions and Source Conditions	106
Figure 4.3	BIOREDOX and MT3D Comparison: Plan View Contours (Layer 1)	108
Figure 4.4	BIOREDOX and MT3D Comparison: Cross-Section Contours (Row 20)	108
Figure 4.5	BIOREDOX and MT3D Comparison: Observation Nodes (Toluene)	109

Figure 4.6	BIOREDOX and MT3D Comparison: Observation Nodes (PCE)	110
Figure 4.7	BIOREDOX Simulation of Solute Distributions: Cross-Section (Row 20)	111
Figure 4.8	Comparison of NAPL Source Models to A Constant Concentration Source	113
Figure 4.9	RT3D and BIOREDOX Model Domain	114
Figure 4.10	Comparison of RT3D and BIOREDOX Simulations	115
Figure 5.1	Vejen Landfill site location and monitoring transect orientation.	118
Figure 5.2	Landfill leachate and groundwater perimeter monitoring wells.	120
Figure 5.3	Electrical conductivity profile in groundwater below south side of landfill.	123
Figure 5.4	Chloride plume delineation along vertical transect.	126
Figure 5.5	NVOC corrected concentrations along downgradient groundwater flowpath. Measured NVOC concentrations were corrected to remove the effects of dispersion based on chloride concentrations.	127
Figure 5.6	Transient variations in NVOC and chloride measured concentrations at permanent monitoring stations.	128
Figure 5.7a	Concentration vs. depth profiles for NVOC, oxygen, and nitrate at boring locations B1, B3, and B9. Interpolated from charts presented in Lyngkilde and Christensen, 1992a	130
Figure 5.7b	Concentration vs. depth profiles for NVOC and sulfate at boring locations B1, B3, and B9.	130
Figure 5.8a	Concentration vs. depth profiles for dissolved Mn^{2+} and Fe^{2+} at boring locations B1, B3, and B9. Interpolated from charts presented in Lyngkilde and Christensen, 1992a	133
Figure 5.8b	Concentration vs. depth profiles for sulfide and methane at boring locations B1, B3, and B9.	133
Figure 5.9	Estimated redox zonation in groundwater. Source:	137

Lyngkilde and Christensen, 1992a

Figure 5.10	Groundwater flowpath location and total iron concentration in sediment samples. Source: Heron and Christensen, 1995	139
Figure 5.11	Iron(II) mineral species extract concentrations. Source: Heron and Christensen, 1995	141
Figure 5.12	Iron(III) mineral species extract concentrations. Source: Heron and Christensen, 1995	142
Figure 5.13	Noncrystalline iron(III) concentrations in different redox zones. Source: Christensen et al., 1994	143
Figure 5.14	Average concentrations of iron(II) and iron(III) mineral species along flowpath downgradient from landfill. Source: Heron and Christensen, 1995	144
Figure 5.15	Simulation model domain.	146
Figure 5.16	Flow and transport boundary conditions.	147
Figure 5.17	Simulated electron acceptor concentration contours at the end of the simulation period (t = 15 years) for the Base Case input parameters.	153
Figure 5.18	Redox zone visualization colour scheme.	156
Figure 5.19	Validation of BioRedox method for visualizing redox zonation based on electron acceptor threshold concentrations for each TEAP.	158
Figure 5.20	Transient redox zone development (from one to 15 years of the Base Case simulation).	165
Figure 5.21	Influence of Fe(II) production on simulated redox zonation.	170
Figure 5.22	Simulation of landfill cap influence on groundwater intrinsic remediation.	174

NOMENCLATURE

α_w	Freundlich exponent for solute w [dimensionless]
C	Substrate concentration [ML^{-3}]
C_a	Concentration of electron acceptor a [ML^{-3}]
C_d	Dissolved-phase concentration of electron donor d [ML^{-3}]
C_m	Equivalent aqueous-phase concentration of mineral solute m [ML^{-3}]
$C_{m,k}$	Mineral-phase concentration of electron donor k , ML^{-3}
$C_{a,bck}$	Background concentration for electron acceptor a [ML^{-3}]
$C_{a,ijk}^t$	Concentration of electron acceptor a at cell block ijk at time t [ML^{-3}]
$C_{a,min}$	Minimum concentration needed to support the reduction of electron acceptor a [ML^{-3}]
Cr	Courant number
$C_{sat,i}$	Saturated groundwater concentration for solute i [ML^{-3}]
$C_{s,w}$	Dissolved-phase concentration of sources/sinks for solute w [ML^{-3}]
C_w	Dissolved-phase concentration of solute w [ML^{-3}]
C_{w-l}	Dissolved-phase concentration of the parent solute $w-l$ [ML^{-3}]
$C_{w,k}$	Dissolved concentration of electron donor k , ML^{-3}
$D_{ij,w}$	Hydrodynamic dispersion coefficient for solute w [L^2T^{-1}]
f_{oc}	Fraction of organic carbon in the porous medium [MM^{-1}]
f_i	Efficiency factor for solute i that accounts for bulk mass transfer limitations [%]
G_{oxc}	Total number of electron equivalents transferred to the electron acceptors during the oxidation of all available electron donors [eq. $\text{L}^{-3}\text{T}^{-1}$]
$G_{R,m}$	General transformation reaction term for solute m [$\text{ML}^{-3}\text{T}^{-1}$]

$G_{R,w}$	General reaction term for solute w , including biotransformations and rate-limited NAPL dissolution [$\text{ML}^{-3}\text{T}^{-1}$]
$G_{Ro,a}$	Chemical reaction term for the oxidized species of electron acceptor a [$\text{ML}^{-3}\text{T}^{-1}$]
$G_{Rr,a}$	Chemical reaction term for the reduced species of electron acceptor a [$\text{ML}^{-3}\text{T}^{-1}$]
$ID_{a,min}$	Minimum Redox Zone ID No. for the predominant electron acceptor a (e.g. $ID_{a,min}$ for oxygen is 1.0)
ID'_{ijk}	Redox Zone ID No. for cell block ijk at time t
K	Maximum substrate utilization rate [T^{-1}]
$K_{f,w}$	Freundlich constant for solute w [units depends on exponent a_w]
$K_{l,w}$	Langmuir constant for solute w [L^3M^{-1}]
$K_{oc,w}$	Organic-carbon partitioning coefficient for solute w [L^3M^{-1}]
K_s	Half-saturation constant [ML^{-3}]
MW_k	Molecular weight of electron donor k , M mole^{-1}
$MW_{o,a}$	Molecular weight of the oxidized species of electron acceptor a [M mole^{-1}]
$MW_{r,a}$	Molecular weight of the reduced species of electron acceptor a [M mole^{-1}]
MW_w	Molecular weight of solute w [M mole^{-1}]
MW_{w-l}	Molecular weight of the parent solute $w-l$ [M mole^{-1}]
n_i	Number of moles of solute i present in the NAPL mixture [mol]
N	Total number of moles in the NAPL mixture [mol]
N_s	Total concentration of sorption sites available [MM^{-1}]
q_s	Volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative) [T^{-1}]
r_{REF}	Reaction rate at reference temperature [$\text{ML}^{-3}\text{T}^{-1}$]

r_T	Reaction rate at temperature of T °C [ML ⁻³ T ⁻¹]
R_k	Retardation coefficient for electron donor k , dimensionless
R_w	Retardation coefficient for solute w [dimensionless]
S_k	Sorbed-phase concentration of electron donor k , MM ⁻¹
S_i	Solubility limit of solute i [ML ⁻³]
ST ₀	Total initial mass in storage
ST _t	Total mass in storage at time t
S_w	Sorbed-phase concentration of solute w [MM ⁻¹]
S_{w-l}	Sorbed-phase concentration of the parent solute $w-l$ [MM ⁻¹]
T	Time [T]
Δt	Time-step duration [T]
T	Temperature [°C]
x_i	Distance along the respective Cartesian coordinate axis [L]
X	Biomass concentration [ML ⁻³]
X_i	Mole fraction of solute i in the NAPL phase [mol/mol]
X_m	Mineral-phase concentration of solute m [MM ⁻¹]
Y	Yield of biomass growth per mass of substrate utilized [MM ⁻¹]
α_L	Longitudinal dispersivity of the porous medium
β_a	Number of moles of reduced electron acceptor species produced from the reduction of 1 mole of the oxidized species of the electron acceptor
β_w	Number of moles of daughter solute w produced during the transformation of 1 mole of the parent solute $w-l$ [mole mole ⁻¹]
δ_a	Number of electron equivalents utilized during the reduction of 1 mole of electron acceptor a [eq. mole ⁻¹]

δ_k	Number of electrons donated during the oxidation of 1 mole of electron donor k , equivalence mole ⁻¹
n_{donor}	Number of electron donors undergoing kinetic oxidation
$\lambda_{a,w}$	First-order, dissolved-phase degradation rate of solute w [T ⁻¹]
$\lambda_{a,w-l}$	First-order, dissolved-phase degradation rate of the parent solute $w-l$ [T ⁻¹]
λ_{fld}	First-order degradation rate based on field tests [T ⁻¹]
λ_{max}	Maximum first-order decay rate of all solutes included in a BIOREDOX simulation
λ_m	First-order degradation rate for solute m [T ⁻¹]
$\lambda_{m,k}$	First-order, mineral-phase degradation rate of electron donor k , T ⁻¹
$\lambda_{NAPL,i}$	First-order NAPL dissolution coefficient for solute i [T ⁻¹]
$\lambda_{s,w}$	First-order, sorbed-phase degradation rate of solute w [T ⁻¹]
$\lambda_{s,w-l}$	First-order, sorbed-phase degradation rate of the parent solute $w-l$ [T ⁻¹]
$\lambda_{w,k}$	First-order, dissolved-phase degradation rate of electron donor k , T ⁻¹
$\lambda_{s,k}$	First-order, sorbed-phase degradation rate of electron donor k , T ⁻¹
μ_{ad}	Stoichiometric ratio expressed in mass of electron acceptor consumed per mass of electron donor utilized [MM ⁻¹]
μ_{max}	Maximum specific growth rate [T ⁻¹]
μ_w	Stoichiometric coefficient for the transformation of parent solute $w-l$ to solute w [MM ⁻¹]
v_i	Average linear groundwater velocity [L/T]
θ	Temperature-activity coefficient [dimensionless]
θ	Saturated porosity of the porous medium [L ³ L ⁻³]
ρ_b	Dry bulk density of the porous medium [ML ⁻³]

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Subsurface contamination with petroleum hydrocarbons, chlorinated solvents, or landfill leachate is a widespread problem in North America. Organic chemicals are commonly introduced to the environment through events such as surface spills, historical dumping prior to legislated disposal practices, or long-term leaking from underground storage tanks or landfills.

Extensive research has been conducted over the past 15 years on the naturally-occurring biodegradation of organic pollutants in groundwater. Microorganisms are indigenous to subsurface soils, and result in the microbial consumption of many organic substrates, depending on whether conditions are favourable for biodegradation.

Natural attenuation refers to the overall processes that result in the natural reduction of pollutant mass or concentrations in the subsurface (thereby reducing potential risks to downgradient receptors). Biodegradation plays a key role in the natural attenuation of petroleum hydrocarbons and chlorinated solvents. In fact, the United States Environmental Protection Agency (USEPA) will only accept natural attenuation as a groundwater remedy if the proponent can demonstrate that pollutant mass is being destroyed which occurs through biodegradation processes for many organic compounds. Naturally-occurring biodegradation is sometimes referred to as *intrinsic bioremediation*.

The USEPA refers to Monitored Natural Attenuation (MNA) as the legislated groundwater remedy that proponents may put forward as the preferred site alternative. Lines of evidence are used to demonstrate to regulators that biodegradation processes are

effectively destroying contaminant mass, and that potential risks to downgradient receptors are within acceptable parameters. The USEPA (1999) states that active source control measures must be considered when MNA is put forward as a groundwater remedy for a site. Therefore, it is possible that intrinsic bioremediation is a suitable remedy for a downgradient portion of a plume, while active source control measures are utilized to contain or remediate highly-concentrated portions of the plume.

Remediation timeframe is also a key issue when proposing MNA as a groundwater remedy. The USEPA (1999) states that MNA will only be acceptable if the remediation timeframe is “comparable” to the timeframe that would be required for more active measures. The quantification of remediation timeframe can be challenging, particularly given the uncertainty in the composition, spatial and temporal heterogeneity, and duration of the pollutant source in the subsurface. Computer models can be valuable tools for evaluating potential ranges in remediation timeframe for MNA and active remediation technologies.

The biodegradation of organic pollutants in groundwater involves a complex sequence of interactions involving inorganic chemicals such as oxygen, nitrate, manganese, iron, sulfate, and methane. The effectiveness of the biodegradation process is strongly dependent on groundwater oxidation-reduction potential (ORP), and also depends on other factors such as available supplies of microbial substrates and inorganic chemicals that ultimately result in microbial growth. Extensive occurrence of biodegradation will cause a significant shift in groundwater redox conditions. The interdependence between biodegradation performance and groundwater geochemistry makes it difficult to evaluate current and future performance of intrinsic bioremediation.

The intrinsic bioremediation of petroleum hydrocarbons is well documented, and appears to be relatively ubiquitous in the subsurface environment (Wiedemeier et al., 1998). MNA is expected to be a suitable remedy for petroleum hydrocarbon plumes at approximately 80% of contaminated sites (Wiedemeier et al., 1999). Effective intrinsic bioremediation of chlorinated solvents, however, is not as widespread. Wiedemeier et al. (1999) indicate that approximately 20% of sites contaminated with chlorinated solvents will be suitable for MNA.

A complicating factor with the intrinsic bioremediation of chlorinated solvents is that sometimes these processes can result in the transformation of one species to a daughter product that is more toxic and more mobile in groundwater. For example, the incomplete reductive dechlorination of tetrachloroethene (PCE) through trichloroethene (TCE) and cis-1,2-dichloroethene (DCE), may result in the accumulation of vinyl chloride, which is more toxic than the parent species.

An additional complicating factor for the anaerobic bioremediation of some chlorinated solvents is that there must be a suitable substrate available in order for microorganisms to consume the chlorinated solvents. Examples of suitable substrates include benzene, toluene, ethylbenzene, and xylene (BTEX) compounds, organic-rich landfill leachate, or native organic matter in the soil. In some cases, the fortuitous occurrence of co-mingled sources with both BTEX and chlorinated solvents, results in effective intrinsic bioremediation of all pollutants.

A potential drawback to co-mingled plumes is that active source control may effectively remove the microbial substrate (e.g. BTEX) that is needed for continued intrinsic biodegradation of chlorinated solvents in the downgradient portion of the plume.

Thus active remediation activities may result in a change to substrate (and geochemical) conditions, resulting in a significant reduction in efficiency of intrinsic bioremediation of chlorinated solvents. Predicting the effect of active remediation activities on MNA is becoming more recognized as a valuable exercise during MNA assessments; however, adequate computer models which facilitate the prediction of redox-dependent intrinsic bioremediation for chlorinated solvents, including the effects of active source control measures, are not readily available.

Historically, the assessment of intrinsic bioremediation performance was conducted using single solute models with first-order decay of each organic species. However, it has become apparent that these simple models are not adequate for predicting the complex processes which govern the fate and transport of petroleum hydrocarbons and chlorinated solvents in groundwater.

Several models have been developed and made widely available to practitioners for evaluating redox-dependent intrinsic bioremediation of petroleum hydrocarbons. RT3D (Clement et al., 1998) and BIOPLUME III (Rifai et al., 1998) are both capable of predicting redox-dependent biodegradation of total BTEX. BIOPLUME III is only suitable for modeling intrinsic bioremediation of one or two hydrocarbons. RT3D models redox-dependent total BTEX biodegradation. RT3D also includes a separate option to simulate sequential transformation reactions for chlorinated ethenes (PCE, TCE, DCE, and vinyl chloride), but these reactions are not coupled to oxidation-reduction reactions involving electron donors and acceptors.

However, neither of these models are suitable for simulating redox-dependent biodegradation mechanisms, rates, and pathways for chlorinated solvent reactions. Also,

there are no readily available models that facilitate the prediction of effects from source control measures on downgradient redox conditions, and the corresponding effects on intrinsic bioremediation of the downgradient portion of a plume.

1.2 PURPOSE AND SCOPE

The purpose of this research was to develop a groundwater reactive transport model that facilitates the assessment of redox-dependent biodegradation of organic pollutants in groundwater, including petroleum hydrocarbons, chlorinated solvents, and organic-rich landfill leachate. The principal component of this work involved the development of a model with sufficient flexibility to permit handling of site-specific reaction mechanisms, pathways, and rate kinetics. This model represents an important advancement relative to other available reactive transport models, which have fixed reaction options that are often not adequate for simulating the wide range of chemicals and reaction scenarios found at different sites.

The coupled biodegradation-redox transport model developed as part of this research is called BioRedox-MT3DMS (henceforth referred to as BioRedox). BioRedox was developed based on the widely used three-dimensional transport model MT3DMS (Zheng and Wang, 1998). MT3DMS is a multispecies transport code that was specifically developed with a modular framework, to allow incorporation of complex reaction modules into the existing framework, which simulates processes of advection, dispersion, source/sink mixing, and simple reactions.

The scope for this work included modification of the FORTRAN source code of an existing transport model to allow for a sophisticated representation of coupled

biodegradation-redox reactions, and verification through benchmarks with existing analytical and numerical codes. BioRedox was also validated as part of this research by simulating landfill leachate natural attenuation, and subsequent redox zonation that occurred at the Vejen Landfill site in Vejen, Denmark. The Vejen landfill site is one of the most extensively monitored sites for groundwater redox zonation (John T. Wilson, personal communication, 1997), and provides a suitable candidate site for validation of the BioRedox model because of the detailed characterization of the hydrogeochemical regime within and below the landfill. This work also included a hypothetical simulation of different capping options for this landfill, to permit an evaluation of how source control at the landfill may influence downgradient redox zonation and pollutant biodegradability.

BioRedox is intended to be applicable for predictions involving a wide range of petroleum hydrocarbons, chlorinated solvents, organic matter in native soils or landfill leachate, and some metals. The emphasis of this thesis is on specific applications of BioRedox for simulating the intrinsic bioremediation of chlorinated ethenes. These processes were specifically selected because they are more complex than those involving petroleum hydrocarbons, and because of the widespread problems associated with chlorinated ethene contamination in Canada and the United States.

1.3 ORGANIZATION

The remainder of this thesis is organized as follows:

- Chapter 2 Provides a comprehensive literature review on the biodegradation process, including microbial characteristics, occurrence and modeling of redox zonation, and redox-dependent biodegradation processes for chlorinated ethenes.

- Chapter 3 Documents the algorithm and governing equations for the BioRedox model.
- Chapter 4 Presents the verification of the BioRedox code based on a testing strategy developed by the USEPA.
- Chapter 5 Documents the validation of the BioRedox code through simulation of redox zonation in the aquifer underlying the Vejen Landfill, and presents hypothetical simulations that demonstrate the influence of landfill source control on intrinsic bioremediation performance downgradient from the source area.

CHAPTER 2

BIODEGRADATION PROCESS

2.1 OVERVIEW OF MICROBIAL PROCESSES

2.1.1 Types of Microorganisms

There are numerous types of microorganisms that are indigenous to subsurface soil materials. Soil microorganisms can be categorized as originating from either animal or plant matter. Plant microorganisms play the most significant role in the biodegradation of organic chemicals. Types of plant microorganisms that exist in soils include bacteria, actinomycetes, molds (fungi), and algae (Dragun, 1988). Table 2.1 presents a summary of the size of microorganism populations found in soils.

Cryophilic bacteria operate between temperatures of -2°C to 30°C , with optimum growth occurring between temperatures of 12°C and 18°C . *Mesophilic* bacteria operate between temperatures of 20°C to 45°C , and thus play a less significant role in groundwater biodegradation in relatively cold climates.

2.1.2 Cell Structure

Microorganisms such as bacteria are single-cell organisms that are generally structured as follows (Metcalf and Eddy, 1979):

- a cell wall, which may be either a rigid or flexible membrane; if the cells are motile, they typically possess flagella (hair-like appendage) for locomotion;
- the interior of the cell primarily consists of a cytoplasm fluid, which is comprised largely of water with colloidal suspensions of proteins, carbohydrates, and other complex organic compounds;
- the cytoplasmic area contains ribonucleic acid (RNA), which is used for the synthesis of proteins; and
- the cell also contains a nuclear region containing deoxyribonucleic acid (DNA), which contains all of the information necessary for the reproduction of the cell.

Table 2.1 – Microorganism Population Sizes in Soil and Groundwater.

Organism	Population Size	
	<i>Typical</i>	<i>Extreme</i>
----- Surface Soil (cells / gram soil) -----		
Bacteria	0.1 – 1 billion	> 10 billion
Actinomycetes	10 – 100 million	100 million
Molds (fungi)	0.1 - 1 million	20 million
Algae	10,000 - 100,000	3 million
----- Subsoil (cells / gram soil) -----		
Bacteria	1000 – 10,000,000	200 million
----- Groundwater (cells / ml) -----		
Bacteria	100 - 200,000	1 million

Two groups of microorganisms (bacteria and blue-green algae) have cells that differ from the cells of other organisms in several respects. Most notably, these microorganisms have a poorly defined nucleus (i.e. the nucleus is not bound by a membrane lining). These microorganisms are referred to as *prokaryotic* cells, whereas cells with a well-defined nucleus are called *eukaryotic* cells.

2.1.3 Energy and Carbon Sources

Microorganisms require both carbon and energy for the synthesis of new cellular material. The carbon is necessary for cell growth, and energy is required to sustain basic metabolic activities of the cell.

Microorganisms are classified based on their source of carbon: *autotrophic* organisms use carbon dioxide as their carbon source; *heterotrophic* organisms use carbon released during the decomposition of organic matter.

Most subsurface microorganisms are heterotrophic. That is, they utilize carbon derived from the decomposition of native organic matter in soils or anthropogenic organic compounds in the environment. In situations where organic matter is limited, cellular mass itself may be broken down to produce energy. The overall process of net decrease in cellular mass is called *endogenous respiration*.

Energy for cell metabolism in soils is generated through coupled oxidation-reduction reactions (as described in Sections 2.1.4 and 2.1.5).

Microorganisms may also be classified based on their dependence on oxygen for the generation of energy:

- *aerobes* are microorganisms that only grow in the presence of oxygen;
- *anaerobes* are microorganisms that only grow when oxygen is exhausted; and
- *facultative* microorganisms do not depend on oxygen – they grow regardless of whether oxygen is present or not.

Other essential elements required as nutrients for cell synthesis include: nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, copper, zinc, boron, molybdenum, chlorine, and cobalt (Dragun, 1988). The influence of inorganic and organic nutrients on biodegradation of organic contaminants varies substantially (Wiedemeier et al., 1999), and in some cases the addition of nutrients into the subsurface environment has been shown to have little or no effect on biodegradation rates of petroleum hydrocarbons (Swindoll et al., 1988; Miller, 1990).

2.1.4 Concept of Gibb's Free Energy

The decomposition of organic compounds ultimately provides energy that is used for microbial metabolism. The decomposition of organic matter can be considered as a two-step process:

- chemical bonds are broken in the reactant molecules; and
- new chemical bonds are formed in the product molecules.

Each molecule of organic matter contains a number of elements (e.g. carbon, hydrogen, oxygen, chloride, etc.). These elements are bound together to form a three-dimensional molecular structure. The chemical bonds that hold these elements together represent stored energy, and each bond is defined as having quantitative *bond energy*.

The magnitude of a bond energy is based on the difference in electronegativity of the two atoms bonding together. The larger the bond energy, the more energy is required to break the chemical bond.

Bond energy is also referred to as *free energy* because it is available to do work. We refer to free energy as G (i.e. *Gibb's free energy*), in honor of Josiah Willard Gibb who developed the concept of free energy. ΔG_r represents the difference between the sum of bond energies in products, and sum of bond energies in reactants.

If the total free energy stored in chemical bonds of the products, is less than the original free energy in the reactants, then a finite amount of free energy (i.e. ΔG_r) must be liberated. This liberated energy is then available for microbial metabolism.

In other words, a negative value for ΔG_r implies that energy is released during the transformation from reactants to products. Microorganisms will only catalyze reactions that result in the release of energy (i.e. $\Delta G_r < 0$).

2.1.5 Oxidation-Reduction Reactions

Oxidation or reduction reactions are defined as the loss or gain of electrons, respectively. Oxidation reactions must always be coupled with reduction reactions in nature (and are thus referred to as *redox* reactions). During a coupled redox reaction, electrons are transferred from an *electron donor* (which is said to be *oxidized* because it loses an electron), to an *electron acceptor* (which is said to be *reduced* because it gains an electron).

The oxidation of an electron donor does not necessarily imply that oxygen is involved. This name was derived because oxygen has a high affinity for electrons (it is the second-most electronegative element), and thus serves as an excellent electron acceptor. Because of its effectiveness in this role, its name was used as the basis for all reactions of this type, even those that do not involve oxygen as an electron acceptor.

Microbially-catalyzed redox reactions are critical to the biodegradation process because they result in the liberation of free energy, which is then available for microbial metabolism processes.

2.1.6 Physiology of Substrate Uptake By Microorganisms

Soil microorganisms will catalyze the decomposition of organic compounds to obtain carbon and energy in support of cell growth and metabolism. For microbial degradation to occur, the organic chemicals must come in direct contact with specific cellular enzymes. Some microorganisms rely on extracellular enzymes (i.e. enzymes outside the outer cell membrane) to decompose large substrate molecules into forms that

are small enough to be transported across the outer membrane. However, many microorganisms rely on intracellular chemical reactions to metabolize organic pollutants.

The general steps involved with intracellular decomposition of organic compounds are:

- the organic molecule is transported into the cell via passive diffusion or active uptake (which requires expenditure of cellular energy);
- the molecule is degraded to end-products through oxidation-reduction reactions that are catalyzed by one or more enzymes; and
- the end-products are transported out of the cell via diffusion or active transport.

The biochemical reactions between enzymes and substrates are described in more detail in the following section.

2.1.7 Role of Enzymes in Catalyzing Decomposition Reactions

Microbial cells are analogous to functioning chemical factories; each cell may catalyze hundreds of chemical reactions that drive the metabolic and synthesis processes of the cell. Reactions that ultimately result in the release of energy (i.e. $\Delta G_r < 0$) are typically not spontaneous. Some of these reactions may occur very slowly without microbial intervention. Microbes actually catalyze these thermodynamically favorable reactions, so that they occur much more rapidly. Therefore, microbial degradation may play a significant role in the natural or enhanced bioremediation of a wide variety of organic pollutants.

To understand how this catalyst reaction occurs, we consider the energy input first required to break the chemical bonds during the decomposition of organic matter. The magnitude of the required input of energy is called the *energy of activation*.

Microorganisms use *enzymes* to reduce the energy of activation, thereby reducing the barrier for the decomposition of the organic molecule. Figure 2.1 illustrates the conceptual reduction in energy of activation as a result of microbial catalysis. This figure also demonstrates that the free energy stored in the end products is less than the free energy in the reactants, indicating that some free energy (equal to ΔG_r) is liberated during the biotransformation reaction.

Enzymes are large protein molecules that catalyze decomposition reactions. In order for decomposition to occur, the enzyme must form a temporary bond with one or more of the reactants. This bond lowers the activation energy, thus allowing the reaction to occur more rapidly.

The forces that bind the enzyme and the substrate together may be hydrogen bonds, ionic bonds, and/or mutual attraction of hydrophobic regions of two molecules. Due to the weakness of these bonding mechanisms, the substrate molecule must fit precisely into a complementary surface of the enzyme. This process is analogous to the fitting of a key into a lock.

Figure 2.1 – Energy relationship for the burning of metabolic respiration of a carbohydrate such as glucose (CH_2O). *Source: Kimball (1983)*

The rapid decomposition reaction between substrate and enzyme results in the formation of a product, which is then released from the bond with the enzyme. In many cases, a complex sequence of enzymatic reactions will occur before the final end products are created. Figure 2.2 presents a conceptual illustration of the enzymatic binding/reaction process.

Figure 2.2 – Conceptual process of substrate binding to enzyme, undergoing a chemical transformation, and the subsequent release of new products from the enzyme. *Source: Kimball (1983)*

The required complementarity between enzyme and substrate explains the *specificity* of most enzymes. That is, most intracellular enzymes are compatible with only one or a few different types of chemicals. Extracellular enzymes may have a broader specificity, meaning that they are capable of reacting with a wide range of organic compounds.

Substrate decomposition is known to be catalyzed in some cases because of a shift in the molecular alignment that occurs as the organic molecule binds to the enzyme molecule. This change in molecular configuration may increase the separation distance between several atoms, thus reducing the energy of activation required to break the

chemical bond between these atoms within the organic molecule. This is just one example of how the catalysis may occur.

The requirement for a brief, close union between enzyme and substrate is one reason why we see *competitive inhibition*. This process refers to the cessation or slowing of biodegradation of one chemical, due to the presence of a more preferred substrate. That is, if an enzyme is capable of reacting with two different chemicals, and one chemical bonds preferentially to the enzyme, then the other chemical will not be transformed until the preferentially-bound chemical is significantly depleted.

Enzyme catalysis of reactions is a very rapid process. One enzyme molecule can catalyze the decomposition of millions of organic molecules in less than one minute. The ability of microbial cells to re-use enzymes in such a rapid manner enables the cells to survive with very small quantities of each enzyme. Thus one cell can store many different types of enzymes, allowing it to catalyze up to 1000 different chemical reactions.

2.1.8 Energy Storage Within the Cell

Microorganisms utilize chemical charge “recycling” to capture the energy released during enzyme-catalyzed redox reactions, and to make this energy available for metabolic activities (including the synthesis of new cells).

Released energy is most commonly captured within the cell by an organic compound called adenosine diphosphate (ADP). As soon as this chemical captures the released energy, it transforms to a charged state called adenosine triphosphate (ATP).

The energy contained in ATP compounds is then expended to support cell synthesis, maintenance, and motility. After release of this energy, the ATP molecule will

then convert back to its discharged state (ADP), which becomes available again for capturing energy.

2.1.9 Growth Phases of Individual Populations

Bacteria reproduce predominantly through a process called binary fission, in which one cell divides to become two new organisms.

Figure 2.3 illustrates the four general growth phases for a pure culture: the lag phase, log-growth phase, stationary phase, and the log-death phase.

Figure 2.3 – General phases of population growth. Source: Metcalf and Eddy (1979)

Lag Phase – represents the time required for bacteria to acclimate to new environmental conditions. If a new chemical is introduced to the subsurface environment, it may take on the order of hours to months before significant biodegradation begins to occur (Dragun, 1988). This lag period may be reduced by the presence of organisms that have already been pre-exposed to the chemical of concern. }

Log-Growth Phase – during this period, cells divide at a rate determined by their generation time and their ability to process substrates (constant percentage growth rate) (Metcalf and Eddy, 1979).

Stationary Phase – the population growth reaches steady-state (i.e. the growth of new cells is equal to the rate of death of existing cells). This period is reached when substrates or nutrients become limiting with respect to new growth.

Log-Death Phase – the bacteria death rate exceeds the rate of production of new cells because of insufficient supply of substrate or nutrient conditions.

2.1.10 Concept of the Microbial Consortium

Many different types of microorganism populations are known to co-exist naturally in subsurface soils. Each different population will have specific conditions which are most favorable for population growth. For example, aerobic bacteria will be active (i.e. will grow) in environments where oxygen is present. Anaerobic bacteria may be present in aerobic environments, but exist in a dormant state until the oxygen has become depleted.

For example, nitrate-reducing bacteria will only begin to function once the concentration of oxygen is reduced below a level that inhibits the enzymes required for nitrate utilization (e.g. 0.5 mg/L; Wiedemeier et al., 1999). As discussed in Section 2.2.1, the depletion of electron acceptors during microbial activity results in a decrease in

groundwater redox potential. This will cause a succession of active bacterial populations, which are adapted to specific regimes and electron acceptors.

Under anaerobic conditions, most organic compounds are degraded by groups of interacting microorganisms referred to as a consortium (Wiedemeier et al., 1998).

Individual populations within a consortium carry out complex, specialized functions that may ultimately result in the complete mineralization of organic compounds. The metabolic diversity within a consortium of microorganisms results in the natural biodegradation of a wide variety of organic compounds. The integrated metabolic functions between different populations may be so tightly linked that the consortia can mistakenly be identified as a single species (Wiedemeier et al., 1998).

Wiedemeier et al. (1998) identify key advantages of a consortium as:

- microenvironments may be created where certain types of organisms can survive in otherwise hostile conditions;
- reactions that are not favorable on their own, may be catalyzed by the occurrence of other biochemical reactions in the diverse consortium; and
- linking the diverse enzyme reactions in the consortium may reduce the lag time that occurs when a new chemical is introduced to the environment, relative to the time required for a single species to evolve a new enzyme pathway capable of degrading the substrate.

2.1.11 General Growth Kinetics

Monod (1949) presented the differential equations describing the utilization of a single rate-limiting substrate, and resulting growth of a pure culture of microorganisms suspended in liquid at a constant temperature:

$$\frac{dC}{dt} = -\frac{\mu_{\max}}{Y} X \left[\frac{C}{K_s + C} \right] \quad (2.1)$$

$$\frac{dX}{dt} = \mu_{\max} X \left[\frac{C}{K_s + C} \right] \quad (2.2)$$

where C = substrate concentration $[\text{ML}^{-3}]$;
 t = time $[\text{T}]$;
 $\mu_{\max}$ = maximum specific growth rate (T^{-1}) ;
 Y = yield of biomass growth per mass of substrate utilized $[\text{MM}^{-1}]$;
 X = biomass concentration $[\text{ML}^{-3}]$; and
 K_s = half-saturation constant $[\text{ML}^{-3}]$.

Based on the Monod formulation, the rate of transformation increases with substrate concentration, C , but as C grows large, the rate asymptotically approaches a maximum value given by $(\mu_{\max}/Y)X$. The half-saturation constant, K_s , is equivalent to the substrate concentration at which the transformation rate is one-half of the maximum value.

The equation for substrate utilization (Eq. 2.1) is often simplified by combining the constant maximum specific growth rate and biomass yield terms to give

$$\frac{dC}{dt} = -kX \left[\frac{C}{K_s + C} \right] \quad (2.3)$$

where k = maximum substrate utilization rate $[\text{T}^{-1}]$.

It is apparent from inspection of Eq. 2.3 that linear approximations can be made for certain situations, depending on the relative values for K_s and C . When $C \ll K_s$, then Eq. 2.3 may be approximated by the first-order reaction equation

$$\frac{dC}{dt} = -\left(\frac{kX}{K_s} \right) C \quad (2.4)$$

The bracketed term on the right-hand side is often replaced by λ , which represents the first-order degradation rate for the substrate $[\text{T}^{-1}]$. The important relationship to note

with the first-order degradation equation is that the degradation rate is directly proportional to the substrate concentration.

When $C \gg K_s$, Eq. 2.3 may be approximated by the zero-order reaction equation

$$\frac{dC}{dt} = -kX \quad (2.5)$$

Temperature and pH play a vital role in the life and death of bacteria. The rate of reaction for microorganisms increases with increasing temperature. Metcalf and Eddy (1979) provide the following equation for estimating temperature effects on biological reaction rates:

$$r_T = r_{REF} \theta^{(T-REF)} \quad (2.6)$$

where r_T = reaction rate at temperature of T °C [$\text{ML}^{-3}\text{T}^{-1}$];
 r_{REF} = reaction rate at reference temperature [$\text{ML}^{-3}\text{T}^{-1}$];
 θ = temperature-activity coefficient [dimensionless]; and
 T = temperature [°C].

The typical values of θ for activated sludge, aerated lagoons, and trickling filters are 1.02, 1.08, and 1.08, respectively (Metcalf and Eddy, 1979). Based on this range in values for θ , an increase in temperature of 10°C would result in an increase in biological degradation rate of 1.2 to 2.2. Jakobsen et al. (1998) indicate that temperature will have physiological affects, as well as an affect on thermodynamic equilibrium with reduction reactions that involve hydrogen as an electron donor. Bekins et al. (1998) cite different experiments where it was determined that an increase in temperature of 10°C caused an increase in reaction rate of 150 to 300%.

2.2 MECHANISMS OF BIODEGRADATION

Four primary mechanisms that are generally involved with the degradation of organic compounds: oxidation, fermentation, cometabolism, and reductive dehalogenation.

Oxidation involves a transfer of electrons from the organic substrate (also referred to as the electron donor), to organic or inorganic compounds that act as electron acceptors. *Fermentation* occurs when the organic compound acts as both the electron donor and electron acceptor. *Cometabolism* refers to degradation reactions that do not provide direct benefit to microorganisms. Cometabolic reactions occur when an enzyme responsible for the degradation of the primary substrate results in the fortuitous degradation of other compounds (because of a broad enzyme specificity). *Reductive dehalogenation* occurs when a halogen (e.g. chloride ion) is cleaved from a halogenated molecule and replaced with H^- . Reduction of halogenated compounds may occur co-metabolically, or when the halogenated species acts as an electron acceptor.

The processes involved with each of these biodegradation mechanisms are explained in Sections 2.2.1 through 2.2.4, respectively. Section 2.2.5 presents a summary of the redox-dependent biodegradation mechanisms that play a role in the fate of chlorinated ethenes in groundwater.

2.2.1 Oxidation

There is typically an abundance of inorganic electron acceptors that may be available to support the biodegradation of organic compounds. In general, microbes will

only use those electron acceptors that will result in the greatest release of energy for microbial metabolism.

Typical electron acceptors available in groundwater, in the order of their preferential utilization by microorganisms, are as follows: dissolved oxygen, nitrate, manganese oxide and iron hydroxide coatings on soil sediments, dissolved sulfate, and carbon dioxide (Baedecker and Back, 1979a; Lyngkilde and Christensen, 1992a). Metabolic by-products that may be formed during reduction of these electron acceptors include dissolved manganese, iron, hydrogen sulfide, and methane.

Long-term oxidation of organic substrates results in depletion of the supply of available electron acceptors in a step-wise, or sequential manner, such that the redox potential in groundwater becomes more reducing during the biodegradation process. The sequential development of predominant redox zones downgradient from a source of organic matter is termed *redox zonation* (Jakobsen et al., 1998). If conditions are sufficiently reducing, the following zones are expected to exist in sequence downgradient from the source (Lyngkilde and Christensen, 1992a):

- i. methanogenic zone (methane produced from the reduction of carbon dioxide);
- ii. sulfidogenic zone (sulfate-reducing);
- iii. ferrogenic zone (Fe(III)-reducing);
- iv. manganogenic zone (Mn(IV)-reducing);
- v. nitrate-reducing zone; and
- vi. aerobic zone.

Each redox zone is characterized by the dominant terminal electron accepting process (TEAP). The biodegradation mechanisms, rates, and pathways for organic pollutants are strongly dependent on groundwater redox conditions. Therefore, it is important to evaluate redox zonation when assessing the potential for organic pollutant

natural attenuation. When evaluating natural or active remediation technologies, it is also important to consider the inter-dependence between biodegradation and geochemical reactions.

Specific reactions involved with each TEAP are described below.

2.2.1.1 Oxygen-Reducing Zone

Oxygen reduction provides a large amount of energy for microbial metabolism, and often occurs very rapidly. In some cases, the aerobic biodegradation of petroleum hydrocarbons is so rapid relative to groundwater velocity that it can be assumed to be an instantaneous reaction (Wiedemeier et al., 1999). Because oxygen depletion occurs very quickly during aerobic biodegradation, it is likely that oxygen supply will become the limiting factor for aerobic biodegradation.

Wiedemeier et al. (1999) suggest the following conditions must be met before aerobic biodegradation will occur:

- aerobic bacteria must be present;
- oxygen must be present at concentrations greater than 0.5 mg/L; and
- biodegradable organic carbon must be present.

If any of these conditions are violated, then anaerobic biodegradation is likely to predominate (assuming conditions are favorable).

2.2.1.2 Nitrate-Reducing Zone

Nitrate does not form insoluble minerals and does not sorb significantly to organic matter in soils (Appelo and Postma, 1993). Therefore, nitrate is readily available for

reduction during organic matter biodegradation. Nitrate is predominantly reduced to nitrogen gas (N_2) via the overall reaction

Nitrate reduction proceeds through a complex sequence of intermediate reactions involving NO_2^- , NO , and N_2O . These intermediate species are relatively unstable, so the predominant reaction product is N_2 .

Nitrate reduction from reaction with reduced species such as $Fe(II)$, H_2S , and CH_4 may occur in groundwater; however, the kinetics for these abiotic reactions are uncertain and are expected to be slow. Recent evidence (Gouy et al., 1984) indicates that $Fe(II)$ oxidation via nitrate reduction may be biologically mediated (and thus of potential significance), although more experimental work is required to better understand this process.

Nitrate reduction is expected to occur at significant rates during the oxidation of organic matter, pyrite, and $Fe(II)$ -silicates. The energy yield for organic matter oxidation via nitrate reduction is higher than the yield for pyrite oxidation, so organic matter oxidation is expected to occur preferentially when biodegradable organic matter is present (Appelo and Postma, 1993).

Microbially-mediated nitrate reduction to ammonia is a well known process in microbiology (Zhender, 1988), and in some cases has been shown to be a significant process in aquifers (e.g. Smith et al., 1991). However, N_2 appears to be the dominant product of nitrate reduction (Appelo and Postma, 1993).

2.2.1.3 Manganese-Reducing Zone

When the groundwater has become significantly depleted of dissolved oxygen and nitrate, then conditions will be sufficiently reducing for the reductive dissolution of manganese oxide and iron hydroxide coatings to occur. These reactions will result in the mobilization of manganese and ferrous iron in groundwater. The mobilization of manganese will begin prior to that of iron because manganese reduction yields a larger amount of energy for microbial metabolism. However, the concentration of dissolved iron in groundwater is often higher than that of manganese because soil sediments typically consist of a higher iron content (Hem, 1985).

There are several forms of mineral-phase manganese in soil, each having an oxidation state of +4. Pyrolusite (MnO_2 , also known as Mn(IV)-oxide) is the most common manganese coating in soil. Manganite (MnOOH) is an oxyhydroxide coating, but appears to have little significance to organic matter biodegradation.

Manganese reduction in soil involves the reductive dissolution of Mn(IV) to aqueous-phase Mn(II). Once dissolved into solution, Mn(II) is relatively stable until it enters the aerobic zone, where it is subject to second-order oxidation in the presence of oxygen. The oxidation rate of Mn(II) depends partially on pH, which results in a slow rate of Mn(II) oxidation in natural waters relative to the oxidation of Fe(II). Therefore, Mn(II) has a tendency to travel farther distances before it is oxidized and precipitates as MnO_2 (Hem, 1985).

2.2.1.4 Iron-Reducing Zone

Fe(III), also known as *ferric iron*, will act as an electron acceptor during the biodegradation of organic matter. Fe(III) reduction will result in the transformation to *ferrous iron* (henceforth referred to as Fe(II)), which is relatively mobile in reduced groundwater if there is no HS^- or CO_3^{2-} .

Dissolved or chelated Fe(III) is thought to be more biologically reactive than mineral-phase Fe(III) (Ehrlich, 1996). However, at the near-neutral groundwater pH conditions found at many sites, Fe(III) is very insoluble and thus is found predominantly in the mineral phase.

Amorphous Fe(III) [$\text{Fe}(\text{OH})_3$] refers to minerals that have only recently precipitated on soil coatings. These Fe(III) coatings will gradually transform to more crystalline forms over time. The amorphous forms are considered to be significantly more reactive than the more crystalline forms because of their higher energy yield during Fe(III) reduction. Reduced surface area in the more crystalline form is thought to play a role in the reduction in reactivity (Rohen and Zachara, 1996).

Kennedy et al. (1998) provide the following examples of mineral-phase Fe(III) in increasing order of crystallinity (and decreasing order of reactivity): ferrihydrite rust, $\text{Fe}(\text{OH})_3$ (henceforth referred to as iron hydroxide); lepidocrocite and akageneite, γ - and β - FeOOH ; goethite, α - FeOOH ; and hematite, α - (Fe_2O_3) . The form of Fe(III) in soil is important to the extent and rate of iron reduction, and may also play a role in the simultaneous occurrence of iron and sulfate reduction. (Refer to Section 2.2.1.7 for a discussion of the role that hydrogen plays in competition between iron and sulfate reduction.)

The bioavailability of different forms of mineral-phase Fe(III) is determined partially by their reactivity, and also by their spatial distribution. Fe(III) must be available for direct enzymatic reduction. For example, a significant portion of Fe(III) may be present as a coating on silicate minerals such as quartz; therefore, only the outermost layer will be immediately accessible to bacteria (Kennedy et al., 1998).

Based on the limited bioavailability of Fe(III), it is difficult to quantify the proportion of total Fe(III) in soil that is available for microbial reduction. It is also difficult to assess the amount of Fe(III) reduction by measuring Fe(II) in groundwater, because much of the reduced Fe(II) may precipitate in new minerals such as iron sulfides (FeS or FeS₂), siderite (FeCO₃), or magnetite (Fe₃O₄), or may be exchanged with other cations through the process of ion exchange.

It is also important to note that another potential sink for Fe(III) may be through reaction with HS⁻ produced upgradient due to sulfate reduction, and subsequent formation of FeS_(s). Refer to Section 2.2.1.5 for a more detailed description of this process. Increases in iron sulfide mineral content have been documented in aquifers contaminated with iron-rich landfill leachate (e.g. Heron and Christensen, 1995).

The mobility of Fe(II) in groundwater is also strongly influenced by redox potential and pH conditions. Fe(II) oxidation downgradient from the iron-reducing zone (and subsequent precipitation as amorphous iron hydroxide) occurs almost immediately in the presence of oxygen. Fe(II) will also react quickly with sulfide dissolved in groundwater to form pyrite because this mineral is relatively insoluble under reducing conditions; this reaction is particularly important under strong reducing conditions where

dissolved hydrogen sulfide may be present in abundant quantities because of sulfate-reduction.

Ion exchange reactions can have a significant influence on the attenuation of Fe(II) in groundwater (Deutsch, 1997; Heron and Christensen, 1995). Heron and Christensen (1995) conducted a detailed study to determine the speciation of Fe(II) downgradient from a landfill where most of the iron hydroxides had been reduced, and found that up to 20% of the Fe(II) had been attenuated from groundwater through ion exchange processes. Deutsch (1997) suggests that ion exchange of iron can be a significant attenuation process, provided that the cation exchange capacity does not become depleted.

2.2.1.5 Sulfate-Reducing Zone

Sulfate reduction occurs based on the half-reaction equation

Although sulfate concentrations are expected to decrease during sulfate reduction, it is the observation of the author that sulfate concentrations can show an increasing trend during organic matter biodegradation. In some cases, increasing sulfate concentrations have been observed even when dissolved sulfide was observed in groundwater at significant levels, indicating that sulfate reduction was occurring. One potential reason for increasing or stable sulfate concentrations during sulfate reduction involves the dissolution of gypsum ($CaSO_4$) minerals, as a result of increased alkalinity and carbonate equilibrium processes (Apello and Postma, 1993). Another possibility for increased

sulfate concentrations is aqueous complexation with calcium, resulting in the supersaturation of sulfate-bearing minerals.

A significant portion of the hydrogen sulfide produced during sulfate reduction will react with Fe(III) minerals in the soil to form iron sulfide minerals. Lovley et al. (1991) and Appelo and Postma (1993) indicate that nonenzymatic reduction of FeOOH by hydrogen sulfide will maintain low concentrations of hydrogen sulfide in groundwater. The equation for this oxidation-reduction reaction is

FeS is less stable than pyrite (FeS₂) but forms kinetically very fast. Over time, FeS undergoes oxidation to pyrite via the reaction

Because FeS is relatively insoluble under typical groundwater conditions, hydrogen sulfide will also react rapidly with Fe(II) to precipitate as FeS. Therefore, measuring Fe(II) or HS⁻ in groundwater is not a good means of quantifying the total extent of iron and sulfate reduction that has occurred in an aquifer.

2.2.1.6 Methanogenic Zone

Methanogenesis is generally characterized by the use of carbon dioxide (CO₂) as an electron acceptor, resulting in the formation of methane (CH₄) as a metabolic by-product. Methanogenesis may also result in the fermentation of acetate (a common metabolite of organic matter fermentation) to methane according to the reaction

Appelo and Postma (1993) cite a study by Iversen and Jorgensen (1985) which indicates that methane was used as an electron donor when coupled with sulfate reduction in marine sediments. The kinetics of anaerobic methane oxidation are uncertain, although Lyngkilde and Christensen (1992a) state that the oxidation of methane coupled with nitrate or sulfate reduction is expected to be slow.

2.2.1.7 Role of Hydrogen in Mediating TEAPs

Our understanding of the role that hydrogen (H_2) plays in mediating TEAPs has advanced considerably in the past decade. Hydrogen also plays an important role in driving the reductive dechlorination of chlorinated ethenes, which is discussed in Section 2.2.4.

Previously, it was assumed that the oxidation of organic matter such as landfill leachate or BTEX was directly coupled with the reduction of electron acceptors. It was also previously thought that the driving force for sequential redox zonation was the differing energy yields associated with each TEAP. These concepts have proven to be useful for understanding the qualitative nature of coupling between geochemical and biological processes. In addition, Lovley and Chapelle (1995) emphasized the importance of physiological controls on microbial metabolism, and competition between different types of microorganisms for electron donors, for the segregation of TEAPs.

Our current understanding has evolved in that we now know organic matter biodegradation generally occurs as a general two-step process, at least when coupled with anaerobic TEAPs (Postma and Jakobsen, 1996):

- organic matter undergoes fermentation, resulting in the production of hydrogen and other metabolites such as acetate and formate; and

- the oxidation of these intermediate metabolites is directly coupled to different TEAPs.

Fermentation can actually involve additional intermediate steps, which are discussed in more detail in Section 2.2.2. The overall production of intermediate metabolites such as hydrogen, acetate, and formate is the same, however.

The intermediate metabolites are typically measured at very low levels in groundwater. Postma and Jakobsen (1996) provide examples indicating that hydrogen is typically measured on the order of nanomoles (nM), acetate and formate are measured on the order of micromoles, and inorganic electron acceptors are normally consumed on the millimole scale.

Hydrogen is a very efficient electron donor (Wiedemeier et al., 1999). Jakobsen et al. (1998) postulate that hydrogen is the most important metabolite governing TEAPs because it is consumed much more rapidly than acetate or formate. This assumption is based on the observation that hydrogen is measured at much smaller concentrations (on the order of nanomoles, or nM) than acetate or formate (on the order of μM), and thus is likely to be oxidizing at a more rapid rate. This is confirmed by Chapelle et al. (1995), who report that the half-life for hydrogen is on the order of seconds.

Postma and Jakobsen (1996) suggest that low metabolite concentrations in groundwater is an indication that the TEAP is significantly faster than the fermentation step. They also hypothesize that the coupled fermentative and TEAP steps represent a partial equilibrium process, where fermentation determines the overall rate, and equilibrium is approached during the reduction of the terminal inorganic electron acceptors.

The energy yield of fermentation is relatively small under natural conditions, and is independent of the TEAP (Postma and Jakobsen, 1996). The principal energy released for microbial metabolism arises from the second step (i.e. reaction of the fermentation metabolite products with individual TEAPs).

Wiedemeier et al. (1999) indicate that interspecies hydrogen transfer between fermenters and hydrogen-utilizing bacteria is a syntrophic process. Hydrogen is a high-energy electron donor that is readily utilized by nitrate-reducers, iron-reducers, sulfate-reducers, and methanogens. Lovley and Goodwin (1988) cite recent experiments which indicate that manganese-reducers use hydrogen almost as efficiently as nitrate-reducers.

Wiedemeier et al. (1999) suggest that the fermenters also benefit from oxidation of hydrogen, because low hydrogen concentrations allow the energetics of the fermentation reaction to remain thermodynamically favorable. Fennell and Gossett (1998) confirm that the fermentation rate of electron donors was observed to decrease when hydrogen concentrations increased in their laboratory bioreactor.

Lovley and Goodwin (1988) hypothesized that reducing microorganisms which function under different TEAPs have different efficiencies for oxidizing hydrogen, resulting in TEAP-specific hydrogen concentration ranges. Lovley and Goodwin (1988) indicate that nitrate- and manganese-reducers oxidize hydrogen so efficiently that steady-state concentrations of hydrogen are maintained below 0.1 nM. Once the nitrate and manganese are depleted, iron-reduction will become the dominant TEAP. Because iron-reducers are not as efficient in scavenging dissolved hydrogen, the steady-state concentrations of hydrogen will rise to a level between 0.2 and 0.8 nM.

Postma and Jakobsen (1996) indicate that the efficiency of Fe(III)-reducers for oxidizing hydrogen is directly dependent on the stability (which correlates with reactivity) of the Fe(III) minerals in soil. As the amorphous Fe(III) coatings become depleted, the remaining (i.e. less reactive) Fe(III) is not as efficient in oxidizing hydrogen, causing gradual increases in hydrogen concentrations. When hydrogen levels increase to the minimum threshold concentration required for sulfate-reducing microorganisms to grow, sulfate reduction will begin to occur concomitantly with Fe(III) reduction.

Postma and Jakobsen (1996) indicate that the extent of the transition zone between Fe(III) reduction and sulfate reduction will depend on the range of reactivity of Fe(III) minerals in soil. A narrow range of stability (and thus a narrow range in reactivity of Fe(III)) will result in a sharp transition between Fe(III) reduction and sulfate reduction. A wide range in Fe(III) reactivity will result in a more diffuse transition zone between these two TEAPs.

Sulfate-reducing bacteria are expected to maintain steady-state hydrogen concentrations between 1 and 4 nM, and methanogenic bacteria will maintain hydrogen concentrations between 5 and 20 nM.

Competition between sulfate reducers and methanogens depends on the abundance of the electron donor supply, as well as the levels of sulfate in groundwater. Vroblecky et al. (1996) reported a site with high electron donor concentrations and low sulfate levels (1.4 mg/L), where concomitant sulfate reduction and methanogenesis was observed. This concomitant activity lasted for approximately 7 months. Vroblecky et al. (1996) suggest that this acclimation time was required for the population of sulfate

reducing bacteria to reach a critical threshold level, at which time they were capable of utilizing all of the substrate (to the competitive exclusion of methanogens).

Vroblesky et al. (1996) also reported that when electron donor supply was limited, sulfate reducers were capable of sequestering all electron flow from hydrogen oxidation (even with very low sulfate concentrations), preventing methanogenesis from occurring. This indicates that the concomitant occurrence of sulfate reduction and methanogenesis will depend on the availability of electron donors, sulfate concentration, and size of the sulfate-reducing population.

It is conceivable that stagnant groundwater zones exhibiting one TEAP may exist within a larger TEAP. For example, Jakobsen et al. (1998) report that a small amount of methane was being produced in an anaerobic aquifer. It was determined that methanogenesis was not energetically favorable, leading the authors to conclude that methanogenesis was occurring in small stagnant groundwater zones within the large-scale plume. As a hypothetical example, it is also conceivable that the heterogeneous distribution of Fe(III) hydroxides will result in varying rates of Fe(III) depletion in neighbouring zones in an aquifer, potentially leading to micro-zones where sulfate-reduction is occurring within a large Fe(III)-reducing zone.

Cozzarelli et al. (2000) indicate that TEAP distribution can vary over small spatial and temporal scales. For example, Cozzarelli et al. (1999) stated that depletion of iron oxyhydroxides in thin vertical zones less than one metre in thickness allowed sulfate reduction to occur. Bekins et al. (1999) found through microbiological profiles of soil at a crude oil spill site that aerobic, iron-reducing, and methanogenic bacteria exhibited spatial zonation on the scale of tens of centimetres.

When investigating the occurrence of TEAPs in the field, it is important to assess the predominant TEAP segregation. The sequence and extent of dominant TEAPs in an aquifer may have a significant influence on the redox-dependent biodegradation of organic pollutants. Although concomitant TEAPs may occur in an aquifer, it is still reasonable to assume that one TEAP will dominate in each specific redox zone (Thomas Christensen, personal communication, 1999).

2.2.1.8 Modeling of Multiple TEAPs

Abrams and Loague (2000) provide a comprehensive review of multispecies reactive transport models that are capable of predicting redox-dependent reactions. These models may be classified as either microbiologically-based or geochemically-based models. It was interesting to note that only one of the 17 transport models reviewed by Abrams and Loague (2000) was three-dimensional; several other three-dimensional models (Lu et al., 1999; Waddill and Widdowson, 1998) are discussed in this section.

Microbiologically-based models (e.g. Essaid et al., 1995) tend to focus on the microbiological aspects of the problem, and thus place less emphasis on evaluating TEAP occurrence based on thermodynamic considerations. The geochemically-based models provide more emphasis on the use of thermodynamic equilibrium to predict inorganic chemical speciation and oxidation-reduction potential. The benefits and limitations of each of these processes are discussed below.

Microbiologically-Based Models

The most well-known reactive transport model used to simulate natural attenuation reactions is RT3D (Lu et al., 1999). The general concepts used to formulate the governing equations for this model will be discussed here, as they are common to other microbiologically-based models.

RT3D provides the capability of simulating TEAP-specific first-order decay rates for a lumped constituent that represents total BTEX concentrations in an aquifer. The BTEX transformation model in RT3D is first-order, and RT3D uses Michaelis-Menten kinetics to represent the influence of electron acceptor concentrations on BTEX utilization. RT3D also uses inhibition coefficients to simulate the inhibitory effects of more energetically-efficient electron acceptors on a specific TEAP.

The RT3D model calculates the rate of BTEX oxidation that occurs in all TEAPs at each time step, in each finite difference grid block. If oxygen concentrations are relatively high, then the predominant TEAP will be aerobic, although RT3D will assume simultaneous oxidation of BTEX is occurring to some degree for all anaerobic TEAPs. The degree of simultaneous BTEX oxidation in each TEAP is dependent on the TEAP-specific inhibition constants used in the model. That is, the total BTEX oxidation rate in one grid cell block at any time step is calculated by the equation

$$r_{BTEX} = r_{BTEX,O_2} + r_{BTEX,NO_3} + r_{BTEX,Fe^{3+}} + r_{BTEX,SO_4} + r_{BTEX,CH_4} \quad (2.12)$$

where r_{BTEX} = total substrate utilization rate [$ML^{-3}T^{-1}$];
 r_{BTEX,O_2} = substrate utilization rate under oxygen reduction [$ML^{-3}T^{-1}$];
 r_{BTEX,NO_3} = substrate utilization rate under nitrate reduction [$ML^{-3}T^{-1}$];
 $r_{BTEX,Fe^{3+}}$ = substrate utilization rate under Fe(III) reduction [$ML^{-3}T^{-1}$];
 r_{BTEX,SO_4} = substrate utilization rate under sulfate reduction [$ML^{-3}T^{-1}$];
 r_{BTEX,CH_4} = substrate utilization rate under methanogenesis [$ML^{-3}T^{-1}$];

The substrate utilization rate for aerobic oxidation is calculated using

$$r_{BTEX, O_2} = -k_{O_2} C_{BTEX} \frac{C_{O_2}}{K_{O_2} + C_{O_2}} \quad (2.13)$$

where k_{O_2} = first-order degradation rate for aerobic BTEX oxidation [T^{-1}];
 C_{BTEX} = aqueous concentration of total BTEX [ML^{-3}];
 C_{O_2} = aqueous concentration of oxygen [ML^{-3}];
 K_{O_2} = half-saturation constant for oxygen [ML^{-3}];

There is no inhibition of aerobic BTEX oxidation because this TEAP is more energetically-favourable than the other TEAPs (nitrate, Fe(III), and sulfate reduction, and methanogenesis). For brevity, only the equation for methanogenic consumption of BTEX will be shown here. The equation for this TEAP is:

$$r_{BTEX, CH_4} = -k_{CH_4} C_{BTEX} \frac{C_{CO_2}}{K_{CH_4} + C_{CO_2}} \left(\frac{K_{i, O_2}}{K_{i, O_2} + C_{O_2}} \right) \left(\frac{K_{i, NO_3}}{K_{i, NO_3} + C_{NO_3}} \right) \left(\frac{K_{i, Fe^{3+}}}{K_{i, Fe^{3+}} + C_{Fe^{3+}}} \right) \left(\frac{K_{i, SO_4}}{K_{i, SO_4} + C_{SO_4}} \right) \quad (2.13)$$

where k_{CH_4} = first-order degradation rate for methanogenic BTEX consumption [T^{-1}];
 C_{CO_2} = aqueous concentration of total BTEX [ML^{-3}];
 K_{CH_4} = half-saturation constant for methanogenesis [ML^{-3}];
 K_{i, O_2} = inhibition constant for oxygen [ML^{-3}].

The variables in the inhibition terms for anaerobic TEAPs follow an analogous convention to those used for the concentration and inhibition constant for oxygen.

The use of inhibition constants in RT3D does not have a physico-chemical basis for representing the complex competition between multiple TEAPs, as discussed in Section 2.2.1.7. There are no known studies that validate the mathematical relationship used in RT3D for simulating concomitant TEAPs in groundwater.

RT3D does not explicitly represent solid Fe(III) and CO₂ concentrations. As an alternative, the model simulates concentrations of aqueous Fe(II) and CH₄, and uses the concentrations of these dissolved metabolites to approximate the capacity for Fe(III) reduction and methanogenesis. The explicit concentration for Fe(III) in Eq. 2.13 is calculated by subtracting the simulated concentration of Fe(II) from the maximum Fe(II) measured in the field. This difference in Fe(II) concentrations is assumed to represent the potential capacity for Fe(III) reduction. This formulation does not consider the actual Fe(III) redox buffering capacity in soil. The concentration for CO₂ used in Eq. 2.13 is calculated in an analogous manner to the calculation of Fe(III) concentration, using the simulated and maximum CH₄ concentrations.

RT3D calculates the oxidation capacity of each of these TEAPs based on differences between simulated concentrations at each grid block, and the maximum concentration of dissolved Fe(II) and methane observed at a site. This implementation has an inherent limitation because it assumes an infinite supply of Fe(III), and thus may not be suitable for simulating long-term intrinsic remediation performance.

The applicability of RT3D for simulating petroleum hydrocarbon biodegradation is limited because there is no basis (or validated input parameters) for the inhibition constants used in Eq. 2.13. This model is also limited because only one lumped constituent can be used to represent the reactive transport of benzene, toluene, ethylbenzene, and xylenes, each of which have widely varying degradation rates, sorption coefficients, and clean-up criteria.

RT3D does have an additional option for simulating first-order sequential transformations of chlorinated ethene species. However, this option does not allow for

coupled simulation of TEAPs, and thus is not appropriate for simulating redox-dependent transport of chlorinated solvents. This RT3D option does allow for spatially-fixed aerobic and anaerobic degradation rates; however, the user must define the boundaries for these zones based on observations in the field, and there is no facility in RT3D to simulate the effect of remediation alternatives on electron donor supply, and subsequent effects on redox zonation.

Essaid et al. (1995) document the application of a sophisticated reactive transport model (BIOMOC) at the Bemidji, Minnesota crude oil spill site. The BIOMOC application simulated volatile and non-volatile organic matter consumption under aerobic conditions, manganese and iron reduction, and methanogenesis in a two-dimensional cross-section. BIOMOC is a two-dimensional transport model.

BIOMOC uses a multiple Monod formulation to simulate single or multiple hydrocarbon consumption, including the effects of competitive and non-competitive inhibition, and the growth of reducing bacteria specific to each TEAP. BIOMOC does not represent sequential first-order transformation reactions.

Similar to RT3D, BIOMOC uses inhibition constants to segregate between the simultaneous consumption of hydrocarbons in all TEAPs. BIOMOC uses a different form for the inhibition constant calculation, although the application presented by Essaid et al. (1995) used inhibition constants such that all TEAPs occurred concomitantly. As discussed in Section 2.2.1.7, the segregation between TEAPs is related to complex thermodynamic equilibrium, and is also a function of mineral speciation and hydrogen concentrations. The inhibition function used in BIOMOC does not have a physical basis; it is simply a fitting parameter (Abrams et al., 1998).

The BIOMOC simulation did provide a general match to trends observed in the field. However, it is not certain that the model provides a valid representation of TEAP segregation given that a total of 27 input parameters were estimated based on literature values to represent the oxidation of one substrate in four different TEAPs (average of six input parameters per TEAP).

Waddill and Widdowson (1998) present the governing equations for a reactive transport model called SEAM3D. This model represents an add-on reaction package to the widely used three-dimensional transport model MT3DMS (Zheng and Wang, 1998). The biokinetic package in SEAM3D is very complex, and includes representation of Michaelis-Menten kinetics for multiple hydrocarbon electron donors, nutrient inhibition, electron acceptor inhibition (similar formulation to the RT3D model), microbial growth, and the formation of metabolic by-products such as Fe(II), hydrogen sulfide, and methane.

SEAM3D uses a very complex biokinetic representation that, similar to RT3D, does not account for the thermodynamic equilibrium which drives segregation between TEAPs, and their simultaneous performance. For the hypothetical transport scenario presented by Waddill and Widdowson (1998), a total of 45 input parameters were required to represent the oxidation of one hydrocarbon in five different TEAPs (average of 9 input parameters per TEAP).

Geochemically-Based Models

Abrams and Loague (2000) suggest that geochemically-based models are advantageous for simulating redox zonation because they utilize thermodynamic

principles to determine which TEAP is most favorable at any point in space and time. The disadvantage of geochemically-based models is that very few of them permit simulation of kinetic reactions during organic matter biodegradation; most geochemically-based models assume equilibrium reactions.

Another inherent limitation with some of these models is that they require calculation of a redox variable (e.g. pE) to determine the oxidation-reduction potential in the aquifer. This pE variable is then used as the decision variable to determine the favorable redox reactions that will occur (e.g. McNab and Narasimhan, 1994). Given that groundwater systems are typically in stable disequilibrium (Lindberg and Runnels, 1984), this calculation in a transport model may not be representative or accurate.

Abrams and Loague (2000) describe a compartmentalized reactive transport model called COMPTRAN, which can accommodate any number of kinetic reactions that compete for dissolved organic carbon, without the use of empirical reaction inhibition. Each reaction can have its own rate parameters and different kinetic formulations. Competing reactions can be either kinetically or thermodynamically limited, including lower-energy redox reactions that lose the thermodynamic competition with higher-energy redox reactions. COMPTRAN also simulates geochemical speciation reactions for inorganic chemicals within each compartment of the model.

To simulate redox zones, the COMPTRAN segregates the TEAPs occurring in the model into different compartments, such that each compartment contains two potential TEAPs (classified as a high-energy and low-energy yielding TEAPs). Each compartment contains overlapping TEAPs. For example, to simulate oxygen, nitrate, Mn(IV) and Fe(III) TEAPs, the model will use 3 compartments: Compartment 1 simulates oxygen

and nitrate reduction; Compartment 2 simulates nitrate and Mn(IV) reduction; and Compartment 3 simulates Mn(IV) and Fe(III) reduction.

The redox reactions in an aerobic aquifer will first be modeled using Compartment 1 TEAPs. The organic matter consumption is simulated as occurring simultaneously with oxygen and nitrate reduction. This process is first modelled using kinetic reactions for each TEAP (Monod or first-order). Then the concentrations of the electron acceptors will be checked, to ensure that thermodynamic equilibrium was not violated. If it is, then the organic matter oxidation will be restricted to occur kinetically, until thermodynamic equilibrium is reached.

The redox zonation will cycle from Compartment 1 to Compartment 2, once the high-energy yielding electron acceptor (i.e. oxygen) is reduced in concentration to a level that is less than a user-defined proportion of the nitrate concentration. Once the simulation has cycled to Compartment 2, nitrate and Mn(IV) reduction will occur simultaneously, following kinetic and thermodynamic constraints.

The advantages of this modeling system, as defined by Abrams et al. (1998), are:

- redox zone development can be simulated without having to calibrate inhibition coefficients;
- simultaneous TEAPs can be simulated
- a global pE variable was not simulated

Overall, COMPTRAN represents the most advanced and flexible model available for simulating coupled biological and geochemical reactions. Potential disadvantages of this modeling system are:

- the assumption that at least two TEAPs occur concomitantly at all times contradicts what occurs at some sites, where one TEAP is considered to be dominant over the lower energy-yielding TEAP (e.g. oxygen and nitrate reduction);

- thermodynamic equilibrium (i.e. free energy of reaction equals zero) rarely occurs in microbially-mediated redox reactions; Jakobsen et al. (1998) and Fennell and Gossett (1998) suggest that a minimum energy threshold is required for microorganisms to store energy as ATP; and
- to accurately determine thermodynamic constraints for each TEAP, one would need to simulate organic matter fermentation, followed by the equilibrium reaction between hydrogen oxidation and the individual TEAP.

The benefits and limitations of microbiologically-based and geochemically-based models were used to develop an alternative reactive transport model, BioRedox, for simulating redox-dependent intrinsic bioremediation of organic matter in groundwater. Refer to Chapter 3 for a description of BioRedox functionality and governing equations.

2.2.2 Fermentation

Fermentation occurs when the organic compound acts as both the electron donor and electron acceptor. As discussed in Section 2.2.1.7, the fermentation of organic matter is an important process that supplies high-energy electron donors such as hydrogen for anaerobic TEAPs.

BTEX compounds are common fermentation substrates at chlorinated solvent sites, although there are many other hydrocarbon substrates that are naturally fermented at sites and result in the generation of hydrogen (Wiedemeier et al., 1999). Examples of easily fermentable organics include acetone, sugars, and fatty acids from landfill leachate.

2.2.3 Cometabolism

It is widely recognized that chlorinated aliphatic hydrocarbon (CAH) compounds are susceptible to aerobic cometabolism in the presence of a suitable substrate.

Monooxygenase enzymes secreted by aerobes during the utilization of substrates such as

methane, toluene, and phenol, have a broad specificity that allow them to rapidly and fortuitously decompose the CAH compounds.

In some cases, methane formed in a source zone may be transported to a downgradient aerobic zone, resulting in the natural cometabolism of CAH compounds. However, this situation has not been observed often in the field (Ron Buchanan, personal communication, 2000). Given that oxygen is rapidly depleted during this reaction, aerobic cometabolism of CAH compounds must typically be an engineered process (Wiedemeier et al., 1999).

2.2.4 Reductive Dehalogenation

Anaerobic reductive dehalogenation is the most important biodegradation reaction for CAH compounds. Reductive dehalogenation can occur via two mechanisms:

- as a cometabolic reaction; or
- the CAH compound is reduced as an alternative electron acceptor, and is coupled with the oxidation of fermentation metabolites such as hydrogen.

The microorganisms responsible for cometabolic reductive dehalogenation are ubiquitous in subsurface soils (Gossett and Zinder, 1996). This process is relatively slow however, and often results in incomplete transformation of chlorinated solvents (Gossett and Zinder, 1996).

The other mechanism for reductive dehalogenation, where CAH compounds act as alternative electron acceptors, has been termed halorespiration (Wiedemeier et al., 1999). This process is driven by dechlorinating bacteria that utilize hydrogen as an electron donor. It is only recently that researchers have begun to understand the importance of hydrogen in the halorespiration process (Gossett and Zinder, 1996).

Although a few other compounds are known to serve as electron donors for dechlorinators (e.g. acetate, formate), these compounds are also products of fermentation (Wiedemeier et al., 1999).

As discussed above, there are many bacteria that utilize hydrogen as an electron donor. Therefore, dechlorinators must compete with other bacteria during halo-respiration. The competition between these bacteria is partially determined by the free energy released during the reduction of the organic and inorganic electron acceptors.

Table 2.2 presents the Gibbs Free Energy for reduction half-reactions for the inorganic TEAPs, and for the chlorinated ethene halo-respiration reactions. From Table 2.2 we can see that amorphous iron hydroxide results in a significantly larger release of energy than more stable forms of iron, such as lepidocrocite (FeOOH) or crystalline goethite (Fe(OH)₃). Refer to Section 2.2.1.4 for a discussion of forms and stabilities of mineral-phase Fe(III).

Table 2.2 – Reduction half-reactions for organic and inorganic electron acceptors.

Electron Acceptor	Reaction	ΔG°_r (kcal/mol e ⁻)
Oxygen	$4e^- + 4H^+ + O_2 \rightarrow 2H_2O$	-28.3
Nitrate	$5e^- + 6H^+ + NO_3^- \rightarrow 0.5N_2 + 3H_2O$	-28.7
Mn(IV)	$2e^- + 4H^+ + MnO_2 \rightarrow Mn^{2+} + 2H_2O$	-28.3
Amorphous Goethite	$e^- + 3H^+ + Fe(OH)_{3,amph} \rightarrow Fe^{2+} + 3H_2O$	-21.5
Lepidocrocite	$e^- + 3H^+ + FeOOH \rightarrow Fe^{2+} + 2H_2O$	-15.0
PCE	$C_2Cl_4 + H^+ + 2e^- \rightarrow C_2HCl_3 + Cl^-$	-14.8
TCE	$C_2HCl_3 + H^+ + 2e^- \rightarrow C_2H_2Cl_2 + Cl^-$	-14.5
DCE	$C_2H_2Cl_2 + H^+ + 2e^- \rightarrow C_2H_3Cl + Cl^-$	-12.1
Vinyl Chloride	$C_2H_3Cl + H^+ + 2e^- \rightarrow C_2H_4 + Cl^-$	-13.8
Crystalline Goethite	$e^- + 3H^+ + Fe(OH)_{3,cline} \rightarrow Fe^{2+} + 3H_2O$	-11.8
Sulfate	$8e^- + 9H^+ + SO_4^{2-} \rightarrow HS^- + 4H_2O$	-5.7
CO ₂	$8e^- + 8H^+ + CO_{2,g} \rightarrow CH_{4,g} + 2H_2O$	-3.9

Table 2.2 also indicates that the energy yield for chlorinated ethene halorespiration is only slightly less than the energy released by the reduction of lepidocrocite, and is greater than the energy released by the reduction of crystalline goethite. The energy yield for halorespiration is significantly greater than the reduction of sulfate or methanogenesis. Table 2.3 (Wiedemeier et al., 1999) provides the overall Gibbs Free Energy of various reduction reactions coupled with hydrogen oxidation. This table also confirms that halorespiration results in an energy yield that is similar to Fe(III) reduction. The form of Fe(III) used to calculate the Gibbs Free Energy shown in Table 2.3 is not known.

Table 2.3 – Free energy for reduction reactions coupled to hydrogen oxidation.

Electron Acceptor	Reaction	ΔG°_r (kcal/mol e^-)
Oxygen	$\frac{1}{2}\text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O}$	-28.5
Nitrate	$\frac{2}{5}\text{NO}_3^- + \frac{2}{5}\text{H}^+ + \text{H}_2 \rightarrow \frac{1}{5}\text{N}_2 + \frac{6}{5}\text{H}_2\text{O}$	-27.0
Fe(III)	$2\text{Fe}^{3+} + \text{H}_2 \rightarrow 2\text{Fe}^{2+} + 2\text{H}^+$	-19.6
PCE	$\text{C}_2\text{Cl}_4 + \text{H}_2 \rightarrow \text{C}_2\text{HCl}_3 + \text{H}^+ + \text{Cl}^-$	-19.7
TCE	$\text{C}_2\text{HCl}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 + \text{H}^+ + \text{Cl}^-$	-19.4
DCE	$\text{C}_2\text{H}_2\text{Cl}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{H}^+ + \text{Cl}^-$	-17.1
VC	$\text{C}_2\text{H}_3\text{Cl} + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}^+ + \text{Cl}^-$	-18.7
Sulfate	$\frac{1}{4}\text{SO}_4^{2-} + \frac{3}{8}\text{H}^+ + \text{H}_2 \rightarrow \frac{1}{8}\text{H}_2\text{S} + \frac{1}{8}\text{HS}^- + \text{H}_2\text{O}$	-4.8
CO ₂	$\frac{1}{4}\text{CO}_2 + \text{H}_2 \rightarrow \frac{1}{4}\text{CH}_4 + \frac{1}{2}\text{H}_2\text{O}$	-4.1

However, given the reliance of halorespiration on hydrogen utilization, it is unlikely that the relative competition between dechlorinators and iron reducers, sulfate reducers, and methanogens will depend solely on thermodynamics.

As discussed in Section 2.2.1.7, different types of bacteria require minimum threshold concentrations of hydrogen before becoming active. For example, Fennell and

Gossett (1998) observed in an experiment that the minimum hydrogen threshold concentration required for halorespiration was “at least as low” as 1.5 nM. This is comparable to the minimum level of 1 nM required for sulfate reduction.

Given the similar energy yields for halorespiration and less reactive forms of Fe(III), it is conceivable that halorespiration may occur when Fe(III) reduction is the dominant TEAP, assuming significant depletion of the amorphous (and more reactive) iron hydroxides has occurred causing hydrogen concentrations to increase above the minimum threshold required for dechlorinators. More research is required to determine the extent to which halorespiration may occur during Fe(III) reduction.

The dechlorinators appear to be more efficient in scavenging hydrogen than sulfate reducers and methanogens. Therefore, halorespiration is expected to occur concomitantly with sulfate reduction and methanogenesis.

The kinetic relationships used to describe dechlorination, including competitive inhibition between chlorinated species and potential competition between dechlorinators and other bacteria, are described in Section 2.3.

2.2.5 Chlorinated Ethene Biodegradation Mechanisms

The previous sections discussed various biodegradation mechanisms responsible for the degradation of organic pollutants in groundwater. Chlorinated ethene compounds undergo redox-dependent biodegradation mechanisms that vary in complexity at different sites. These compounds are common contaminants in groundwater at sites across North America. For this reason, the BioRedox model described in Chapter 3 was specifically designed with the flexibility needed to represent each of the biodegradation mechanisms

involved with these chlorinated ethenes. This section presents a discussion of the mechanisms responsible for the biodegradation of chlorinated ethene compounds (i.e. PCE, TCE, DCE, and vinyl chloride).

The anaerobic reduction of PCE and TCE to ethene (through sequential intermediate products of DCE and vinyl chloride) has been observed at many sites (Ellis, 1996), although the transformations may be incomplete. The processes responsible for dechlorination past DCE are not yet well understood (Gossett and Zinder, 1996). McCarty (1996) provides a general review of the redox-dependent biodegradability of chlorinated ethenes. In summary, the complete transformation from PCE and TCE to ethene will occur only under methanogenic conditions. Under less reducing conditions, such as in the ferrogenic or sulfate-reducing zones, PCE and TCE may be transformed to DCE, but will not be transformed further to vinyl chloride or ethene. Reductive dechlorination of these chlorinated ethenes will not occur in the nitrate-reducing zone.

The aerobic co-metabolism of chlorinated ethenes is generally of little significance unless a suitable electron donor (e.g. methane, ammonia, or phenol) is present (McCarty, 1996). Thus it is important to consider that, in the absence of a suitable electron donor, PCE, TCE, and to a lesser extent DCE, appear to be essentially non-degradable if they reach the nitrate-reducing or aerobic zones. Vinyl chloride is known to undergo rapid oxidation in the aerobic zone, and it is suspected that DCE will also undergo aerobic oxidation if the required bacteria are present (Wiedmeier et al., 1999).

Vinyl chloride and DCE are also known to undergo oxidation under anaerobic conditions when iron (III) is the electron acceptor (Bradley and Chapelle, 1996; Wiedemeier et al., 1999).

Transformation Rates

In general, the rates of reductive dechlorination are most rapid under methanogenic conditions, and become slower with increasing redox potential (Semprini et al., 1995). Also, a higher degree of chlorination generally results in a faster rate of reductive dechlorination (Vogel et al., 1987). Thus the reduction of PCE and TCE occurs at faster rates than the reduction of vinyl chloride.

Based on a survey of multiple sites where the reductive dechlorination of chlorinated ethenes had been identified, Ellis (1996) determined the average half-lives for PCE, TCE, DCE, and vinyl chloride to range from 1.0 to 1.3 years. Based on a similar survey, Wilson et al. (1996) identified the upper range for “reasonable” rates of attenuation of chlorinated ethenes to be 7.3 y^{-1} (equivalent to a half-life of approximately 1 month).

2.3 HALORESPIRATION MODELS

The two most common approaches for representing chlorinated solvent transformations in transport models are Monod or first-order kinetics. Selection of the appropriate reaction representation is based in large part on the objectives of the modeling study, as well as the scale at which chemical transport is to be predicted. The reactive transport model developed for this thesis is intended for prediction of large-scale

plumes in the field. For the purpose of this study, a large-scale plume is defined as being on the order of tens to thousands of metres in length.

This section presents a critical comparison between Monod and first-order kinetic representations for simulating chemical transformations in the field. Section 2.3.1 describes a sophisticated Monod-based transformation model that was successfully validated to chlorinated ethene transformations observed during controlled laboratory experiments. The potential applicability of this sophisticated type of representation for predicting chemical transformations in the field is also discussed. Section 2.3.2 presents a critical analysis that demonstrates first-order degradation kinetics are more appropriate than Monod kinetics for predicting plume transport in the field.

2.3.1 Sophisticated Monod Kinetic Models

Fennell and Gossett (1998) present a comprehensive model for chlorinated ethene halorespiration under methanogenic conditions. The Fennell and Gossett Model (F&G Model) is capable of predicting the fermentation of electron donors, coupled with competition for hydrogen utilization between hydrogenotrophic dechlorinators and methanogens. The F&G Model governing equations employ Michaelis-Menten type kinetics, hydrogen threshold limits, and thermodynamic limitations on donor fermentation.

The F&G Model was successfully validated by simulating laboratory batch reactors of chlorinated ethene dechlorination resulting from addition of different types of electron donors (i.e. butyrate, ethanol, lactate, and propionate). The F&G Model

confirmed that the ability of dechlorinators to use “low levels” of hydrogen at appreciable rates provides dechlorinators with a competitive advantage over methanogens.

This finding is important because it provides a potential explanation as to why halorespiration rates tend to increase with increasingly stronger reducing conditions (Vogel et al., 1987). Halorespiration rates under sulfate-reducing conditions may be relatively slow because dechlorinators have less competitive advantage over sulfate reducers (which also utilize low levels of hydrogen at appreciable rates). Halorespiration under methanogenesis may occur at faster rates because the dechlorinators are capable of sequestering a higher percentage of hydrogen from the fermentation reaction.

Fennell and Gossett (1998) suggest that the F&G Model is particularly useful for evaluating dechlorination performance based on amendments with different electron donors. The authors also suggest that this model is “promising” as a useful and more descriptive biokinetic component that could be incorporated into fate and transport models used for predicting natural or enhanced bioremediation.

The key advantage to the F&G Model is that it simulates the syntrophic relationship between hydrogen-producing microorganisms (fermenters), and hydrogen-utilizing microorganisms (dechlorinators and methanogens). The micro-scale model provides a valuable tool for evaluating the relative performance of dechlorination in the presence of electron donors.

One limitation of the F&G Model is that it does not consider the influence of additional fermentation products such as acetate or formate on dechlorination. The only electron donor assumed to be utilized by dechlorinators was hydrogen. Also, this model did not consider different populations of dechlorinators that may exist in microbial

consortia, nor did it consider the effects of concomitant or transitioning between TEAPs. The model did not consider competitive inhibition between different chlorinated species, although the laboratory experiments were conducted in a manner that minimized the effects of competitive inhibition.

Perhaps the most important limitation of the F&G Model is that it was applied based on empirical input parameters derived from controlled laboratory experiments using a liquid bioreactor at 35°C. The validity of this model has not been demonstrated under field conditions and the inherent complexity associated with large-scale plumes. Factors influencing biotransformation reactions in the field include: complex interaction between biodegradation reactions and groundwater geochemistry; microbial consortia; competition with multiple (and potentially concomitant) TEAPs; competitive inhibition with daughter products of halorespiration, presence of other organic and inorganic chemicals, desorption and diffusion limitations associated with biodegradation in porous media, heterogeneous flow and transport properties, etc.

Fennell and Gossett (1998) also did not indicate how one might apply such a sophisticated model to a field study. Calibration of the F&G model, which involves many input parameters, would be highly non-unique. It may also be possible to use empirical input parameters based on laboratory experiments to represent conceptual “What if” scenarios, but degradation parameters determined based on laboratory studies rarely represent the actual biodegradation rates observed in the field (as demonstrated in Section 2.3.2).

2.3.2 Comparison of Monod and First-Order Kinetic Models

General Representation

Bekins et al. (1998) and Haston and McCarty (1999) suggest that transport models using first-order degradation rates are not appropriate for simulating biodegradation. This hypothesis is based on historical experimental research which has demonstrated that ideal biodegradation processes follow Monod kinetics. However, these and other authors fail to acknowledge the difficulty in deriving input parameters for the Monod kinetic model based on field-scale testing. Nor do they consider that first-order kinetics may actually be just as representative as Monod kinetics, if not more so, when taking into account all of the non-ideal behaviour which influences biodegradation rates in the field. (Refer to Section 2.3.1 for a list of some non-ideal processes and properties that influence biodegradation reactions in the field.)

The obvious difficulties that arise when predicting field-scale biodegradation reactions are often not considered by researchers conducting controlled experiments in the laboratory. Experimental research is very important to elucidate the processes that govern complex biodegradation reactions. However, it is the opinion of this author that there is a distinct need for more bridging between the results of this controlled experimental work, and the development of our understanding of the additional complexities associated with predicting these processes in the field.

Estimating Input Parameters for Modeling Transport in Field

The advantage of using first-order rate kinetics is that there are simple methods available (e.g. Wiedemeier et al., 1998) for calculating site-specific degradation rates

based on measured chemical attenuation between pairs of upgradient and downgradient monitoring wells. These methods account for the different attenuation caused by dispersive and biotransformation processes.

Another advantage of using a first-order kinetic representation, particularly when insufficient data is available to calculate site-specific rates, is the large number of studies reported in the literature which document field-measured first-order rates for a variety of chemicals.

The obvious disadvantage in using Monod kinetics is that estimation of site-specific parameters for the reaction model is not straightforward, and sometimes is not even feasible. Based on the redox-dependent nature of biodegradation kinetics alone, it would be very difficult to determine TEAP-specific Monod kinetic parameters in the field. Adding the complicating effects of competitive inhibition between substrates and TEAPs, heterogeneous properties, time-varying source conditions, and difficulties in measuring specific microbial populations within the soil consortia, it is not feasible at this time to determine input parameters (with a sufficient degree of confidence) for a reactive transport model that incorporates Monod kinetics.

If Monod kinetics are to be represented in a large-scale transport model, then it becomes necessary to estimate rates based on laboratory experiment results reported in the literature. However, perhaps the most imposing limitation in estimating Monod parameters is that the maximum substrate utilization rate, kX , is directly proportional to the microbial population size. The size of different microbial populations may vary by orders of magnitude between different laboratory and field experiments; therefore, it is not appropriate to assume that values for kX are applicable at different sites. It may be

possible to use a fitting model to estimate kX and K_s for a chemical, but calibrating these dependent parameters may result in a non-unique solution.

The following example illustrates the difference between transformation rates that would be predicted using empirical Monod parameters determined in the laboratory, and a range of field-measured first-order degradation rates for chlorinated ethenes.

Comparing Empirical Monod Parameters to Field-Based First-Order Rates

Haston and McCarty (1999) determined Monod kinetics for chlorinated ethene biodegradation in liquid batch reactors at 25°C. Maximum substrate utilization rates (kX) and 95% confidence intervals for PCE, TCE, DCE, and vinyl chloride were determined to be 77 ± 5 , 59 ± 11 , 14 ± 3 , and 13 ± 3 $\mu\text{M}/\text{day}$, respectively. Half-saturation constants (K_s) were determined to be 0.11 ± 0.04 , 1.4 ± 0.9 , 3.3 ± 2.2 , and 2.6 ± 1.9 μM , respectively.

The anaerobic mixed culture used in these experiments was capable of completely dechlorinating PCE to ethene, and was seeded with aquifer material from a PCE-contaminated site in Victoria, Texas. This site had been bioremediated under sulfate-reducing conditions through the addition of benzoate. Haston and McCarty (1999) did not report whether the dechlorinators in these reactors were competing with methanogens for hydrogen from the fermentation reactions. It is assumed that sulfate was not available to support sulfate reduction in the batch reactors.

Haston and McCarty (1999) suggest that the lower kX and higher K_s values for DCE and vinyl chloride may partially explain why incomplete PCE transformation occurs in the field. However, they do not discuss the findings of other researchers, which

indicate that a specific type of dechlorinating bacteria must be present to catalyze DCE dechlorination to vinyl chloride (David Major, Personal Communication, 2000).

A simple spreadsheet was developed to compare substrate utilization rates that would be calculated using Monod kinetics based on the Haston and McCarty values determined in the laboratory, and using first-order kinetics based on a typical range of rates observed in the field.

The Monod equation (Eq. 2.3) was re-arranged to give

$$\frac{dC}{dt} = -\left(\frac{kX}{K_s + C}\right)C \quad (2.14)$$

Eq. 2.14 is arranged in a manner which, facilitates the calculation of an equivalent first-order decay rate that would occur based on the input parameters for the Monod model.

That is, the equivalent first-order decay rate is calculated using

$$\lambda_{eq} = \left(\frac{kX}{K_s + C}\right) \quad (2.15)$$

Using Eq. 2.15, equivalent first-order decay rates were calculated for each chlorinated ethene, based on concentrations values that were specified to range from 1 to 100,000 ug/L. The kX and K_s values derived by Haston and McCarty for each of the chlorinated ethenes (PCE, TCE, DCE, and vinyl chloride) were used in Eq. 2.15.

Figure 2.4 presents the equivalent first-order half-lives that were calculated for each of the chlorinated ethenes as a function of species concentration. The effects of competitive inhibition and temperature were not included in this calculation.

The purpose of this analysis is to demonstrate (Figure 2.4) that the equivalent first-order rate decreases with increasing species concentration. This can easily be confirmed by the simple relationship shown in Eq. 2.15.

The implication of this relationship is that if a first-order degradation is calculated in the field in the vicinity of a source area (where concentrations are highest), the calculated first-order rate will be conservatively slow. In other words, if biodegradation is occurring near a source area following simple Monod kinetics, and a monitoring well

Figure 2.4 – Chlorinated ethene equivalent half-life values for Monod kinetics.

pair near the source area is used to calculate an equivalent first-order degradation rate, then the use of a first-order kinetic model will result in underestimation of the amount of biodegradation occurring near the source area.

The corollary is that a first-order rate calculated based on field-measured concentrations farther downgradient of the source (where concentrations are significantly lower), and the application of this estimated rate in a first-order degradation model, may result in overestimation of the extent of biodegradation occurring in the immediate vicinity of the source.

Another interesting thing to note from Figure 2.4 is that the equivalent half-lives range from 0.001 to 100 days. As discussed in Section 2.2.5, Wilson et al. (1996)

indicate that the lower range for chlorinated solvent biodegradation half-lives, based on field-calculated values, is on the order of 1 month (approximately 30 days). Therefore, using the Monod parameters determined by Haston and McCarty would significantly overestimate the biodegradation rate for chlorinated ethenes when concentrations are less than 10 mg/L.

To assess the effect of temperature, the substrate utilization rates were calculated for temperatures of 10 and 25°C using Eq. 2.15. The Monod rates were then compared to substrate utilization rates calculated using a first-order relationship with half-lives equal to one month and one year (based on field-measured rates presented in Section 2.2.5), using the equation

$$\frac{dC}{dt} = -\lambda_{fd} C \quad (2.16)$$

where λ_{fd} = first-order degradation rate based on field tests [T^{-1}].

Figures 2.5 through 2.8 present the calculated substrate utilization rates for each model, as a function of concentration, for PCE, TCE, DCE, and vinyl chloride, respectively. Inspection of each of these figures indicates that using first-order rates measured at field sites results in significant underestimation of the overall substrate utilization that would be calculated using Monod kinetics based on the laboratory-based Haston and McCarty parameters.

Conclusions that may be inferred from this finding:

- Monod parameters measured in the laboratory may not be representative of general conditions in the field; and
- using field-measured first-order degradation rates is conservative (i.e. underpredicts biodegradation rates) relative to Monod kinetics when the first-order rates are estimated based on near-source concentration trends.

Figure 2.5 – PCE utilization rate versus concentration: comparison between Monod and first-order relationships. First-order half-lives of 1 month and 1 year were used to estimate rapid and slow biodegradation trends.

Figure 2.6 – TCE utilization rate versus concentration: comparison between Monod and first-order relationships. First-order half-lives of 1 month and 1 year were used to estimate rapid and slow biodegradation trends.

Figure 2.7 – DCE utilization rate versus concentration: comparison between Monod and first-order relationships. First-order half-lives of 1 month and 1 year were used to estimate rapid and slow biodegradation trends.

Figure 2.8 – Vinyl chloride utilization rate versus concentration: comparison between Monod and first-order relationships. First-order half-lives of 1 month and 1 year were used to estimate rapid and slow biodegradation trends.

The advantage of utilizing a first-order kinetic representation is that it facilitates representation of field-based estimates of degradation rates (either site-specific rates that are calculated when sufficient data is available, or degradation rates measured in the field at other sites). Field-based estimates of degradation rates serve as bulk parameters that not only incorporate the effects of solute biodegradation, but they also implicitly include the effects of non-ideal behaviour.

Field-based estimates of Monod kinetics are difficult to determine, and are not readily available in the literature. Using empirically-based Monod parameters are more likely to represent biodegradation rates that would occur under ideal and controlled conditions, and will not represent the effects of non-ideal behaviour that inhibits biodegradation rates in the field.

Thus transport models that incorporate empirically-based Monod kinetics to represent idealized biodegradation processes should also incorporate representation of non-ideal processes such as competitive inhibition, rate-limited diffusion and desorption processes, heterogeneity, geochemical reactions that influence ORP and pH, etc, which ultimately reduce the biodegradation rate.

2.4 SUMMARY

The objective of the literature review presented in the preceding sections was to define the important processes influencing the intrinsic bioremediation of chlorinated solvents in groundwater, and to provide insight into limitations of various approaches for predicting the performance of this process.

The general findings of this literature review, in the context of developing a field-scale predictive model, are discussed briefly here.

2.4.1 Redox Zonation

In general, the sequential development of zones follows the relative energy yields associated with different TEAPs. Based on typically available inorganic electron acceptors, TEAPs will be utilized in the following order: oxygen reduction, nitrate reduction, Mn(IV) reduction, Fe(III) reduction, sulfate reduction, and methanogenesis.

Compounds thought previously to act as electron donors, such as landfill leachate or BTEX, are now known to undergo fermentation reactions to produce hydrogen, acetate, and formate. These intermediate metabolites are then utilized as electron donors by anaerobic TEAPs. Hydrogen is the most important of these fermentation metabolites because bacteria are thought to oxidize hydrogen at significantly faster rates than the other intermediate metabolites.

The overall process causing redox zonation may be described as the decomposition of organic matter (e.g. BTEX, landfill leachate, or native organic matter in soil), and the corresponding electrons are transferred to inorganic terminal electron acceptors. This process results in redox zonation in aquifers.

It is possible for concomitant iron and sulfate reduction to occur, depending on the range of stabilities of Fe(III) minerals in the aquifer material. It is also possible for concomitant sulfate reduction and methanogenesis to occur because an acclimation period is required for sulfate-reducing bacteria increase to a minimum threshold level,

because of micro-zones where conditions differ from the bulk of the plume, or because sulfate concentrations are low and electron donor concentrations are high.

Although TEAPs may occur concurrently, it is reasonable to assume that one TEAP dominates in each bulk redox zone in groundwater.

Multiple sinks may reduce the amount of bioavailable Fe(III) during organic matter biodegradation (e.g. reaction with aqueous hydrogen sulfide to cause transformation to iron sulfide minerals). The amount of bioavailable Fe(III) is difficult to quantify with laboratory analysis. Therefore, the implication of iron sulfide mineral formation on organic matter biodegradation is difficult to determine.

There are multiple sources of sulfate that should be considered when evaluating redox zonation, including upgradient or infiltrating recharge, gypsum dissolution arising from alkalinity increases during organic matter biodegradation, or pyrite oxidation near the water table.

Numerous sinks exist for metabolic by-products such as Fe(II), HS^- , and CH_4 . Therefore, the ability to predict mobilization and transport of these parameters during individual TEAPs is limited. It is possible that these metabolic by-products may react with inorganic electron acceptors, thereby reducing the supply of electron acceptors for organic matter oxidation. However, the kinetics of these reactions are not well known, and are expected to be relatively slow.

2.4.2 Chlorinated Ethene Halorespiration

The biodegradation mechanisms, rates, and pathways for chlorinated ethenes are strongly dependent on groundwater redox conditions. All chlorinated ethenes will

undergo halorespiration under strongly anaerobic conditions. TCE, DCE, and vinyl chloride will undergo rapid aerobic cometabolism in the presence of substrates such as methane, toluene, or phenol. Vinyl chloride and DCE will undergo oxidation under aerobic and iron-reducing conditions, although the number of sites at which these reactions are likely to occur is uncertain at this time.

The micro-scale biodegradation processes generally follow Monod substrate utilization kinetics. Factors that reduce the rate of dechlorination in controlled laboratory experiments include competitive inhibition between products of dechlorination, competition for hydrogen between dechlorinators and other bacteria, and decreases in temperature.

Using site-specific first-order degradation rates in transport models is likely to be conservative, relative to Monod kinetics based on empirical parameters determined in the laboratory. First-order degradation rates determined in the field implicitly account for non-ideal behaviour and heterogeneity at the field scale, whereas Monod kinetics determined in the laboratory do not.

More research is required to determine if Monod kinetic transport models are reliable and practical for evaluating field-scale performance of intrinsic remediation.

CHAPTER 3

MODEL DEVELOPMENT

BioRedox is a three-dimensional, multicomponent solute transport model that was developed to represent coupled biodegradation-redox reactions associated with the microbial consumption of organic pollutants. BioRedox is also capable of representing the sequential, redox-dependent biotransformation of chlorinated solvents, with the option of utilizing substrate-limited reaction kinetics.

This chapter presents the development history, general functionality and applicability, governing equations, and solution algorithm for the BioRedox code. Section 3.1 summarizes the general features of the BioRedox model, and Section 3.2 presents a discussion of specific solute classes and phases that may be represented in a BioRedox simulation. Section 3.3 outlines the governing transport equations for aqueous and mineral solutes, and Section 3.4 presents the sorption isotherms. Section 3.5 describes the transformation reaction equations, and Section 3.6 presents the NAPL dissolution and leachate source models incorporated into BioRedox. Section 3.7 presents the numerical implementation details.

3.1 GENERAL

3.1.1 Code Features

BioRedox was developed to provide a predictive tool for evaluating the intrinsic and enhanced bioremediation of organic compounds in groundwater, including petroleum hydrocarbons, chlorinated solvents, and organic matter in landfill leachate. BioRedox

was designed using a unique flexibility for the reaction module that allows BioRedox to be applied to widely varying field situations and biodegradation reaction schemes.

The general principal behind BioRedox is that it explicitly simulates coupled oxidation-reduction reactions using an electron conservation approach. The user defines the number and type of electron donors (i.e. organic substrates), as well as the TEAP half-reduction reactions and the preferential utilization sequence for the list of TEAPs.

BioRedox assumes that one dominant TEAP occurs at any specific point in time and space; that is, BioRedox will not simulate concomitant TEAPs. The selection of predominant TEAP during the simulation is simply based on the user-defined sequence of TEAPs. When the electron acceptor concentration for the first TEAP in the sequence decreases below the user defined threshold concentration, then the code will simulate the kinetic oxidation of electron donors using the next TEAP in the user-defined sequence. Reductions in electron acceptor concentrations, and optional simulation of reduced species formation, are based on electron conservation and stoichiometric coefficients in the oxidation and reduction half-reactions.

This simplified approach solves the problem identified by Abrams and Loague (2000) for microbiologically-based models, which do not consider the energetic favourability of different TEAPs when simulating organic matter consumption. There is no need for inhibition coefficients in BioRedox, because only one TEAP is simulated at any point in time and space. There is also no need to simulate a redox variable such as pE, because the code uses simple logic based on electron acceptor concentrations and threshold criteria as decision variables for driving the sequential utilization of each TEAP.

The strength behind BioRedox is in the flexibility of the reaction algorithm.

Users may define any number of electron donors, electron acceptors, chlorinated solvents, and halogens. The oxidation of multiple substrates is simulated by assuming there is no competition between them when coupled to the dominant TEAP.

Users have the option to define TEAP-specific reaction kinetics, mechanisms (oxidation, cometabolism, or reductive dechlorination), and pathways. For example, the biodegradation options for all solutes are specified for each TEAP, and may include consideration of the following options.

- TEAP-specific kinetics: Either first-order or instantaneous reactions are simulated in each TEAP. Different first-order rates may be specified for each TEAP.
- TEAP-specific mechanisms: Oxidation is represented explicitly through coupling with a TEAP half-reaction, or through simple first-order decay that is not coupled directly with a TEAP. Cometabolism is simulated by specifying one first-order degradation rate when a substrate such as methane is in the aerobic zone above a threshold level, and a different rate when the substrate is below the threshold level. Reductive dechlorination is specified as a first-order reaction with one optional daughter product and the option to represent chloride accumulation. The difference between reductive dechlorination and oxidation for chlorinated solvents is that reductive dechlorination will only occur when a sufficient supply of electron donor is available.
- TEAP-specific pathways – optional daughter products and halogen accumulation (e.g. chloride) may be simulated.
- TEAP-specific substrate-limited kinetics – a Michaelis-Menten formulation may be used to specify the effect of substrate or electron acceptor concentrations on the first-order decay rate (based on the concentration and half-saturation constant of the substrate or electron acceptor).
- TEAP-specific inhibition reaction – simulates one first-order decay rate if an inhibitor solute is above a threshold criteria (e.g. zero for benzene if toluene is present), and a different first-order rate if the inhibitor solute is below the threshold criteria.

The reaction module has been designed to be as simple or as sophisticated as the user needs. For example, BioRedox can be used to simulate single solute first-order decay

with no representation of TEAPs, or it can be used as a fully reactive, multispecies transport model.

In addition to the flexible reaction module in BioRedox, important redox zone visualization capabilities have been incorporated into BioRedox to facilitate the analysis and presentation of complex models involving redox-dependent transport of multiple solutes. Solute property and redox reaction databases have been incorporated into BioRedox to simplify the preparation of model input files. A flexible input structure eliminates the need for hardwiring reaction options into the program, providing a broad scope of applicability for the BioRedox code. A global mass balance report provides information for analyzing and documenting model simulations.

New source models have been incorporated into BioRedox to enhance the options available for simulating time-varying source concentrations. A recharge source term has been developed to simulate exponentially-decaying landfill leachate concentrations recharging to an underlying aquifer. Another source model represents immobile, multicomponent NAPL dissolution based on equilibrium or rate-limited kinetics. The NAPL constituent dissolution flux is calculated at each time step based on the mole fraction and solubility of each constituent in the multicomponent NAPL phase.

BioRedox does not support the input of transformation kinetics that are dependent on spatial location within the model domain. As an alternative, BioRedox allows the user to specify transformation kinetics (i.e. rates and pathways of transformation) that are dependent on simulated redox conditions, the presence and concentration of other substrates, and/or inhibitors of biodegradation. This is more of a process-based representation, and allows for prediction of the influence that active source control

measures may have on downgradient redox zonation, and the subsequent influence of changes in redox zonation on organic pollutant biodegradability.

3.1.2 Model Applications

BioRedox was specifically designed to have a broad base of potential applications, with a focus on the simulation of natural or enhanced bioremediation of BTEX, CAH compounds, and organic-rich landfill leachate in groundwater. General applications for BioRedox can be segregated into three categories:

- (a) single solute transport (i.e. same functionality as MT3D);
- (b) multicomponent transport of chlorinated solvents with sequential transformation pathways (without representation of coupled biodegradation-redox reactions); or
- (c) multicomponent transport to simulate redox zone development (based on the coupled oxidation of electron donors and the sequential reduction of electron acceptors), with the option to incorporate redox-dependent biodegradation kinetics and transformation pathways for co-contaminants such as chlorinated solvents.

BioRedox is capable of simulating the production of methane in the methanogenic zone, and the corresponding transport of the dissolved methane downgradient from this zone. The simulation of methane transport is important if an aerobic zone exists downgradient from a methanogenic zone in an aquifer, because of the potential for methanotrophic co-metabolism of chlorinated solvents under aerobic conditions.

BioRedox is also capable of representing the production of aqueous Fe(II) in the Fe(III)-reducing portion of an aquifer, as well as the coupling between ferrous iron oxidation and the reduction of oxygen. This coupled reaction has an important influence on the extent of the anaerobic zone downgradient from a source area, and can therefore be important when predicting the sequential anaerobic-aerobic treatment of chlorinated solvents in groundwater.

3.1.3 Model Limitations

BioRedox provides partial representation of the complex physical, biological, and geochemical processes that influence the biodegradation of organic compounds in groundwater. Although this model may have important applications as a predictive tool, it is important that the limitations of this model be considered relative to the purpose and scope of the desired applications.

As discussed in Chapter 2, we have observed concomitant iron and sulfate reduction, or sulfate reduction and methanogenesis at field sites. This is partially based on the range of Fe(III) stabilities in soil, complex physiological and thermodynamic considerations, and heterogeneity in Fe(III) and sulfate distributions. Obviously, BioRedox is limited in this respect because it is based on the assumption that only one TEAP may occur at any point in space and time. This is in agreement with the general understanding that one TEAP remains dominant, even when concomitant TEAPs may be occurring (Thomas Christensen, personal communication, 1999).

The key point to consider is the affect that concomitant TEAPs may have on the biodegradation of organic pollutants represented in the simulation model. For example, TCE may not undergo halorespiration when an abundant supply of amorphous Fe(III) is present (refer to Tables 2.2. and 2.3). However, when the amorphous Fe(III) is significantly depleted, the remaining Fe(III) will be less reactive, and thus may be reduced concomitantly with sulfate reduction and/or halorespiration of TCE (because of an increase in hydrogen concentrations).

In BioRedox, it is possible to specify that TCE will not undergo reductive dechlorination when Fe(III) concentration is above a user-defined threshold. The

threshold concentration can be used to represent conditions during which amorphous iron reduction maintains hydrogen levels below the threshold required for halorespirators. The user may then define a finite first-order rate for TCE when simulated Fe(III) concentrations decrease below the user-defined threshold, indicating that halorespiration will occur during reduction of the less reactive Fe(III) minerals. So although BioRedox does not represent concomitant TEAPs, it is possible to use the substrate-dependent rate option to simulate approximate dechlorination trends anticipated to occur during depletion of electron acceptor concentrations in the Fe(III) or sulfate reducing TEAPs.

Another limitation of BioRedox is that it does not provide explicit representation of the complex geochemical processes that influence the bioavailability of electron acceptors, such as mineral precipitation and dissolution, aqueous speciation, ion exchange, and surface complexation. The utilization of BioRedox to provide a simplified representation of groundwater redox conditions must be made with caution, and only after a site-specific assessment of groundwater geochemistry confirms that this conceptual model provides a suitable representation of site conditions for the purpose of the application.

BioRedox represents equilibrium partitioning between the aqueous and sorbed phases. The rate-limited desorption of organic pollutants has been observed to be an important process that influences the bioavailability of these species, and should be carefully considered when evaluating simulation results using BioRedox.

Also, BioRedox and MT3DMS are both based on the assumption that all solutes in a multispecies simulation have equal diffusion coefficients. This may limit the applicability of these codes when simulating multispecies transport in diffusion-

dominated situations (e.g. transport through silt or clay zones where groundwater velocity is very slow).

3.1.4 Development History

The original version of BioRedox, Version 1.0, was developed in 1998 based on the public domain version of MT3D (Version DoD_1.5), which is a three-dimensional model for simulating the transport of a single solute in groundwater (Zheng, 1990). MT3D provided an excellent platform for adding multispecies biodegradation-redox reactions and NAPL dissolution source models, because the original MT3D code was developed using a modular format that allowed for easy code modification and expansion.

In June 1998, MT3DMS DoD_3.00.A (Zheng and Wang, 1998) was released to the public domain. MT3DMS includes valuable technological advancements that significantly improve some of the mathematical formulations for simulating contaminant transport in saturated porous media. MT3DMS was also developed with a framework for supporting multispecies simulations, and now serves as the base module for several reactive transport subroutines that have been developed in conjunction with the MT3D/MT3DMS technology.

In 1999 BioRedox was revised so that it is now directly integrated with the MT3DMS source code. The primary components of BioRedox include the Reaction module and the NAPL dissolution source module. BioRedox (V2.0) provides some of the advanced features included in MT3DMS for solving the advection term of the

transport equation, as well as the sophisticated reaction and NAPL dissolution capabilities provided by the BioRedox code.

The features that are included in MT3DMS Release DoD_3.00.A, but not included in BioRedox V2.0, include:

- implicit finite difference formulations;
- dual-domain mass transfer reactions; and
- non-equilibrium sorption reactions.

The sophisticated features that BioRedox brings to the integrated BioRedox-MT3DMS transport code are discussed in the following section.

3.2 SOLUTE DEFINITIONS

3.2.1 Solute Classes

There are four types of solute classes for BioRedox simulations: electron donors, electron acceptors, general solutes, and halogens. *Electron donors* and *electron acceptors* participate in coupled oxidation and reduction half-reactions, respectively. BioRedox simulations will include one or more electron donor and electron acceptor solutes when it is necessary to simulate the development of redox zones in an aquifer. The redox zone TEAPs simulated using BioRedox are defined based on the dominant electron accepting processes.

General solutes are defined as solutes that do not directly participate in the coupled oxidation-reduction reactions; however, it is possible to simulate biodegradation reactions for general solutes that are directly dependent on the redox conditions (i.e. the TEAP) simulated for each model grid block. For example, it is possible to simulate

biodegradation rates and transformation pathways for TCE (a general solute) that vary within each simulated redox zone.

Halogens are defined as conservative solutes (such as chloride or bromide), which are produced during the transformation of halogenated parent compounds. For example, using BioRedox it is possible to simulate the straight-chain sequential transformation of TCE to DCE (both general solutes), as well as the corresponding release of chloride (a halogen solute). Refer to Section 3.5.4 for a description of the halogen reaction model incorporated into BioRedox.

3.2.2 Solute Phases

BioRedox simulations may include both *aqueous* and *mineral* solutes. Aqueous solutes are present in the dissolved phase in groundwater, and some aqueous solutes may also be present in a sorbed phase if organic carbon partitioning occurs between the dissolved phase and sediment organic matter. Aqueous solutes are subject to all relevant transport processes, which may include advection, dispersion, sorption, sinks/sources, and transformation reactions.

Mineral solutes are assumed to be immobile in soil and exist solely in a solid state. Mineral solutes are subject only to transformation reactions, and should not be confused with the sorbed phase of an aqueous solute. BioRedox is capable of representing the phase transition that may occur during these reaction mechanisms (e.g. from the aqueous to the mineral phase, or vice versa). For example, it is possible to represent the reductive dissolution of mineral-phase ferric hydroxide coatings ($\text{Fe}(\text{OH})_3(\text{s})$) to dissolved ferrous iron (Fe^{2+}). Representation of this phase transition is accomplished

through a mass conservation equation, which represents the mass transfer from a solute in one phase to a second solute in the other phase. This is explained further in Section 3.5.

Coupled transformation reactions involving aqueous and mineral solutes is accomplished in BioRedox by converting the mineral-phase solute concentrations (typically reported in dimensions of mass-solute per mass-soil) to an equivalent aqueous-phase concentration (dimensions of mass-solute per volume-groundwater) using

$$C_m = \frac{X_m \rho_b}{\theta} \quad (3.1)$$

where C_m is the equivalent aqueous-phase concentration of mineral solute m [ML⁻³];
 X_m is the mineral-phase concentration of solute m [MM⁻¹];
 θ is the saturated porosity of the porous medium [L³L⁻³]; and
 ρ_b is the dry bulk density of the porous medium [ML⁻³].

3.3 GENERAL TRANSPORT EQUATIONS

3.3.1 Aqueous Solutes

The partial differential equation describing the advection, dispersion, sink-source mixing, retardation, and transformation reactions for aqueous solutes (denoted by the index w) can be written as (Zheng, 1990)

$$R_w \frac{\partial C_w}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij,w} \frac{\partial C_w}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C_w) + \frac{q_s}{\theta} C_{s,w} \pm G_{R,w} \quad (3.2)$$

where C_w is the dissolved-phase concentration of solute w [ML⁻³]
 t is time [T];
 R_w is the retardation coefficient for solute w [dimensionless];
 x_i is the distance along the respective Cartesian coordinate axis [L];
 $D_{ij,w}$ is the hydrodynamic dispersion coefficient for solute w [L²T⁻¹];
 v_i is the average linear groundwater velocity [L/T];
 q_s is the volumetric flux of water per unit volume of aquifer representing sources (positive) and sinks (negative) [T⁻¹];
 $C_{s,w}$ is the dissolved-phase concentration of sources/sinks for solute w [ML⁻³];
 and

$G_{R,w}$ is the general reaction term for solute w , including biotransformations and rate-limited NAPL dissolution [$\text{ML}^{-3}\text{T}^{-1}$].

The retardation coefficient is further defined as

$$R_w = 1 + \frac{\rho_b}{\theta} \frac{\partial S_w}{\partial C_w} \quad (3.3)$$

where S_w is the sorbed-phase concentration of solute w [MM^{-1}].

3.3.2 Mineral Solutes

The general equation describing the transformation reactions for immobile mineral solutes (denoted by the index m) is given by

$$\frac{\partial C_m}{\partial t} = \pm G_{R,m} \quad (3.4)$$

where $G_{R,m}$ is the general transformation reaction term for solute m [$\text{ML}^{-3}\text{T}^{-1}$].

3.4 SORPTION ISOTHERMS

Zheng (1990) provides a thorough review of the general assumptions and isotherms describing linear and non-linear partitioning between the dissolved and sorbed solute phases, and a portion of this work is summarized in this section.

It is assumed that the mechanisms driving mass transfer between the dissolved and sorbed phases follow an equilibrium process. BioRedox incorporates the effects of sorption through the retardation factor R_w , and three types of sorption isotherms are available: linear, Freundlich, and Langmuir.

3.4.1 Linear Isotherm

The linear sorption isotherm assumes that the sorbed concentration for solute w is directly proportional to the dissolved concentration of solute w , as indicated by

$$S_w = K_{oc,w} f_{oc} C_w \quad (3.5)$$

where $K_{oc,w}$ is the organic-carbon partitioning coefficient for solute w [L^3M^{-1}]; and f_{oc} is the fraction of organic carbon in the porous medium [MM^{-1}].

The retardation factor for the linear sorption isotherm is then defined as

$$R_w = 1 + \frac{\rho_b}{\theta} K_{oc,w} f_{oc} \quad (3.6)$$

3.4.2 Freundlich Isotherm

The Freundlich isotherm is a non-linear isotherm, and is expressed as

$$S_w = K_{f,w} C_w^{\alpha_w} \quad (3.7)$$

where $K_{f,w}$ is the Freundlich constant for solute w [units depends on exponent α_w]; and α_w is the Freundlich exponent for solute w [dimensionless].

Both $K_{f,w}$ and α_w are empirical constants. When α_w is equal to 1, the Freundlich isotherm is equivalent to the linear isotherm. The retardation factor for the Freundlich isotherm is defined as

$$R_w = 1 + \frac{\rho_b}{\theta} \alpha_w K_{f,w} C_w^{\alpha_w-1} \quad (3.8)$$

3.4.3 Langmuir Isotherm

The Langmuir isotherm is described by

$$S_w = \frac{K_{l,w} N_s C_w}{1 + K_{l,w} C_w} \quad (3.9)$$

where $K_{l,w}$ is the Langmuir constant for solute w [L^3M^{-1}]; and
 N_s is the total concentration of sorption sites available [MM^{-1}].

The retardation factor for the Langmuir isotherm is defined as

$$R_w = 1 + \frac{\rho_b}{\theta} \left[\frac{K_{l,w} N_s}{(1 + K_{l,w} C_w)^2} \right] \quad (3.10)$$

3.5 TRANSFORMATION REACTIONS

The options available in BioRedox for specifying reaction rates and sequential transformation pathways are specific to each solute class. As discussed in Section 3.2.2, BioRedox is capable of representing phase transitions between aqueous and mineral solutes during these transformation reactions. This transition is readily accomplished because aqueous and mineral solutes are represented in BioRedox with consistent dimensions, as shown by Equation 3.1.

The following sections present the transformation reaction models available for electron donors, electron acceptors, general solutes, and halogens. Differences in equations representing various reaction mechanisms for aqueous and mineral solutes, where they occur, are noted in the following sections.

3.5.1 Electron Donors

BioRedox provides two kinetic models for representing the transformation of electron donors: instantaneous reactions (limited by the electron acceptor supply) and

first-order reactions. The models for each of these reactions are described in the following sections.

3.5.1.1 Instantaneous Reaction Model

The instantaneous reaction model may only be specified for the dissolved-phase of aqueous electron donors because it involves a coupling with the reduction of an electron acceptor solute. It is assumed that instantaneous kinetic reactions are not applicable to solid-phase electron donors (such as native organic matter) or to the sorbed-phase of aqueous electron donors.

The fundamental concept behind this model is that the oxidation of the electron donor will occur very rapidly relative to groundwater flow, and is only limited by the available supply of the electron acceptor. In other words, the time required to mineralize the electron donor (assuming a sufficient supply of electron acceptor is available) approaches an instantaneous reaction. For example, this model is sometimes used to represent the oxygen-limited aerobic biodegradation of petroleum hydrocarbons such as benzene.

The instantaneous reaction model is defined as

$$G_{R,w} = \frac{C_a}{\mu_{ad}\Delta t} \quad (3.11)$$

where C_a is the concentration of electron acceptor a [ML⁻³];
 μ_{ad} is a stoichiometric ratio expressed in mass of electron acceptor consumed per mass of electron donor utilized [MM⁻¹]; and
 Δt is the time-step duration [T].

Equation 3.11 is restricted by the condition

$$G_{R,w}\Delta t \leq C_d \quad (3.12)$$

where C_d is the dissolved-phase concentration of electron donor d [ML^{-3}].

3.5.1.2 First-Order Reaction Model

Aqueous Solutes

The complete reaction equation for aqueous solutes, incorporating the effects of both solute degradation and solute production from the straight-chain, sequential degradation of a parent solute, is given by

$$G_{R,w} = -\lambda_{a,w} C_w - \lambda_{s,w} \frac{\rho_b}{\theta} S_w + \mu_w \lambda_{a,w-1} C_{w-1} + \mu_w \lambda_{s,w-1} \frac{\rho_b}{\theta} S_{w-1} \quad (3.13)$$

where $\lambda_{a,w}$ is the first-order, dissolved-phase degradation rate of solute w [T^{-1}];
 $\lambda_{s,w}$ is the first-order, sorbed-phase degradation rate of solute w [T^{-1}];
 μ_w is the stoichiometric coefficient for the transformation of parent solute $w-1$ to solute w [MM^{-1}];
 $\lambda_{a,w-1}$ is the first-order, dissolved-phase degradation rate of the parent solute $w-1$ [T^{-1}];
 C_{w-1} is the dissolved-phase concentration of the parent solute $w-1$ [ML^{-3}];
 $\lambda_{s,w-1}$ is the first-order, sorbed-phase degradation rate of the parent solute $w-1$ [T^{-1}]; and
 S_{w-1} is the sorbed-phase concentration of the parent solute $w-1$ [MM^{-1}].

The equation describing the stoichiometric coefficient (μ_w) for the transformation of the parent solute $w-1$ to solute w is

$$\mu_w = \frac{MW_w}{MW_{w-1}} \beta_w \quad (3.14)$$

where MW_w is the molecular weight of solute w [M mole^{-1}];
 MW_{w-1} is the molecular weight of the parent solute $w-1$ [M mole^{-1}]; and
 β_w is the number of moles of daughter solute w produced during the transformation of 1 mole of the parent solute $w-1$ [mole mole^{-1}].

If a parent solute does not exist, then Eq. 3.13 may be simplified to

$$G_{R,w} = -\lambda_{a,w} C_w - \lambda_{s,w} \frac{\rho_b}{\theta} S_w \quad (3.15)$$

BioRedox provides the option to represent substrate-limited reaction kinetics based on a simple Monod term that is defined by the substrate concentration divided by the sum of the substrate half-saturation constant and substrate concentration.

Mineral Solutes

It is possible to represent the first-order oxidation of mineral-phase electron donors, such as native organic matter in the soil sediments. The first-order oxidation model for mineral solutes is given by

$$G_{R,m} = -\lambda_m C_m \quad (3.16)$$

where λ_m is the first-order degradation rate for solute m [T⁻¹].

3.5.2 Electron Acceptors

The biodegradation (i.e. oxidation) of an electron donor in groundwater is always coupled with the reduction of an electron acceptor. Therefore, it is possible to have two different species of an electron acceptor present in groundwater: the *oxidized* species, which is the state that exists prior to the reduction of the electron acceptor; and the *reduced* species, which is the state that exists after the reduction of the electron acceptor.

BioRedox is capable of representing both the oxidized and reduced species of an electron acceptor as two distinct solutes. The oxidized species is defined as an electron acceptor solute, and the reduced species must be defined as an electron donor solute. In this manner, the downgradient transport (and subsequent oxidation) of the reduced

species of an electron acceptor, such as methane or ferrous iron, may be represented in a BioRedox simulation.

In BioRedox, the reduction of electron acceptors is coupled to the oxidation of one or more electron donors through a system of mass conservation equations. These equations are presented below. A detailed algorithm describing the steps that are followed for the solution of these equations is presented in Section 3.7.3.

The number of electrons transferred during the first-order oxidation of aqueous-phase electron donors, $G_{OXC,w}$, is determined using the equation

$$G_{OXC,w} = \sum_{k=1}^{ndonor} \left[\left(\lambda_{w,k} C_{w,k} + \lambda_{s,k} \frac{\rho_b}{\theta} S_k \right) \frac{\delta_k}{R_k MW_k} \right] \quad (3.17)$$

where $ndonor$ is the number of aqueous-phase electron donors undergoing kinetic oxidation;

$\lambda_{w,k}$ is the first-order, dissolved-phase degradation rate of electron donor k , T^{-1} ;

$C_{w,k}$ is the dissolved concentration of electron donor k , ML^{-3} ;

$\lambda_{s,k}$ is the first-order, sorbed-phase degradation rate of electron donor k , T^{-1} ;

S_k is the sorbed-phase concentration of electron donor k , MM^{-1} ;

δ_k is the number of electrons donated during the oxidation of 1 mole of electron donor k , equivalence mole $^{-1}$;

R_k is the retardation coefficient for electron donor k , dimensionless; and

MW_k is the molecular weight of electron donor k , $M \text{ mole}^{-1}$.

The number of electrons transferred during the first-order oxidation of mineral-phase electron donors, $G_{OXC,m}$, is determined using the equation

$$G_{OXC,m} = \sum_{k=1}^{ndonor} \left[\left(\lambda_{m,k} C_{m,k} \right) \frac{\delta_k}{MW_k} \right] \quad (3.18)$$

where $ndonor$ is the number of mineral-phase electron donors undergoing kinetic oxidation;

$\lambda_{m,k}$ is the first-order, mineral-phase degradation rate of electron donor k , T^{-1} ;

$C_{m,k}$ is the mineral-phase concentration of electron donor k , ML^{-3} ;

The total number of electrons transferred during the oxidation of all aqueous and mineral-phase electron donors, G_{OXC} , is given by

$$G_{OXC} = G_{OXC,w} + G_{OXC,m} \quad (3.19)$$

The reaction term describing the reduction of the oxidized species of the electron acceptor is given by

$$G_{Ro,a} = G_{OXC} \frac{MW_{o,a}}{\delta_a} \quad (3.20)$$

where $G_{Ro,a}$ is the chemical reaction term for the oxidized species of electron acceptor α [$ML^{-3}T^{-1}$];
 G_{OXC} is the total number of electron equivalents transferred to the electron acceptors during the oxidation of all available electron donors [eq. $L^{-3}T^{-1}$];
 $MW_{o,a}$ is the molecular weight of the oxidized species of electron acceptor α [$M \text{ mole}^{-1}$]; and
 δ_a is the number of electron equivalents utilized during the reduction of 1 mole of electron acceptor α [eq. mole^{-1}].

The reaction term describing the production of the reduced species of the electron acceptor is

$$G_{Rr,a} = G_{OXC} \frac{MW_{r,a}}{\delta_a} \beta_a \quad (3.21)$$

where $G_{Rr,a}$ is the chemical reaction term for the reduced species of electron acceptor α [$ML^{-3}T^{-1}$];
 $MW_{r,a}$ is the molecular weight of the reduced species of electron acceptor α [$M \text{ mole}^{-1}$];
 δ_a is the electron equivalents utilized during the reduction of 1 mole of electron acceptor α [eq. mole^{-1}] and
 β_a is the number of moles of reduced electron acceptor species produced from the reduction of 1 mole of the oxidized species of the electron acceptor.

3.5.3 General Solutes

BioRedox allows for the specification of first-order transformation reactions for general solutes using the same formulations defined for electron donors in Equations 3.13 through 3.16, inclusive. Similarly, it is possible to define substrate-limited reaction rates based on a maximum degradation rate, the concentration of an organic substrate, and the substrate half-saturation constant. It is also possible to define different first-order degradation rates based on the presence or absence of inhibitory solutes, within a user-defined range of threshold concentrations.

3.5.4 Halogens

BioRedox represents the release of halogens during the transformation of halogenated solutes (either electron donors or general solutes) using a formulation analogous to formation of a daughter product during the degradation of the parent solute (Equations 3.13 and 3.14).

3.6 BOUNDARY AND INITIAL CONDITIONS

The boundary and initial conditions for BioRedox are similar to those specified for the MT3DMS model. BioRedox also incorporates a solute source model to provide the capability of representing multicomponent NAPL dissolution into groundwater. A leachate source model has also been incorporated into BioRedox, to represent time-varying leachate constituent concentrations in recharge water to aquifer systems. The general formulations for these new source models are described in Section 3.6.1 and 3.6.2, respectively.

3.6.1 NAPL Dissolution Source Model

Characterizing the presence and composition of light or dense non-aqueous phase liquids (NAPLs) in the field is very challenging, and can sometimes be an impracticable task. However, there are some applications where it may be useful to evaluate the effects of long-term NAPL dissolution on the performance of site remediation alternatives (such as source flushing). For this reason, a multicomponent NAPL dissolution model has been incorporated into BioRedox.

The NAPL source model in BioRedox is based on the work presented by MacKay et al. (1991). The assumptions used to define the NAPL dissolution model include the following:

- groundwater is sufficiently dilute so that the density and molecular mass of the aqueous solution are approximately those of pure water;
- NAPL is not present in an emulsified state in groundwater;
- Raoult's Law is applicable in defining the saturated concentrations for each component of a multicomponent NAPL source; and
- component solubility limits are less than a mole fraction of 1%.

The assumption that Raoult's Law is applicable is reasonable when the species in the NAPL are chemically similar (i.e. from the same class of organic compounds). A significant dissimilarity between chemical species will result in a Raoult's Law activity coefficient for the NAPL phase that is greater than unity, and will thus contribute to some error when ideality (i.e. Raoult's Law) is assumed.

For equilibrium NAPL dissolution, the saturated groundwater concentration for each solute is calculated using

$$C_{sat,i} = S_i f_i X_i \quad (3.22)$$

where $C_{sat,i}$ is the saturated groundwater concentration for solute i [ML⁻³];
 S_i is the solubility limit of solute i [ML⁻³];

- f_i is an efficiency factor for solute i that accounts for bulk mass transfer limitations [%]; and
 X_i is the mole fraction of solute i in the NAPL phase [mol/mol].

The mole fraction for each component in a NAPL mixture is defined by

$$X_i = \frac{n_i}{N} \quad (3.23)$$

- where n_i is the number of moles of solute i present in the NAPL mixture [mol];
 N is the total number of moles in the NAPL mixture [mol];

Rate-limited NAPL dissolution is assumed to follow first-order kinetics, and the source dissolution to the aqueous phase is linked through the general reaction term $G_{R,w}$, based on the relationship

$$G_{R,w} = \lambda_{NAPL,i} (C_{sat,i} - C_w) \quad (3.24)$$

- where $\lambda_{NAPL,i}$ is the first-order NAPL dissolution coefficient for solute i [T^{-1}].

3.6.2 Landfill Source Model

An exponential decay model has been incorporated to reflect the time-varying concentrations of landfill leachate percolating to underlying aquifers. The landfill source model assumes that user-defined leachate constituents percolate readily through the base of the landfill, and dilution or dispersion in the vadose zone between the landfill and the water table surface is ignored.

The model assumes that leachate constituents in the landfill decay exponentially, from a starting concentration at the beginning of the simulation. The leachate constituent concentrations are calculated using the source model at each time step, and are specified as recharge concentrations for the transport model. The model will automatically

calculate the dilution that occurs when contaminants percolate from the vadose zone into the water table aquifer.

3.7 NUMERICAL IMPLEMENTATION

The finite difference method is used to solve the BioRedox partial differential equations representing solute transport. The numerical implementation in BioRedox for this finite difference approximation is similar to the implementation used for the MT3DMS code as described by Zheng and Wang (1998). It is assumed that the reader is familiar with the MT3DMS numerical implementation details; therefore, these details are only presented briefly in this chapter.

3.7.1 Grid and Time Step Discretization

The spatial and temporal discretization for the BioRedox model is consistent with the discretization used for MT3DMS, with the exception that BioRedox does not provide an implicit finite difference formulation. The fixed grid system is based on a block-centered formulation, and BioRedox permits the use of a deformed mesh in the vertical direction (as does MT3DMS and MODFLOW).

The temporal discretization for BioRedox is also consistent with MT3DMS. Stress periods are defined as periods where all external stress parameters are constant. Stress periods are discretized into time steps if the flow simulation is transient, and each time step of the flow simulation model is divided into individual transport steps, during which groundwater hydraulic heads are considered constant. The length of each transport step can be specified in the model input files, or automatically determined by the model

using a minimum allowable stepsize based on the stability criterion presented in Section 3.7.4.1. The user-specified step size will only be used when it is smaller than the maximum allowable step size determined by the model.

3.7.2 General Solution

A fully explicit central finite difference approximation is used to determine a numerical solution to the transport equation. The explicit solution refers to the temporal discretization of the differential approximations, indicating that solute concentrations at a new time step are calculated by using concentrations at the previous time step to approximate the individual terms of the transport equation (i.e. advection, dispersion, and sink/source terms).

Although the explicit scheme is readily incorporated into computer code, it is subject to the stability and accuracy criterion presented in Section 3.7.4. The following presents an algorithm of the general solution for a BioRedox transport simulation.

1. Define the simulation:
 - 1.1 Define solute properties database and redox reactions database.
 - 1.2 Define solutes for each class, and define all reaction rates/pathways.
 - 1.3 Define model dimensions and simulation options.
2. Allocate storage space for data arrays
3. Read and Prepare all other input data relevant to the entire simulation.
4. For each stress period:
 - 4.1 Read and Prepare input data relevant to each stress period.
 - 4.2 For each time step in a transient flow simulation:

- 4.2.1 Read and Prepare input data relevant to each time step.
- 4.2.2 If first stress period, calculate initial mass in storage.
- 4.2.3 Calculate dispersion coefficients constant within each time step.
- 4.2.4 For each transport step:
 - 4.2.4.1 For each aqueous solute:
 - 4.2.4.1.1 Solve for the advection term.
 - 4.2.4.1.2 Solve for the dispersion term.
 - 4.2.4.1.3 Solve for the sink/source term.
 - 4.2.4.1.4 Proceed to next aqueous solute.
 - 4.2.4.2 Solve for the reactions of all aqueous and mineral solutes.
 - 4.2.4.3 Calculate mass budgets.
 - 4.2.4.4 Output relevant data.
 - 4.2.4.5 Proceed to next transport step.
- 4.2.4 Proceed to next time step.
- 4.3 Proceed to next stress period.
- 5. End simulation.

The numerical implementation used to solve the advection, dispersion, and sink/source terms is described in Zheng and Wang (1998). A more comprehensive solution was required to solve the coupled oxidation-reduction-biodegradation reactions for multicomponent solutions, and is described in detail in the next section.

3.7.3 Evaluation of the Reaction Term

GENERAL REACTION ALGORITHM

(This algorithm is applied to each model cell block for each transport time step.)

1. Determine the most preferred electron acceptor available in the model cell block at time t , based on the user-specified sequence. [Further references to electron acceptors in this algorithm, unless otherwise specified, refer to the oxidized species of the preferred electron acceptor.]
2. If there are no electron acceptors available to support the oxidation of electron donors, proceed to Step No. 9.
3. If there is a limited supply of the electron acceptor, calculate the available oxidation capacity supplied by the electron acceptor (OXC_{av}).
4. If there are electron donors that oxidize instantaneously in the presence of the electron acceptor:
 - 4.1 If the supply of the electron acceptor is unlimited:
 - 4.1.1 Simulate the exhaustion of the electron donors that degrade instantaneously.
 - 4.1.2 Simulate the production of the reduced species of the electron acceptor (optional) by coupling to the oxidation of the electron donors assuming mass conservation.
 - 4.1.3 Proceed to Step No. 5.
 - 4.2 Calculate the total oxidation capacity that would be required to support the complete oxidation of all electron donors that degrade instantaneously (OXC_{req});
 - 4.3 If the required oxidation capacity (OXC_{req}) is greater than or equal to the available supply from the electron acceptor (OXC_{av}):
 - 4.3.1 Simulate the exhaustion of the oxidized species of the electron acceptor.
 - 4.3.2 Simulate the production of the reduced species of the electron acceptor (optional).

- 4.3.3 Simulate the coupled oxidation of the electron donor(s) assuming mass conservation and negligible competitive effects between multiple electron donors.
- 4.3.4 Proceed to Step No. 1.
- 4.4 If the required oxidation capacity (OXC_{req}) is less than the available supply from the electron acceptor (OXC_{av}):
 - 4.4.1 Simulate the exhaustion of the electron donor(s).
 - 4.4.2 Simulate the coupled reduction of the electron acceptor through a mass conservation equation and re-calculate the available oxidation capacity (OXC_{av}).
 - 4.4.3 Simulate the production of the reduced species of the electron acceptor (optional).
5. If there are electron donors that undergo first- or second-order kinetic oxidation in the presence of the electron acceptor:
 - 5.1 If the supply of the electron acceptor is unlimited, proceed to Step No. 5.4.
 - 5.2 Calculate the total rate of oxidation capacity utilization (G_{oxc}) required to support the complete oxidation of all electron donors. Note that it is possible for k_{oxc} to equal zero if there are electron donors present, but at concentrations lower than the user-specified minimum threshold limits for these oxidation reactions to occur.
 - 5.3 Calculate the time (t_{oxc}) that would be required to utilize the available oxidation capacity of the electron acceptor, based on OXC_{av} (see Step No. 3) and G_{oxc} .
 - 5.4 If the electron supply is unlimited, or if t_{oxc} is greater than the time-step duration, t_{STEP} , let $t_{oxc} = t_{STEP}$.
 - 5.5 If there is an adequate supply of electron donors (i.e. $G_{oxc} > 0$) then simulate:
 - kinetic oxidation of electron donor(s) over the time period t_{oxc} (assuming negligible competitive effects between multiple electron donors), with the optional production of daughter species and halogens;
 - reduction of the oxidized species of the electron acceptor;
 - production of the reduced species of the electron acceptor (optional);

- kinetic transformations of general solutes which require coupling with the oxidation of one or more electron donors, over time period t_{OXC} , with the optional production of daughter species and/or halogens.
6. If there are general solutes which undergo first- or second-order kinetic transformations as primary substrates, and thus do not require coupling with the oxidation of electron donors (e.g. vinyl chloride oxidation in the aerobic or ferrogenic zones):
 - 6.1 Calculate the time period over which kinetic degradation of the general solutes will occur.
 - 6.2 Simulate the kinetic transformation of these general solutes, with the optional production of daughter species and halogens.
 7. Calculate the amount of time remaining (t_{STEP}) before the end of the transport time step.
 8. If $t_{\text{STEP}} > 0$, proceed to Step No. 1.
 9. RETURN to Main Algorithm.

3.7.4 Stability and Accuracy Criterion

The use of an explicit temporal discretization for solving the transport equation means that the solution is conditionally stable. In other words, the transport step size must be sufficiently small. When the step size exceeds a specified limit, then the numerical errors in the finite difference approximation become amplified as time marches forward, leading to an invalid or unstable solution (Zheng and Bennett, 1995). The step size criteria are evaluated independently for each term in the transport equation, and are presented in Section 3.7.4.1.

Having a stable solution, however, does not necessarily indicate that the solution will be accurate. Numerical dispersion or artificial oscillations that are inherent with the finite difference method may lead to inaccurate solutions if the model grid spacing and

transport time steps are not sufficiently fine. Accuracy criteria are discussed further in Section 3.7.4.2.

3.7.4.1 Stability Criterion

In BioRedox, each of the four step size criterion for the individual terms in the transport equation (advection, dispersion, sink/source, and reaction) are evaluated for each solute and for each active cell. These criterion are then compared to determine the maximum allowed step size for the transport simulation, which is taken as the minimum Δt calculated from the respective criteria.

The stability criterion for the advection, dispersion, and sink/source terms are given by Zheng and Bennett (1995) as:

- Advection:

$$\Delta t \leq \frac{R}{\left(\frac{v_x}{\Delta x} + \frac{v_y}{\Delta y} + \frac{v_z}{\Delta z} \right)} \quad (3.25)$$

- Dispersion:

$$\Delta t \leq \frac{0.5R}{\left(\frac{D_{xx}}{\Delta x^2} + \frac{D_{yy}}{\Delta y^2} + \frac{D_{zz}}{\Delta z^2} \right)} \quad (3.26)$$

- Sink/Source:

$$\Delta t \leq \frac{R\theta}{q_s} \quad (3.27)$$

For problems involving sequential transformation reactions between parent species and daughter products, McNab and Narasimhan (1993) suggest that Δt be equal to

or less than one-third of the shortest half-life in a given transformation chain. Thus the step size criterion used in BioRedox for the reaction term was defined as

$$\Delta t \leq \frac{1}{3} \frac{\ln 2}{\lambda_{\max}} \quad (3.28)$$

where $\lambda_{\max}$ is the maximum first-order decay rate of all solutes included in a BioRedox simulation.

3.7.4.2 Accuracy Criteria

Sharp concentration fronts, or advection-dominated problems, may lead to numerical dispersion or artificial oscillations. The degree of artificial oscillations in a simulation will depend partially on the Peclet number, which is a measure of the degree to which the transport problem is dominated by advection.

The Peclet number is determined using

$$Pe = \frac{\Delta x}{\alpha_L} \quad (3.29)$$

where α_L is the longitudinal dispersivity of the porous medium. Equation 3.29 indicates that the Peclet number may be reduced with a refinement in the spatial discretization.

The corollary of this is that coarse spatial discretizations will result in high Peclet numbers, and will likely lead to oscillatory behavior. In general, when $Pe \leq 2$, oscillatory behavior is eliminated (Huyakorn and Pinder, 1983).

The degree of numerical dispersion in a solution will partially depend on the Courant number, Cr , which is defined using

$$Cr = \frac{v\Delta t}{\Delta x} \quad (3.30)$$

The Courant number can be generally defined as the number of model cell blocks a solute particle is advected through in one time step. To reduce numerical dispersion to an acceptable level, it is generally necessary that the Courant number be less than or equal to a value of 1 (Zheng and Bennett, 1995).

3.7.5 Boundary and Initial Conditions

The boundary and initial conditions for each solute in a BioRedox simulation are consistent with the formulations used in the MT3DMS code (Zheng and Wang, 1998).

3.7.6 Mass Budget

A mass budget is calculated at the end of each transport step, and a summary is provided at user-specified time steps for the total solute mass remaining in storage (dissolved and sorbed phases for aqueous solutes, or the solid phase for mineral solutes), as well as the cumulative mass that has entered or left the groundwater flow system through sinks/sources and transformation reactions.

The mass budget includes a cumulative summary for the following sinks/sources: constant-concentration boundaries, constant-head boundaries, general head-dependent boundaries, wells, drains, rivers, recharge, and evapotranspiration. If redox reactions are simulated, then the mass budget summary will include a cumulative total of the solute mass that is produced or decayed within each individual redox zone. If redox reactions are not simulated, then a total of the cumulative mass that has been produced or decayed for each solute is provided.

The percent error in mass balance is calculated using

$$ERROR = \left[\frac{(IN + ST_o) - (OUT + ST_t)}{0.5(ST_o + IN + OUT + ST_t)} \right] \times 100\% \quad (3.31)$$

where ERROR is the percent error discrepancy.

IN is the total cumulative mass into the groundwater flow system from external sources and produced from reactions;

OUT is the total cumulative mass out of the groundwater flow system through sinks and reactions;

ST_o is the total initial mass in storage; and

ST_t is the total mass in storage at time t;

CHAPTER 4

VERIFICATION

The reliability of groundwater model predictions obtained using BioRedox will depend on three factors (van der Heijde and Kanzer, 1997):

- the degree to which the conceptual model represents processes occurring in the field;
- the availability and quality of model data; and
- the suitability of the predictive tool (i.e. BioRedox).

To provide proper quality assurance (QA) for the development of the BioRedox code, it was necessary to ensure that the final product correctly performs the incorporated functions. A systematic code-testing protocol (van der Heijde and Kanzer, 1997) was followed to provide a rigorous evaluation of code performance.

This chapter documents the quality assurance program that was followed during code development. It also provides detailed documentation of the functionality and applicability of the BioRedox code, so that readers can make an informed decision when evaluating the suitability of BioRedox for specific applications. Section 4.1 outlines the verification strategy, and Sections 4.2 and 4.3 document Level I and Level II test results, respectively. Chapter 5 presents a validation of the model representation of coupled biodegradation-redox processes that was conducted by simulating conditions at Vejen Landfill in Vejen, Denmark.

4.1 VERIFICATION STRATEGY

Table 4.1 presents a detailed functionality list for the BioRedox code. As indicated in Table 4.1, there are various functions for reaction mechanisms and kinetic

models, which provide an important flexibility for site applications. BioRedox also has valuable features that simplify the analysis and reporting of model results. These features include a unique visualization method for evaluating redox-dependent solute biodegradation, and a redox zone mass balance report. BioRedox also has a dynamic link to a solute properties database and a redox reaction database, so that solutes and reactions can easily be added or removed from any simulation.

A comprehensive protocol for groundwater model testing (van der Heijde and Kanzer, 1997) was followed to provide a systematic, efficient approach for testing the performance of the BioRedox code. Where possible, this testing strategy combined the tests required for functionality, performance, and applicability evaluation. A summary of the test objectives, based on the work presented by van der Heijde and Kanzer, is described below.

A three-level code testing strategy was used for this program. The objective of Level I testing was to verify the correctness of coded algorithms, code logic, and programming by: 1) conducting step-by-step numerical tests of all portions of the BioRedox code that represented additions to the MT3D code functions; 2) performing simple, conceptual, and intuitive tests aimed at specific code functions; and 3) comparing BioRedox simulations with independent and accurate benchmarks (e.g. analytical solutions or hand calculations).

The objectives of Level II testing were to verify functions that were not addressed with Level I testing, and to evaluate potentially problematic combinations of functions. At this level, code testing was performed by intracomparison (i.e. comparison between runs with the same code using different functions to represent a particular feature), and

inter-comparison (i.e. comparison between different codes simulating the same problem). Typically, synthetic data sets are used to represent hypothetical problems of a simplified nature.

The objective of Level III testing was to confirm that the theoretical framework for the code provides an adequate level of representation of field-scale processes. Level III tests are typically conducted by simulating laboratory or field-scale experiments and comparing the results.

Sections 4.2 and 4.3 document the Level I and II testing, respectively, that was conducted to verify the performance of the BioRedox code. The verification and validation of a sophisticated transport model such as BioRedox is a rigorous process. Additional tests (Level III) are on-going, with an emphasis on field-scale applications of BioRedox to further validate the comprehensive reaction schemes available in the code, and to assess the needs and requirements for the predictive modeling of natural or enhanced bioremediation alternatives.

Table 4.1 - BioRedox Functionality

Category	Feature	BioRedox
Solution Scheme	MOC, MMOC, HMOC	Yes
	implicit reaction solver	No
Reaction Kinetics	Instantaneous degradation	Yes
	first-order degradation	Yes
	second-order degradation	No
	monod kinetics	No
	redox-dependent rates	Yes
	redox-dependent pathways	Yes
	substrate-dependent rates	Yes
	substrate-dependent pathways	Yes
	inhibitor-dependent rates	Yes
	inhibitor-dependent pathways	Yes
Reaction Mechanisms	multiple electron donors	Yes
	multiple electron acceptors	Yes
	coupled oxidation-reduction half-reactions	Yes
	Oxidation	Yes
	co-metabolism	Yes
	reductive dehalogenation	Yes
	substrate-limited reductive dehalogenation	Yes
	halogen release during reductive dehalogenation	Yes
	straight-chain sequential transformations	Yes
	branched-chain sequential transformations	Yes
	rate-limited adsorption	Yes
	rate-limited desorption	Yes
	microbial transport	No
Source Models	constant concentration	Yes
	landfill exponential decay	Yes
	equilibrium NAPL dissolution (multicomponent)	Yes
	rate-limited NAPL dissolution (multicomponent)	Yes
User Convenience	solute properties database	Yes
	redox reaction database	Yes
	redox zone mass balance reports	Yes
	redox zone visualization approach	Yes

4.2 LEVEL I TEST

Test I was the only Level I test conducted during code verification. Test I involved the benchmarking of BioRedox to an analytical solution of one-dimensional multicomponent transport with first-order, sequential transformation reactions. Van Genuchten (1985) presents the code for a FORTRAN program (CHAIN) which can be used to simulate the complex analytical solution for the transport of up to four species that are involved in sequential, straight-chain first-order transformation reactions.

The CHAIN program was used to simulate the three-species nitrification chain for a one-dimensional soil column using input parameters for a sample problem provided by Van Genuchten (1985). This problem is based on a source of ammonium at the inlet boundary of the column. Ammonium within the soil column is assumed to decay sequentially, under first-order kinetics, to nitrite at a rate of 0.01 h^{-1} , and nitrite in the column decays to nitrate at a rate of 0.1 h^{-1} . It was assumed that nitrate did not decay in the soil column.

The average linear groundwater velocity for this problem was assumed to be 1.0 centimeter per hour (cm/h), and the hydrodynamic dispersion coefficient was assumed to be $0.18 \text{ cm}^2/\text{h}$. The retardation coefficient for ammonium was assumed to equal a value of 2.0, and the retardation coefficients for nitrite and nitrate were both assumed to equal 1.0.

A BioRedox simulation was prepared based on the equivalent input conditions discussed above. The one-dimensional BioRedox model domain was assumed to be 200 cm in length, and was discretized into 400 cell blocks with a uniform width of 0.5 cm

each. The simulation period of 200 hours (h) was discretized into 2000 time steps with a constant step size of 0.1 h.

It is worth noting that the CHAIN model utilizes a third-type (Neumann) boundary condition for the inlet boundary of the column. Van Genuchten (1985) compared the simulation results using CHAIN to a model of the identical problem presented by Cho (1971), which was based on a constant concentration boundary condition at the inlet boundary. This comparison showed that the effect of the different boundary conditions is small for the input parameter values used in this example (Van Genuchten, 1985).

Figures 4.1a, 4.1b, and 4.1c compare the concentration profiles simulated by BioRedox and CHAIN at times of 50 h, 100 h, and 200 h, respectively. These figures illustrate that the BioRedox simulation results closely follow the analytical solution.

Figure 4.1a – Sequential Decay ($t = 50$ hours) Figure 4.1b - Sequential Decay ($t = 100$ hours) Figure 4.1c - Sequential Decay ($t = 200$ hours)

4.3 LEVEL II TESTS

4.3.1 Test II.A - 3D MT3D Comparison

Test II.A involves the intercode comparison between BioRedox and MT3D. The objectives of this test are to verify the three-dimensional, multicomponent solution algorithm for BioRedox, as well as the solute source models (constant source and constant recharge concentrations), and the formulation used in BioRedox to calculate the organic carbon partitioning coefficient (K_d) based on values of K_{oc} and f_{oc} .

The test involved a three-dimensional domain that was 600 m in length, 200 m wide, and 15 m deep. The model was discretized into a regular grid with uniform block dimensions of 5 m length, 5 m width, and 1-m height. Based on this discretization, the total number of cell blocks in the three-dimensional domain was 72,000.

The total duration of the test simulation was 10 years with a regular step size of 4 days, resulting in a total of approximately 920 time steps.

It was assumed for this scenario that there was a shallow source of toluene in the aquifer, which was represented as a constant recharge concentration of 50 mg/L. There was also an assumed DNAPL source of PCE that extended to a depth of 10 m in the aquifer, and this source was represented in both models as a constant concentration of 10 mg/L (specified in the BTN file).

Figure 4.2 illustrates the plan view and cross-section view of the model domain, including the source locations for both toluene and PCE. The aquifer was assumed to have three distinct layers of differing permeability and f_{oc} , as indicated on Figure 4.2. From top to bottom, the values of hydraulic conductivity for the three Hydrogeologic

units were assumed to be 3×10^{-2} , 1×10^{-2} , and 5×10^{-3} cm/s. Also from top to bottom, the values of f_{oc} were assumed to be 0.1%, 0.5%, and 1.0%.

Figure 4.2 - Model Dimensions and Source Conditions

A groundwater flow simulation was conducted using MODFLOW, and was based on a uniform groundwater flow direction from left to right with a horizontal hydraulic

gradient of approximately 0.0022 across the domain. A uniform recharge to the first layer of 210 mm per year resulted in a minor degree of vertical flow in the upper few layers of the domain, although flow through the aquifer was primarily horizontal in nature.

It was assumed that both toluene and PCE were undergoing first-order decay in the aquifer at a rate of $1.9 \times 10^{-3} \text{ day}^{-1}$. The zone-specific K_d values were calculated for toluene and PCE based on K_{oc} values of 1100 and 364 mL/g, respectively; f_{oc} values defined for each hydrogeologic zone; a porosity of 0.30; and a soil dry bulk density of 1.6 g/mL. These calculated values of K_d were then specified in the MT3D model to ensure that each model utilized an equivalent representation of sorption for these two species.

Two MT3D models were developed, one for toluene and the other for PCE. One BioRedox model was developed, including both toluene and PCE in a multicomponent simulation. The BioRedox model also included TCE, DCE, and vinyl chloride as general solutes, and included the representation of chloride as a halogen solute. The BioRedox model assumed that the chlorinated ethenes were undergoing first-order sequential transformations at uniform rates of $1.9 \times 10^{-3} \text{ d}^{-1}$. Although the first-order decay of vinyl chloride was simulated, the production of ethene was not included in this test simulation. It was assumed that one mole of chloride was produced during the dehalogenation of one mole of each of the chlorinated ethene compounds.

Figure 4.3a compares the toluene concentration contours simulated by BioRedox and MT3D for layer 1 at the end of the 10-year simulation period. Similarly, Figure 4.3b compares the PCE concentration contours. Figures 4.4a and 4.4b present a comparison of simulated toluene and PCE concentration contours, respectively, over a cross-section

through the domain. All figures demonstrate that the BioRedox simulations match closely with the MT3D simulations.

Figure 4.3 - BioRedox and MT3D Comparison: Plan View Contours (Layer 1)

Figure 4.4 - BioRedox and MT3D Comparison: Cross-Section Contours (Row 20)

To facilitate another comparison between the simulations, both the MT3D and BioRedox models were specified to output concentration versus time profiles at three cell blocks in the model domain. Each of the three blocks was situated within different layers in the model (layers 3, 6, and 11), and all three blocks were situated at the same horizontal distance downgradient from the source areas.

Figure 4.5 presents a comparison between the concentration versus time profiles for toluene at each of the three observation nodes. The color shading represents MT3D simulated concentrations, and the dark contour lines represent BioRedox simulated concentrations. Based on this figure and a visual inspection of the data files, the simulated concentration profiles between BioRedox and MT3D were identical to an accuracy of at least six significant digits (only six significant digits were printed to the respective output files). Similarly, the concentration profiles for PCE shown in Figure

Figure 4.5 - BioRedox and MT3D Comparison: Observation Nodes (Toluene)

4.6, and a visual inspection of the output data files, also demonstrate an exact match between the BioRedox and MT3D models.

Figure 4.6 - BioRedox and MT3D Comparison: Observation Nodes (PCE)

For demonstration purposes, Figure 4.7 presents the cross-section concentration contours for toluene, PCE, TCE, DCE, vinyl chloride, and chloride that were modeled by BioRedox at the end of the 10-year simulation.

Figure 4.7 - BioRedox Simulation of Solute Distributions: Cross-Section (Row 20)

4.3.2 Test II.B - 2D NAPL Model Verification

Test II.B involves a simple verification of the equilibrium and rate-limited NAPL source models. The objective of this test is to verify that the mathematical formulation for the NAPL source model is correct.

The test involved a three-dimensional domain that was 200 m in length, 100 m wide, and 5 m deep. The model was discretized into a regular grid with uniform block dimensions of 5 meters length, 5 meters width, and 1-meter height. Based on this discretization, the total number of cell blocks in the three-dimensional domain was 4,000.

The total duration of the test simulation was 365 d with a regular step size of 10 d, resulting in a total of 37 time steps.

It was assumed that there was a BTEX source in the aquifer situated in Layers 2, 3, and 4, within the square region between $x = 30$ to 40 m and $y = 45$ to 55 m. Three different simulation models were prepared for this test:

- a constant concentration source of 10 mg/L;
- a NAPL source with equilibrium dissolution, a solubility limit of 100 mg/L, and a bulk efficiency factor of 10%; and
- a NAPL source with rate-limited dissolution, a solubility limit of 100 mg/L, a bulk efficiency factor of 10%, and a first-order dissolution rate equal to R/dt (based on the mathematical formulation, a dissolution rate equal to the retardation factor divided by the time step is equivalent to the equilibrium dissolution model).

A groundwater flow simulation was conducted using MODFLOW, and was based on a relatively uniform groundwater flow direction from left to right with an average linear groundwater velocity of approximately 50 m per year across the domain. A uniform recharge to the first layer of 200 mm per year was also simulated, although flow through the aquifer was primarily horizontal in nature.

It was assumed that BTEX was undergoing first-order biodegradation in the aquifer at a rate of $1.9 \times 10^{-3} \text{ day}^{-1}$. The f_{oc} of the aquifer was assumed to be 0.1%, and the K_{oc} of BTEX was assumed to be 431 mL/g. Based on the assumed porosity of 0.30 and a dry bulk density of 1.6 g/mL, the retardation coefficient for BTEX was 3.2987.

Figure 4.8 compares the simulated BTEX concentrations at a time of 1 year, for each of the three source models. The coinciding concentration contours shown in Figure 4.7 verify that the formulation for the equilibrium and rate-limited dissolution models are correct. An additional test conducted using a slower dissolution rate (not shown here) provided results that were intuitively correct (i.e. the BTEX plume was smaller because the source of BTEX was dissolving into groundwater at a slower rate, so groundwater concentrations at the source nodes remained below the saturated concentration of 10 mg/L).

Figure 4.8 – Comparison of NAPL Source Models to A Constant Concentration Source

Note: Color fill represents concentration contours for the constant concentration model

4.3.3 Test II.C - 2D RT3D Comparison

Clement et al. (1998) conducted a test to benchmark the RT3D model with BIOPLUME II for simulating the coupled transport of BTEX and oxygen, with the instantaneous biodegradation of BTEX occurring under oxygen-limited conditions. Test II.C involves a benchmark between BioRedox and RT3D using the same model scenario that was described by Clement et al. (1998).

The model consists of a two-dimensional, horizontal domain with uniform groundwater occurring across the length of the confined aquifer. The model domain is 510 m long (x-direction), 310 m wide (y-direction), and 10 m thick. The domain was discretized using a regular spacing with 51 grid blocks in the x-direction and 31 grid blocks in the y-direction and an injection rate of 1 m³/day (Figure 4.9). The background oxygen concentration was assumed to be 9 mg/L, and the initial BTEX concentration in the aquifer was assumed to be zero.

Figure 4.9 – RT3D and BioRedox Model Domain

The original benchmark test between RT3D and BIOPLUME III was conducted using the method of characteristics (MOC) package to simulate the advection term. RT3D was used to run the same simulation using the standard finite difference formulation to solve for the advection term to facilitate a direct comparison with BioRedox. The concentration contours of BTEX and oxygen predicted by the two models at the end of the two-year simulation are shown in Figure 4.10a and 4.10b, respectively. This data shows that the concentration profiles predicted by BioRedox agree well with the distribution predicted by RT3D, which verifies that the oxygen-limited reaction formulation incorporated into BioRedox is correct.

Figure 4.10 – Comparison of RT3D and BioRedox Simulations

CHAPTER 5

LANDFILL REDOX ZONATION MODEL

Extensive research previously undertaken by the Technical University of Denmark at the Vejen Landfill site in Vejen, Denmark, has provided an excellent characterization of the hydrogeology and geochemical conditions at the site, including detailed delineation of the redox zonation that was caused by natural attenuation of landfill leachate in the underlying aquifer (e.g. Lyngkilde and Christensen, 1992a).

BioRedox was used to simulate the coupled biodegradation of organic-rich leachate and preferential TEAP-utilization at the Vejen Landfill site. The BioRedox simulation model also predicted the development of sequential redox zones downgradient from the landfill, resulting from these coupled oxidation-reduction reactions. The objectives for simulating the conditions at the site include:

- to validate the conceptual representation incorporated into the BioRedox code for simulating redox zonation during the preferential utilization of available TEAPs;
- to assess the applicability of BioRedox for simulating field-scale redox zonation due to the intrinsic bioremediation of organic matter in groundwater;
- to determine how landfill cap permeability may influence the performance of intrinsic bioremediation of existing plumes in underlying aquifers.

A comprehensive review of the literature revealed few studies where large-scale redox zonation was modeled using a reactive transport model. Therefore, this validation study provides an important test of the applicability of reactive transport models for predicting large-scale redox zonation in groundwater.

Section 5.1 presents a detailed characterization of hydrogeology and geochemical conditions at the Vejen Landfill site. Section 5.2 outlines the development of the

groundwater flow and reactive transport simulation model used to predict the intrinsic bioremediation of landfill leachate and associated redox zonation observed in the underlying aquifer. Section 5.3 documents the results of the base case simulations and the impact of ferrous iron oxidation on the predicted redox zonation. To illustrate the potential effect that source control measures may have on downgradient intrinsic bioremediation performance, Section 5.4 uses the existing Vejen Landfill simulation model to compare the influence of high- and low-permeability landfill caps on the mobility of a hypothetical TCE plume in the underlying aquifer.

5.1 SITE CHARACTERIZATION

The Vejen Landfill is located in the western part of Denmark, in a glacial outwash plain. Figure 5.1 presents a site location map, and identifies the orientation of a transect of groundwater monitoring wells installed to the south of the landfill in the direction of groundwater flow. The base of the landfill was never lined, and leachate was known to have migrated through the landfill base to the underlying aquifer for a period of approximately 15 years before geochemical conditions in the aquifer were characterized.

During this period, the organic-rich leachate underwent microbial degradation in the aquifer, causing the development of sequential redox zones downgradient from the landfill. A transect of monitoring points was installed parallel to groundwater flow downgradient from one section of the landfill. The detailed data collected at the site facilitated the development of a hydrogeochemical conceptual model, which explained the redox zonation observed at the site.

Figure 5.1 – Vejen Landfill site location and monitoring transect orientation.
Source: Lyngkilde and Christensen, 1992a

The data for this site have been published in various studies (Lyngkilde and Christensen, 1992a,b; Larsen et al., 1992; Kjeldsen, 1993; Christensen et al., 1994; Heron et al., 1994a,b; Heron and Christensen, 1995; Nielsen et al., 1995a,b). For example, Lyngkilde and Christensen (1992a) present a detailed delineation of groundwater redox zones along the vertical transect downgradient from the landfill. Heron et al. (1994b) and

Heron and Christensen (1995) present important findings used to characterize the speciation of Fe(II) and Fe(III) minerals along the primary flowpath downgradient from the landfill.

Each of these studies presents information that is pertinent to the construction of a conceptual model to represent reactive transport (i.e. coupled biodegradation-redox reactions) at the site. The site conceptual model was originally developed prior to 1995. Since then, research studies at other sites have improved our understanding of the biogeochemical processes that influence the preferential TEAP-utilization observed during biodegradation of organic matter. Hence, it is imperative that these more recent findings be considered in the conceptual model used to develop the BioRedox reactive transport model for the Vejen Landfill.

The following sections provide a comprehensive compilation of site data relevant to the construction of the reactive transport simulation model. Section 5.1.1 presents a characterization of landfill leachate composition and hydrology. Section 5.1.2 outlines the hydrogeologic properties of the shallow aquifer below the Vejen Landfill. Section 5.1.3 documents the distribution of non-volatile organic carbon (NVOC) and inorganic parameters in groundwater downgradient from the landfill. Section 5.1.4 describes the distribution of redox zones that were interpreted based on groundwater and soil geochemistry data.

5.1.1 Landfill History

The landfill was operated between 1962 and 1981, during which time it received approximately 0.45 megatonnes of waste, including municipal waste, demolition waste,

industrial waste, and chemical waste. The landfill has no engineered leachate collection system, and the base of the landfill is comprised of a mixture of peat and sand soil areas that were present prior to placement of the waste (Kjeldsen, 1993).

Extensive monitoring was conducted in the early 1990's with monitoring wells installed within and on the perimeter of the landfill (Figure 5.2). Leachate quality and recharge estimates were determined, and the extent of landfill impact on the underlying aquifer was assessed (Kjeldsen, 1993).

Figure 5.2 – Landfill leachate and groundwater perimeter monitoring wells.
Source: Kjeldsen, 1993

Based on the landfill monitoring work, a vertical transect of monitoring points was installed in the aquifer directly downgradient from the south section of the landfill. This section of the landfill received household waste and minor amounts of demolition

waste between 1973 and 1977. The upstream length of this area of the landfill is approximately 100 m, and the waste was placed to a height of 6 m above the ground surface. The refuse in this area is currently covered by a soil with varying permeability.

A total of seven leachate wells were installed in the 6-hectare (ha) landfill, and were sampled on three occasions between August 1988 and September 1989. The observed leachate quality data indicate that the landfill is in the methanogenic stage, and is characterized by near-neutral pH, low BOD/COD ratios, high concentrations of dissolved methane and low concentrations of volatile fatty acids. NVOC was measured to range from 90 to 520 mg/L in the portion of the landfill where municipal waste was disposed of, with an average concentration of 250 mg/L. The average concentrations of ammonium and iron in landfill leachate were determined to be 230 and 65 mg/L, respectively. Sulfate was not detected in landfill leachate (above a method detection limit of 5 mg/L) during any leachate sampling events. The principal organic constituents of concern in the leachate are BTEX compounds (average total concentration of 406 µg/L) and the pesticide Mecocrop, or MCPP (average concentration of 370 µg/L). Concentrations of chlorinated solvents were generally very low in the leachate samples.

Based on annual precipitation and evapotranspiration records, Kjeldsen (1993) estimated the annual recharge through the landfill soil cover based on a one-dimensional unsaturated flow model. The annual recharge was estimated to range from 190 to 775 mm between 1960 and 1989, with an average annual recharge value of 420 mm.

5.1.2 Hydrogeologic Setting

The shallow unconfined aquifer underlying the Vejen Landfill is approximately 10 m thick, and is composed of medium- to coarse-grained sand (80%) and fine sand (20%). The aquifer contains small random clay and silt clasts, although clay and silt constitute less than 1% of the aquifer materials. The water table surface elevation is approximately 3 to 5 m below ground surface, and the aquifer is underlain by a competent layer of silt and clay. A small unsaturated zone separates the landfill refuse and shallow aquifer.

The landfill site is situated approximately 5 kilometres from a regional groundwater flow divide. The groundwater velocity in the vicinity of the site is on the order of 150 to 200 m/y. Annual precipitation is on the order of 700 to 900 mm per year. Groundwater elevation contour maps (Kjeldsen, 1993) indicate that groundwater mounds occur below the eastern and central portions of the landfill. The mounding establishes local flow directions in the vicinity of the landfill.

A semi-continuous clay layer 0.5 m in thickness lies below much of the Vejen Landfill at a depth of approximately 4 m. However, this clay layer is absent beneath the portion of the landfill that was contributing to the leachate plume observed in the aquifer transect wells to the south of the landfill.

Figure 5.3 is a three-dimensional figure illustrating electrical conductivity measurements at different vertical intervals in perimeter wells along the south side of the landfill. Figure 5.3 illustrates that the principal leachate recharge to the aquifer is occurring over a relatively narrow section (40 to 50 m in width) on the southern border of

the landfill. The vertical transect is located directly downgradient of this portion of the landfill.

Figure 5.3 – Electrical conductivity profile in groundwater below south side of landfill. Source: Kjeldsen, 1993

The increased electrical conductivity measurements in this section are elevated because (Kjeldsen, 1993): 1. the refuse upgradient of this section has the highest composition of municipal waste, relative to other areas that consist primarily of demolition waste and soils; 2. the base of the landfill in this area consists primarily of high-permeability sandy soils; and, 3. the observed leachate plume coincides with a southerly erosion valley eroded by melt water in the last ice age (the sub-surface clay

layer is missing in this portion of the aquifer). Kjeldsen (1993) indicates that groundwater pollution in the aquifer is primarily derived from only a small 0.5-ha portion of the 6.3-ha landfill.

5.1.3 Groundwater Chemistry Distribution

Two monitoring networks were used to assess the hydrogeochemical regime: a temporary monitoring network was sampled to extract a snapshot of geochemical conditions at the site; and, a permanent network of sampling filters was installed to evaluate transient variations in chemical concentrations.

The temporary sampling network included a total of 160 drive points at 9 different boring locations along a 370-m transect. At each boring location, the average vertical separation between the sampling intervals was 0.5 m. The number of vertical sampling points at each boring location ranged between 13 and 31.

The permanent sampling filters were monitored over a period of approximately one year. All permanent monitoring points were installed along the transect within 130 m of the landfill. Lyngkilde and Christensen (1992a) did not document the number and locations of these permanent sampling filters. The results of this monitoring were inferred by Lyngkilde and Christensen (1992a,b) to indicate that the plume was at relative steady-state conditions.

Trends in the distribution of chloride, NVOC, and geochemical indicator parameters are relevant to the interpretation of groundwater flow and solute transport properties. General trends for each of these parameters are discussed in Sections 5.1.3.1 through 5.1.3.3, respectively.

For comparative purposes, Table 5.1 presents the minimum, maximum, and average concentrations for a number of parameters measured in each redox zone in the aquifer (oxygen, nitrate, nitrite, ammonium, dissolved Mn(II) and Fe(II), sulfate, sulfide, methane, redox potential, NVOC, alkalinity, chloride, and pH). These reported values should be interpreted with caution because they include measurements from monitoring points situated above and below the leachate plume, and thus represent combined results from weakly to strongly polluted groundwater (Lyngkilde and Christensen, 1992a).

Table 5.1 – Range and average concentrations of NVOC and geochemical parameters measured in each redox zone.

Parameter	Aerobic Range Avg. (n = 43)	Nitrate- Reducing Range Avg. (n = 159)	Mn(IV)- Reducing Range Avg. (n = 14)	Fe(III)- Reducing Range Avg. (n = 105)	Sulfate- Reducing Range Avg. (n = 31)	Methano- genic Range Avg. (n = 14)
Oxygen	1.0–7.0 3.01	0.0–0.9 0.15	0.0–0.5 0.13	0.0–0.9 0.07	0.0–0.3 0.06	0.0–0.2 0.05
Nitrate	0.84–29.47 11.973	0–27.70 1.634	0–0.80 0.125	0–0.48 0.042	0–0.29 0.086	0–0.47 0.154
Nitrite	0–0.48 0.032	0–0.20 0.014	0–0.14 0.017	0–0.03 0.002	0–0.02 0.002	0–0.13 0.015
Ammonium	0–0.35 0.021	0–0.95 0.084	0–1.01 0.208	0–81.30 1.094	0–139.40 24.693	0–262.20 77.486
Mn(II)	0–0.5 0.10	0–0.5 0.09	0.3–0.9 0.41	0–1.2 0.35	0–1.6 0.60	0.1–1.8 0.73
Fe(II)	0–5.6 0.64	0–7.1 0.61	0–1.4 0.83	1.5–39.0 8.88	0–76.0 21.00	0.5–38.0 7.54
Sulfate	2–301 42.3	6–95 35.3	6–70 34.6	6–155 57.5	0–156 51.7	1–38 14.5
Sulfide	0 0.00	0 0.00	0 0.00	0–0.2 0.00	0–33.0 3.98	0–4.5 1.05
Methane	0–0.14 0.033	0–1.60 0.064	0–0.51 0.078	0–4.48 0.391	0–5.87 0.550	1.03–6.30 2.524
Redox potential	+103 to +546 +385.0	-91 to +546 +155.1	+20 to +319 +123.0	-83 to +409 +113.0	-29 to +169 +85.3	-55 to +150 +63.1
NVOC	1.2–6.3 2.80	1.2–20.5 2.91	1.3–7.5 2.36	1.2–71.9 6.43	2.1–119.1 32.57	2.3–484.0 104.70
Alkalinity	0.0–1.6 0.28	0.0–5.3 1.81	0.3–5.2 2.48	0.0–10.1 1.92	0.3–23.9 6.46	0.7–42.9 12.08
Chloride	16–71 30.1	14–108 36.3	16–188 48.4	15–341 75.5	13–764 225.3	13–1181 384.7
PH	4.6–7.2 5.27	4.7–8.2 7.00	4.9–8.0 7.18	4.9–7.9 6.38	5.0–7.6 6.27	5.0–7.3 6.51

5.1.3.1 Chloride

Figure 5.4 illustrates the chloride plume along the vertical transect downgradient from the landfill. Chloride concentrations are highest directly below the landfill (greater than 1000 mg/L), and decrease significantly with downgradient distance. It is apparent from inspection of Figure 5.4 that leachate has impacted the entire thickness of the aquifer directly below the landfill. One possible explanation for the deep contamination below the landfill may be that historical leachate strength increased the density of the leachate relative to that of water, resulting in significant downward advection of the leachate.

Figure 5.4 – Chloride plume delineation along vertical transect. Source: Lyngkilde and Christensen, 1992a

The chloride plume decreases in vertical extent and concentration along the flowpath, which suggests that horizontal transverse dispersion (cross-gradient to groundwater flow) may be significant, and that vertical dispersion downgradient from the landfill is relatively minor.

5.1.3.2 NVOC

Figure 5.5 presents a profile of corrected NVOC concentrations versus distance downgradient from the landfill. The NVOC concentrations were corrected to remove the effects of dispersion by using the Conservative Tracer Method (Wiedemeier et al., 1998). Chloride was used as the conservative tracer for correcting NVOC concentrations. Measured NVOC concentrations directly below the landfill ranged from 300 to 500 mg/L, and decreased significantly along the downgradient flowpath.

Figure 5.5 – NVOC corrected concentrations along downgradient groundwater flowpath. Measured NVOC concentrations were corrected to remove the effects of dispersion based on chloride concentrations. Source: Lyngkilde and Christensen, 1992b

The large scatter in NVOC concentrations within 100 m downgradient from the landfill is at least partially explained by the inclusion of low NVOC concentrations from sampling points situated below the leachate plume. Background NVOC concentrations in the naturally aerobic aquifer are approximately 2 mg/L.

The trend of decreasing NVOC corrected concentrations along the flowpath, as shown in Figure 5.5, is due primarily to the biodegradation of NVOC downgradient from the landfill. Historical monitoring over a 285-day period, as shown in Figure 5.6, indicates that the plume is relatively stable in time, thus eliminating the potential for sorption as a significant attenuation mechanism (Lyngkilde and Christensen, 1992b).

Figure 5.6 – Transient variations in NVOC and chloride measured concentrations at permanent monitoring stations. Source: Lyngkilde and Christensen, 1992b

It appears from Figure 5.5 that NVOC concentrations (up to 100 m downgradient from the landfill) are declining at a faster rate than the decline in NVOC concentrations observed farther downgradient from the landfill. Several possible reasons for varying NVOC degradation rates along the flowpath include: 1. rates are redox- or TEAP-dependent; and/or 2. degradation rates are at least partially dependent on NVOC concentrations. Another potential explanation may be related to the chloride concentrations used to correct NVOC concentrations. It is possible that large fluctuations in chloride concentrations may have resulted in the calculation of artificially high NVOC corrected concentrations. Lyngkilde and Christensen (1992b) suggest that significant heterogeneity observed during boring installation may also explain some of the scatter shown in Figure 5.5.

Based on the overall trend shown in Figure 5.5, and the travel time along the flowpath, the degradation half-life for NVOC was calculated to range from 90 to 140 days (corresponding to degradation rates ranging from 5.0×10^{-3} to $7.7 \times 10^{-3} \text{ d}^{-1}$) using an exponential decay spreadsheet model.

5.1.3.3 Electron Acceptors and Metabolic By-Products

The region is highly agricultural, resulting in relatively high concentrations of nitrate in groundwater. Unpolluted groundwater in the shallow portion of the aquifer is typically aerobic, with high dissolved oxygen (7 mg/L), nitrate (20 to 30 mg/L), and sulfate (10 to 100 mg/L) concentrations.

Figures 5.7a and 5.7b compare NVOC and electron acceptor concentrations versus depth at three boring locations, B1, B3, and B9, which are situated approximately

Figure 5.7a – Concentration vs. depth profiles for NVOC, oxygen, and nitrate at boring locations B1, B3, and B9. Interpolated from charts presented in Lyngkilde and Christensen, 1992a

Figure 5.7b – Concentration vs. depth profiles for NVOC and sulfate at boring locations B1, B3, and B9

5, 95, and 360 m downgradient from the landfill, respectively. To facilitate comparison of chemical trends over varying scales, the parameter concentrations were normalized by dividing the measured concentration by a large (parameter-specific) reference concentration. The reference concentration used to normalize the measured solute concentrations are: oxygen, 5.0 mg/L; nitrate, 50 mg/L; sulfate, 250 mg/L; dissolved Mn(II), 2.5 mg/L; dissolved Fe(II), 50 mg/L; sulfide, 5.0 mg/L; and methane, 10.0 mg/L. Normalizing the concentrations allowed them to be plotted using a common concentration axis that ranged from 0 to 1.

Inspection of Figures 5.7a and 5.7b indicates that at boring B1, elevated NVOC concentrations (maximum of 484 mg/L) between elevations of 33 and 36 m Above Mean Sea Level (m AMSL), correlate with depleted concentrations of oxygen, nitrate, and sulfate. This indicates that groundwater conditions are strongly reducing in the vicinity of the landfill.

Comparison of NVOC and sulfate concentrations (Figure 5.7b) at boring B3 (95 metres from the landfill) indicates an opposite trend: sulfate concentrations are elevated and NVOC concentrations are significantly lower relative to the concentrations observed at similar depths in boring B1.

Given that sulfate is depleted in the shallow groundwater at boring B3, and increases in concentration with depth, it is unlikely that the elevated sulfate concentrations at boring B3 are caused by groundwater recharge. It is possible that high alkalinity, arising from biodegradation of leachate-impacted groundwater, causes the dissolution of sulfate-bearing minerals (e.g. gypsum), providing a source of sulfate to groundwater.

Table 5.1 indicates that the maximum sulfate concentration measured in each zone increases downgradient from the methanogenic zone (in the sulfate and Fe(III) reducing zones). This trend does provide some corroboration of the potential for a source of sulfate in groundwater. This has important implications when simulating sulfate-reduction in groundwater, and will be discussed in the context of the model simulations in Section 5.3.

Figure 5.7a also shows that oxygen and nitrate concentrations are elevated in boring B9 (360 m from the landfill), which indicates that the groundwater redox conditions eventually become aerobic downgradient from the landfill.

Figures 5.8a and 5.8b illustrate metabolic by-product (dissolved Mn(II), Fe(II), sulfide, and methane) concentrations versus depth at the same borings (B1, B3, and B9). At boring B1, Mn(II) and sulfide concentrations are highly elevated, dissolved methane concentrations are elevated, and Fe(II) concentrations are relatively low. It is possible that the elevated Mn(II) levels may have been derived from the landfill source. This is corroborated by the very low contribution of Mn(IV) oxides to the total oxidation capacity in sediments near the landfill (Heron et al., 1994).

The high sulfide levels are a strong indication of sulfate-reduction, assuming that they were not derived from the landfill. It is not certain whether sulfide was present in significant quantity in landfill leachate. Kjeldsen (1993) did not report measurement of sulfide concentrations. However, sulfide is a common constituent in landfill gas, and thus may be expected to be present to some degree in landfill leachate.

As will be discussed in the next section, Lyngkilde and Christensen (1992a) interpret high sulfide levels in temporary borings near the landfill to be indicative of

Figure 5.8a – Concentration vs. depth profiles for dissolved Mn^{2+} and Fe^{2+} at boring locations B1, B3, and B9. Interpolated from charts presented in Lyngkilde and Christensen, 1992a

Figure 5.8b – Concentration vs. depth profiles for sulfide and methane at boring locations B1, B3, and B9

sulfate reduction in groundwater. Kjeldsen (1993) reports that sulfate was not measured in landfill leachate above the method detection limit of 5 mg/L. Therefore, if sulfate reduction were occurring below the landfill, sulfate would have to be supplied either from upgradient recharge in the unpolluted portion of the aquifer, or via the dissolution of sulfate-bearing minerals in the reduced portion of the plume.

The significance of a sulfate source is important when evaluating the BioRedox simulations, because the reactive transport model presented in this thesis did not represent potential dissolution of sulfate-bearing minerals as a source of sulfate. Therefore, if this is the principal source of sulfate in the reduced portion of the plume, the model will significantly underestimate the extent of sulfate-reduction occurring in the aquifer (and will overestimate the extent of methanogenesis).

Sulfide was only detected in groundwater in the initial monitoring event at temporary monitoring point installations. Sulfide was not detected in any of the permanent borings, and potential adverse affects caused by well materials or sampling methods were ruled out. Christensen et al. (1994) suggest that temporal variations in leachate strength may be responsible for variation between methanogenic and sulfate-reducing conditions.

Figure 5.8a also shows that dissolved Fe(II) concentrations increase significantly between borings B1 and B3 (i.e. between distances of 5 and 95 metres from the landfill). This increase in Fe(II) levels is likely the result of Fe(III) reduction upgradient or in the vicinity of boring B3. Fe(II) levels at boring B9 are significantly lower, indicating that Fe(II) is significantly attenuated in the nitrate-reducing or aerobic zone.

5.1.4 Observed Redox Zonation

5.1.4.1 Assessment of Dissolved Redox Indicator Concentrations

Lyngkilde and Christensen (1992a) applied criteria for measured redox indicator parameters to estimate the dominant TEAP occurring at each temporary sampling location. Table 5.2 presents a summary of these redox zone criteria. Lyngkilde and Christensen (1992a) acknowledge that this approach for identifying dominant TEAPs is somewhat subjective and prone to uncertainty, particularly given the potential for some redox parameters (e.g. Mn(II), Fe(II), sulfide, and methane) to be transported downgradient from the original point where the reaction occurred.

Table 5.2 - Redox zone criteria for evaluating dominant TEAPs at sampling locations.

Parameter	Aerobic	Nitrate-Reducing	Mn(IV)-Reducing	Fe(III)-Reducing	Sulfate-Reducing	Methanogenic
Oxygen	>1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nitrate-N	^a	--	<0.2	<0.2	<0.2	<0.2
Nitrite-N	<0.1	--	<0.1	<0.1	<0.1	<0.1
Ammonium-N	<1.0	--	--	--	--	--
Mn(II)	<0.2	<0.2	>0.2	--	--	--
Fe(II)	<1.5	<1.5	<1.5	>1.5	--	--
Sulfate	--	--	--	--	--	<40
Sulfide	<0.1	<0.1	<0.1	<0.1	>0.2	--
Methane	<1.0	<1.0	<1.0	<1.0	<1.0	>1.0

^a No criterion is applied.

Cozzarelli et al. (2000) and Jakobsen et al. (1998) both indicate that high dissolved iron concentrations did not necessarily correlate with dominant Fe(III) reduction. Cozzarelli et al. (2000) recommend that a combined program, including

evaluation of redox indicator parameters, hydrogen concentrations, and microbiological assays, will improve the accuracy of the characterization of dominant TEAPs occurring in groundwater.

Jakobsen et al. (1998) and Cozzarelli et al. (2000) determined that groundwater zones with low hydrogen concentrations (at levels that are typically indicative of Fe(III) reduction) were actually characterized as having concomitant sulfate and Fe(III) reduction. Methanogenesis was also observed to occur concurrently with Fe(III) reduction, although Jakobsen et al. (1998) suggest that this is due to micro-scale heterogeneity in stagnant groundwater zones. Jakobsen et al. (1998) determined through thermodynamic calculations that Fe(III) reduction was the dominant process, and sulfate reduction was energetically favourable (but not to the same extent as Fe(III) reduction). These studies underscore the uncertainty in redox zonation characterization that is based solely on redox indicator parameter concentrations.

Based on the analytical data and application of the redox zone criteria shown in Table 5.2, Lyngkilde and Christensen (1992a) delineated the spatial extent of each dominant TEAP interpreted to be occurring in the aquifer. Figure 5.9 presents the redox zonation boundaries, as estimated by Lyngkilde and Christensen (1992a). The distribution of redox zones is characterized as follows:

- a small methanogenic zone directly downgradient from the landfill, followed by a discontinuous sulfate-reducing zone (extending to a distance of up to 100 metres from the landfill);
- a long iron-reducing zone extending as far as 350 metres from the landfill;
- a significant nitrate-reducing zone (length on the order of tens of metres); and
- return to aerobic conditions approximately 400 metres downgradient from the landfill.

Figure 5.9 – Estimated redox zonation in groundwater. Source: Lyngkilde and Christensen, 1992a

5.1.4.2 Assessment of Mineral-Phase Iron Speciation

The quantification of readily reducible Fe(III) oxides in soil is difficult in practice, although it is important to the assessment of long-term redox-buffering capacity of sediments in the presence of biodegrading organic matter.

Heron and Christensen (1995) present some very interesting work that quantifies the quantity and speciation of Fe(III) and Fe(II) minerals in sediments along the flowpath below the Vejen Landfill. They collected 60 sediment samples along the flowpath, which spanned the entire redox sequence. Different extraction techniques (Heron and Christensen, 1995) were utilized to measure the amount and speciation of iron in each sediment sample. The different forms of iron extracted with each method are as follows:

Fe(II) soluble in 1 Mole/Liter (M) CaCl_2 solution – includes Fe(II) in porewater (found to be less than 10% of total Fe(II)) and ion-exchangeable Fe(II). Dissolution of other minerals was not observed during these extraction tests.

Fe(II) and Fe(III) soluble in 0.5 M HCl – dissolves ion-exchangeable Fe(II), ferrous monosulfides, amorphous iron oxides, part of the siderite (FeCO_3), and a small fraction of the crystalline iron oxide minerals. The principal component of the Fe(III) measured with this test represents the noncrystalline iron in sediment.

Fe(II) and Fe(III) soluble in 5 M HCl – in addition to the species extracted in the 0.5 M HCl test, this extraction completely dissolves crystalline iron oxides, siderite, and magnetite. Fe(II) and Fe(III) bound to clays and silicates will be partly dissolved.

Total Iron soluble in Ti(III)-EDTA Solution – includes ferrihydrite ($\text{Fe}(\text{OH})_3$), goethite ($\alpha\text{-FeOOH}$), and hematite (Fe_2O_3). This method is used to measure the contribution of iron and manganese to the total oxidation capacity of sediments.

Figure 5.10 illustrates the approximate flowpath position, as well as the dissolved Fe(II) and total iron measured in sediment samples along the flowpath. Inspection of Figure 5.10 indicates that dissolved Fe(II) varies from 10 to 40 mg/L between 50 and 100 m from the landfill, and appears to decrease to less than 20 mg/L farther downgradient (except for one outlier value measured at a distance of 250 m from the landfill). The total iron concentration in sediments varies from 1 to 4 mg/g up to a distance of 250 m, where it was measured as high as 8 mg/g. The significant increase in total iron concentrations occurs in the vicinity of the transition between Fe(III) and nitrate reducing conditions.

Figure 5.10 – Groundwater flowpath location and total iron concentration in sediment samples. Source: Heron and Christensen, 1995

Figure 5.11 shows the amount of Fe(II) extracted with each method. The ion-exchangeable Fe(II) was relatively small, and was always less than 20% of the total Fe(II) in soil (Heron and Christensen, 1995). The results shown in Figure 5.11 indicate that Fe(II) did not migrate far into the nitrate-reducing and aerobic zones. A significant portion of the Fe(II) appears to have precipitated in the Fe(III) reducing zone, either as iron carbonate or iron sulfide minerals. Separate analyses indicate that the concentration of pyrite was as high as 0.84 mg/g in the methanogenic zone, confirming that iron and sulfide were precipitating in this region of the aquifer (Heron and Christensen, 1995). This has important implications for enhanced bioremediation remedies, and should be considered in reactive transport models used to evaluate the performance of oxygen amendments in groundwater.

Figure 5.12 shows the distribution of Fe(III) measured with the different extraction techniques. These results show a significant trend of increasing Fe(III) with distance from the landfill. The noncrystalline forms of Fe(III) are significantly depleted in the first 150 metres of the flowpath (< 0.1 mg/g), but increase farther downgradient to 0.5 to 3 mg/g in the oxidized section (approximately 300 metres from the landfill). The Ti(III)-EDTA extraction results showed between 1 and 7 mg/g Fe(III) in the oxidized sediments, indicating that more crystalline forms of iron (e.g. goethite and hematite) comprise these sediments (Heron and Christensen, 1995). The Ti(III)-EDTA extracts also showed that more crystalline forms of iron were depleted in the first 150 m of the flowpath (< 0.5 mg/g), indicating that long-term leachate attenuation has reduced even the more crystallized forms of iron. Heron and Christensen (1995) suggest that chemical

stress associated with landfill leachate (i.e. complexing agents in the leachate, low Eh) allowed a large fraction of the iron to undergo reductive dissolution.

Figure 5.11 – Iron(II) mineral species extract concentrations. Source: Heron and Christensen, 1995

Figure 5.12 – Iron(III) mineral species extract concentrations. Source: Heron and Christensen, 1995

Extraction of total Fe(III) with 5 M HCl showed that even the strongly reduced sediments contain as much as 3 mg/g of residual Fe(III). This residual Fe(III) is considered to be relatively unavailable for reduction in the aquifer because it has

remained for such a long period of time. Previous studies indicated that the residual Fe(III) consists of Fe(III) in magnetite or as part of clays and primary minerals (Heron and Christensen, 1994b).

Figure 5.13 shows results from another series of reducible iron extractions from different redox zones (Christensen et al., 1994). These results also indicate that background concentrations of reducible (i.e. amorphous) Fe(III) hydroxides are approximately 3 mg/g in unpolluted sediments.

Figure 5.13 – Noncrystalline iron(III) concentrations in different redox zones.
Source: Christensen et al., 1994

Figure 5.14 illustrates the average speciation between Fe(II) and Fe(III) minerals in the aquifer sediments along the flowpath. Figure 5.14 indicates that only a very small portion of reducible Fe(III) remains in the sediments between 50 and 100 metres from the

landfill, and that the reducible Fe(III) increases significantly (up to 3.5 mg/g) at a distance of 300 metres.

Figure 5.14 – Average concentrations of iron(II) and iron(III) mineral species along flowpath downgradient from landfill. Source: Heron and Christensen, 1995

Based on these results, it is clear that Fe(III) reduction is not occurring significantly in sediments up to 100 m from the landfill. The scatter shown in measured iron in sediments (Figures 5.10 through 5.13) indicate that there is relatively strong heterogeneity in iron concentrations in sediments. Therefore, it is conceivable that microzones with one TEAP may form in a redox zone that is characterized at the large-scale by a different TEAP. The low reactivity of Fe(III) in sediments up to 100 m from the landfill suggests that concomitant (or dominant) occurrence of sulfate reduction and/or methanogenesis is likely.

5.2 SIMULATION MODEL DEVELOPMENT

An integrated simulation model was developed to predict the redox zonation in the aquifer underlying the Vejen Landfill. Groundwater flow and reactive multispecies transport was simulated to evaluate the coupling between leachate biodegradation in groundwater, and the preferential utilization of dominant TEAPs that resulted in the sequential formation of redox zones downgradient from the landfill. A two-dimensional cross-section of the unconfined aquifer was modeled to represent observed conditions along the vertical transect of monitoring wells.

The development of this simulation model is not intended to be a rigorous calibration to observed conditions. This type of reactive transport simulation is likely to be non-unique, in that there may be multiple combinations of parameters that result in similar predictions. The calibration of a reactive transport model is beyond the scope of this study, and would require a more detailed knowledge of site conditions.

This study is intended to provide a representation of the dominant processes that govern redox zonation in the aquifer. Comparison of model simulations to the detailed field observations provides a qualitative validation of the coupled oxidation-reduction reaction scheme incorporated into the BioRedox code, and provides insight into the applicability of BioRedox for predicting large-scale redox zonation in aquifers.

MODFLOW was used to simulate steady-state groundwater flow. BioRedox was used to simulate the fate and transport of the leachate plume in the shallow aquifer, including a representation of the coupling between the oxidation of landfill-derived total organic carbon (TOC) and the reduction of available electron acceptors in groundwater and in the soil. The groundwater velocity distribution simulated using MODFLOW was

used as input to the BioRedox transport model, using the same interface that provides the link between MODFLOW and MT3DMS.

Uniform horizontal and vertical grid spacing of 5 and 1 m, respectively, were specified for the entire model domain. The aquifer was assumed to have a constant thickness of 10 m. Figure 5.15 illustrates the extent of the domains used for the groundwater flow and solute transport simulation models. The groundwater flow model domain was specified as having a longer extent (2000 m) than the transport model domain (1000 m), to ensure that the arbitrary boundary conditions for the flow simulation did not have an adverse influence on the transport model simulation.

Figure 5.15 – Simulation model domain.

Contaminants were assumed to have leached from the uncovered landfill to the shallow aquifer over a 15-year period following the commencement of leachate production (corresponding to the length of time that leachate was known to be impacting

the aquifer below the Vejen Landfill). Other input parameters and simulation methods for groundwater flow, time-varying landfill leachate TOC concentrations, and reactive transport are described in Sections 5.2.1 through 5.2.3, respectively.

5.2.1 Groundwater Flow Model (MODFLOW)

The flow boundary conditions were selected to create a simulated flow system similar to the hydrogeologic regime at the Vejen Landfill. Specific criteria for the flow system were:

- average groundwater velocity of 150 to 200 m/y below the landfill;
- uniform regional infiltration rate of 0.21 m/y; and
- landfill recharge rate of 0.42 m/y.

Figure 5.16 illustrates the boundary conditions assumed for the groundwater flow model.

The simulated groundwater velocity distribution was exported to a MODFLOW-Link file, which is used to import the flow information to transport models such as BioRedox or MT3DMS.

5.2.2 Landfill Leachate Composition Model

As discussed in Section 3.6.2, an exponential decay model was incorporated into BioRedox to represent a source of landfill leachate in recharge to the underlying water table aquifer. This source model does not account for attenuation processes between the base of the landfill and the water table surface of the aquifer. BioRedox does implicitly model the dilution that occurs when vertical leachate migration reaches the water table.

Leachate TOC was represented as a source term for the groundwater model so that the development of redox zones downgradient from the landfill could be simulated. Based on the leachate model presented by Lu et al. (1981), the initial leachate TOC concentration was specified to be 14000 mg/L, and TOC concentrations were specified to decline exponentially with a first-order rate of $7.12 \times 10^{-4} \text{ d}^{-1}$. The decline in concentrations was specified to occur for the first ten years of the landfill simulation.

Following the initial ten-year period, TOC concentrations were assumed to remain constant (1040 mg/L) to reflect the additional electron donor capacity in leachate resulting from the presence of ammonium (Heron and Christensen, 1995). BioRedox also represented constant landfill source concentrations for oxygen, nitrate, and sulfate, which were assumed to be zero at all times.

5.2.3 Solute Transport Model (BioRedox)

TOC was the only organic leachate constituent included in the BioRedox simulation model; inorganic electron acceptors represented as solutes in the model include dissolved oxygen, nitrate, and sulfate. Fe(III) was represented as a mineral-phase species in the simulation model, and was assumed to occur primarily in the form of amorphous ferric hydroxide with a background concentration of 3 mg/g (equivalent aqueous-phase concentration of 13,700 mg/L).

The representation of amorphous Fe(III) reduction will provide a reasonable approximation of the dominant Fe(III) TEAP. As discussed in Section 5.1.4, there are also fractions of less reactive Fe(III) in the sediments below the landfill. However, a study by Cozzarelli et al. (2000) indicates that the reduction of less reactive Fe(III) will occur concomitantly with sulfate reduction and/or methanogenesis. The purpose of this simulation was to represent the dominant TEAPs occurring in the aquifer, which justifies the representation of only the most reactive Fe(III) species in the sediments.

Manganese oxides were not considered as part of this study because Lyngkilde and Christensen (1992a) state that manganese reduction had a relatively small influence on redox zonation relative to iron reduction. It was assumed that carbon dioxide was non-limiting with respect to methanogenic activity. Therefore, carbon dioxide was not represented explicitly in the simulation model. The transport of methane downgradient from the methanogenic zone was not represented

Table 5.3 presents oxidation and reduction half-reactions, and substrate threshold concentrations for each reaction included in the simulation. Stoichiometric coefficients from each redox half-reaction are specified as input parameters for the model using a

redox reaction database. These values are theoretical in nature, and are not expected to change between different sites (assuming the same half-reactions are occurring).

Table 5.3 – Model solutes, oxidation-reduction half-reactions, and reaction threshold concentrations.

<i>Model Solute</i>	<i>Reaction Type</i>	<i>Half-Reaction</i>	<i>Minimum Concentration¹ (mg/L)</i>
TOC	Oxidation	$\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$	2
Oxygen	Reduction	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	0.1
Nitrate	Reduction	$\text{NO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightarrow 0.5\text{N}_2(\text{g}) + 3\text{H}_2\text{O}$	0.1
Iron(III)	Reduction	$\text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+ + \text{e}^- \rightarrow \text{Fe}^{2+} + 3\text{H}_2\text{O}$	1*
Sulfate	Reduction	$\text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{HS}^- + 4\text{H}_2\text{O}$	1
Carbon Dioxide ²	Reduction	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	n/a

NOTE:

¹ Minimum concentration refers to the minimum threshold required for the reaction to occur

² CO₂ oxidation was not explicitly modeled because it was assumed to have an unlimited supply

*equivalent concentration in mass Fe per mass dry soil is 2×10^{-4} mg/g

n/a means not applicable

Table 5.4 presents molecular weight values, and boundary and initial concentrations for the six solutes simulated for this scenario. The total simulation period was 15 years (5475 d), and a constant time step of 0.5 d was used. TOC sorption was assumed to be negligible for all simulations. A porosity of 0.35 and soil bulk dry density of 1.6 kg/L were assumed.

The Base Case simulation was developed using estimated parameters, and a limited sensitivity analysis was conducted to investigate the sensitivity of model simulations to aqueous Fe(II) mobilization and transport. Some fitting was done to develop the Base Case parameters that provided an approximate match between model

and observed conditions. As discussed earlier, a general match between model and field conditions does not imply that the model is calibrated; there are likely to be multiple combinations of parameters that provide similar results, resulting in a non-unique simulation model.

Table 5.4 – Solute molecular weights, and boundary and initial concentrations.

<i>Solute</i>	<i>Molecular Weight (g/mol)</i>	<i>Boundary and Initial Concentrations (mg/L)</i>			
		C_{IN}	C_{RCH}	C_{LF}	$C (t=0)$
TOC	12	0	0	(a)	0
Oxygen	32	7	7	0	7
Nitrate	62	25	25	0	25
Ferric Hydroxide	55.85	N/A	N/A	N/A	13700
Sulfate	96.1	40	40	0	40

Notes: (a) $C = 14000e^{-0.26t}$, $t < 10$ years; $C = 1041$ mg/L, $t > 10$ years

Longitudinal dispersivity was estimated to be a conservatively low value equivalent to 1% of the total plume length (i.e. dispersivity of 3 m). Vertical dispersivity was initially assigned a value of 0.01 m to represent the minimal vertical dispersion observed with the chloride plume.

Organic matter in landfill leachate typically consists of different fractions with varying reactivity. The overall reactivity of organic matter is also known to decrease during the lifespan of a municipal landfill (Christensen et al., 1994). As discussed in Section 5.1.3, the half-life for NVOC in groundwater, after 15 years of landfill operation, was determined to range from 90 to 140 d.

NVOC represents the least reactive fraction of organic matter found in landfills. The early stages of landfill operation result in leaching of highly reactive volatile fatty

acids, which eventually become depleted over the life of the landfill. The simulation model represented organic matter in leachate as TOC, which was assumed to have similar characteristics to the NVOC measured by Lyngkilde and Christensen (1992a).

To provide a rough approximation of the variable reactivity of landfill leachate organic matter, the biodegradation half-life for TOC was specified as follows: a half-life of 30 d when $\text{TOC} \geq 250 \text{ mg/L}$; half-life of 90 d when $\text{TOC} < 250 \text{ mg/L}$ and $\text{TOC} \geq 2 \text{ mg/L}$; and TOC was assumed to be recalcitrant when TOC was less than the background concentration of 2 mg/L.

5.3 SIMULATED REDOX ZONATION

This section illustrates a new approach used by BioRedox to facilitate the visualization of spatial redox zone distribution (Section 5.3.1). Section 5.3.2 presents a comparison of simulated and observed redox zonation, and Section 5.3.3 provides a discussion of how the simulation results provide a qualitative validation of the mathematical representation of preferential TEAP utilization in BioRedox. The results of a limited sensitivity analysis of Fe(II) mobilization and transport are provided in Section 5.3.4.

5.3.1 Redox Zone Visualization Approach

Figure 5.17 presents simulated concentration contours prepared using SURFER, corresponding to the end of the 15-year simulation, for each of the electron acceptors (oxygen, nitrate, mineral-phase Fe(III), and sulfate). The sequential TEAPs are simulated to occur while the specific electron acceptor concentrations are above the user-defined

Figure 5.17 – Simulated electron acceptor concentration contours at the end of the simulation period ($t = 15$ years) for the Base Case input parameters.

minimum threshold concentrations (0.1, 0.1, 1.0, and 1.0, respectively). Inspection of Figure 5.17 indicates that electron acceptor utilization during a specific TEAP results in

rapid depletion of the electron acceptors in the groundwater entering the domain boundary upgradient of the landfill, as evidenced by the strong concentration gradients observed in the contour maps.

When evaluating the results of a redox zonation simulation, it is convenient to visualize the overall extent of each simulated redox zone in groundwater. It is difficult to assess the extent of each redox zone by studying the contour maps for individual electron acceptors (e.g. Figure 5.17). Therefore, an innovative approach was developed and incorporated into the BioRedox code, to facilitate the visualization of simulated redox zonation.

Each redox zone in a BioRedox simulation is assigned an identification number based on the preferred sequence of electron acceptor utilization. The redox zone corresponding to the most preferred electron acceptor (e.g. oxygen) is given an identification number of 1.0, and the remaining redox zones are assigned identification numbers with incremental increases of 1.0 for each zone in the utilization sequence. For example, for a BioRedox simulation which includes oxygen, nitrate, Fe(III), sulfate, and carbon dioxide as electron acceptors, the corresponding values of 1.0, 2.0, 3.0, 4.0, and 5.0 will be assigned as the *minimum* redox zone identification numbers for the aerobic zone, nitrate-reducing zone, ferrogenic zone, sulfate-reducing zone, and the methanogenic zone, respectively.

To provide the additional capability of identifying the distribution of concentrations for the predominant electron acceptors within each individual redox zone, a linear scaling factor was incorporated into BioRedox. For example, this scaling factor makes it possible to identify how oxygen concentrations vary within the aerobic zone,

how nitrate concentrations vary within the nitrate-reducing zone, etc. Therefore, this visualization method can be used to not only delineate the extent of each simulated redox zone, but also to simultaneously assess how electron acceptor concentrations are changing within each individual redox zone.

The scaling factor used in the BioRedox model is calculated based on the change in electron acceptor concentrations relative to the assumed background concentration (which is an input parameter in the model). When coupled redox reactions are simulated, a Redox Zone ID No. is calculated for every model cell block at every time step, using

$$ID_{ijk}^t = ID_{a,min} + \frac{C_{a,bck} - C_{a,ijk}^t}{C_{a,bck} - C_{a,min}} \quad (C.1)$$

where ID_{ijk}^t is the Redox Zone ID No. for cell block ijk at time t ;
 $ID_{a,min}$ is the minimum Redox Zone ID No. for the predominant electron acceptor a (e.g. $ID_{a,min}$ for oxygen is 1.0);
 $C_{a,bck}$ is the background concentration for electron acceptor a [ML⁻³];
 $C_{a,min}$ is the minimum concentration needed to support the reduction of electron acceptor a [ML⁻³]; and
 $C_{a,ijk}^t$ is the concentration of electron acceptor a at cell block ijk at time t [ML⁻³].

The Redox Zone ID No. is saved to the concentration output file, in addition to the concentrations for all solutes included in the simulation, at user-specified simulation times. The benefit of this redox zone scaling factor is that users can visualize how quickly electron acceptor concentrations change near the boundaries of each redox zone. For example, the effects of oxygenated recharge on vertical redox zonation can easily be visualized for cross-section profiles showing contours of the Redox Zone ID Nos. This method has an additional benefit in that it reduces the need for evaluating contour maps for each individual electron acceptor, which is more difficult to analyze when assessing the inter-dependence between concentrations of various electron acceptors.

Figure 5.18 illustrates an example of the colour gradational scheme used to represent varying electron acceptor concentrations within each redox zone. Progressively darker colors in each redox zone represent progressive decreases in the dominant electron acceptor concentration. A uniform colour is used to represent methanogenesis because carbon dioxide was assumed to be available in unlimited supply.

Figure 5.18 – Redox zone visualization colour scheme.

Figure 5.19a illustrates the conceptual redox zones that were identified based on electron acceptor contours corresponding to the minimum threshold concentrations for each TEAP. That is, Figure 5.19a identifies different redox zones based on the following contour lines: oxygen and nitrate isoconcentration contours corresponding to 0.1 mg/L, and Fe(III) and sulfate isoconcentration contours of 1 mg/L. The definition of redox zones based on electron acceptor simulated and the threshold concentrations is identified in Table 5.5. For example, the area identified with in blue in Figure 5.19a represents

Table 5.5 – Simulation model criteria for preferential utilization of TEAPs during TOC oxidation.

	<i>Concentration Thresholds (mg/L)</i>				
	Aerobic	Nitrate-Reducing	Iron(III)-Reducing	Sulfate-Reducing	Methanogenic
Oxygen	C > 0.1	C < 0.1	C < 0.1	C < 0.1	C < 0.1
Nitrate	--	C > 0.1	C < 0.1	C < 0.1	C < 0.1
Iron(III)	--	--	C > 1	C < 1	C < 1
Sulfate	--	--	--	C > 1	C < 1

portions of the domain where oxygen was simulated as being greater than the threshold concentration of 0.1 mg/L. The area identified in yellow in Figure 5.19a represents nitrate reducing conditions (i.e. oxygen is below the threshold concentration, and nitrate is above the threshold concentration of 0.1 mg/L).

Figures 5.19b and 5.19c illustrate the redox zones that were contoured based on Redox ID numbers (1 to 5) output by the BioRedox code during the simulation. The contouring of redox zone codes is based on a complex algorithm that uses a grid spacing, which is more refined than that of the model, to increase the resolution for visualizing

redox zones in vertical cross-sections. Therefore, there are some subtle differences between the zones shown in Figure 5.19a (based on electron acceptor concentration

Figure 5.19 – Validation of BioRedox method for visualizing redox zonation based on electron acceptor threshold concentrations for each TEAP.

contours) and Figures 5.19b,c (based on calculated redox zone codes). In general, however, the similarity in comparisons between Figure 5.19a and 5.19b,c verifies the calculation of these redox zone ID numbers.

The redox zone visualization approach does not illustrate that there is constant recharge of nitrate and oxygen at the water table in the methanogenic and Fe(III)-reducing zones downgradient from the landfill. The redox zone ID number is assigned at each model cell node at the end of each timestep. Thus the visualization of these redox zones does not show that oxygen and nitrate are undergoing reduction at the beginning of each time step in the top layer of the model where conditions are strongly anaerobic. The small concentrations of oxygen and nitrate in diluted recharge are quickly depleted at the beginning of the timestep when TOC concentrations are relatively high.

5.3.2 Discussion of Simulated Redox Zonation

5.3.2.1 Redox Zonation at 15 years

The simulated methanogenic zone (130 m) shown in Figure 5.19c is significantly longer than the zone (20 to 50 m) observed in the field (shown in Figure 5.9). The notable absence of a sulfate-reducing zone in the model, downgradient from the simulated methanogenic zone, is easily explained by the concept behind dominant TEAP zones used to formulate the BioRedox reaction algorithm.

The concept used in BioRedox is that all sulfate must be depleted prior to the occurrence of methanogenesis. Therefore, the model simulated that available sulfate from upgradient recharge is rapidly depleted below the landfill, allowing for methanogenesis to occur. Because the sulfate was exhausted upgradient of the

methanogenic zone, there was no sulfate available to support a sulfate-reducing zone downgradient from the methanogenic zone.

This is in contrast to the common perception that suggests a sulfate-reducing zone is situated downgradient, not upgradient, from the near-source methanogenic zone (e.g. Lyngkilde and Christensen, 1992a). Based on thermodynamic principles, the sequence of redox zones should actually be the reverse. That is, sulfate reduction should occur directly below the source area (assuming that Fe(III) has already been depleted). Once the supply of sulfate is exhausted, methanogenesis will occur downgradient from the source. Assuming that vertical recharge of sulfate is negligible, iron reduction should predominate directly downgradient from the methanogenic zone (unless a geochemical reaction results in sulfate dissolution from aquifer sediments). Nitrate reduction and aerobic zones will occur downgradient from the iron reducing zone, if the vertical recharge of nitrate and oxygen to the anaerobic core of the plume is greater than the rate of depletion of these electron acceptors.

In the field we have observed concomitant sulfate-reducing and methanogenic zones (e.g. Cozzarelli et al., 2000). Based on the concept of preferential TEAP utilization using thermodynamic principals, the occurrence of a sulfate-reducing zone downgradient from a methanogenic zone will occur if a source of sulfate exists, such as gypsum dissolution arising from elevated alkalinity in groundwater. As discussed in Section 5.1.3, measured sulfate levels appear to increase with distance downgradient from the landfill, possibly as a result of mineral dissolution. This would explain the presence of the sulfate-reducing zone observed by Lyngkilde and Christensen (1992a), although this zone was not observed in subsequent events.

The BioRedox model simulated the lack of sulfate reduction downgradient from the methanogenic zone, which is in agreement with the conceptual model used to represent preferential TEAP utilization. The appearance of a small sulfate-reducing zone below and downgradient of the methanogenic zone in Figures 5.19b and 5.19c is an artifact of the contouring method, as shown by the absence of sulfate-reducing conditions in Figure 5.19a. BioRedox will not simulate a sulfate-reducing zone downgradient from a methanogenic zone unless a source of sulfate dissolution is incorporated into the simulation model. The current version of BioRedox does not represent equilibrium processes of mineral precipitation and dissolution.

Although the simulated methanogenic zone (125 m) is significantly longer than the observed zone, the model does provide a reasonable approximation of Fe(III) depletion after 15 years of leachate attenuation. As discussed in Section 5.1.4, average concentrations of noncrystalline Fe(III) were minimal to non-detect in the first 100 m of the flowpath. Also, given the lack of a sulfate reducing zone observed in subsequent monitoring at Vejen Landfill (Christensen et al., 1994), it is conceivable that the actual methanogenic zone in the aquifer is longer than that observed by Lyngkilde and Christensen (1992a).

The simulation model predicted that aquifer redox conditions returned to naturally oxidizing levels approximately 300 m downgradient from the landfill. This underestimates the length of the anaerobic zone, partially because the model did not simulate a significant nitrate-reducing zone downgradient from the Fe(III) reducing zone (in contradiction to field observations made by Lyngkilde and Christensen, 1992a). The Base Case model did not simulate Fe(II) dissolution and downgradient oxidation, which

may explain the difference between the simulated and observed extents of nitrate reduction. This possible explanation is investigated further in the sensitivity analysis.

5.3.2.2 TOC Mass Budget

Table 5.6 provides a cumulative mass budget to illustrate the proportion of TOC undergoing biodegradation in each of the simulated redox zones. Table 5.6 indicates that approximately 85% of the total TOC degraded during the 15-year simulation was transformed under methanogenic conditions, 11% under iron-reducing conditions, and nominal amounts under oxygen, nitrate, and sulfate reduction. By comparison, the total TOC mass degradation in the final year of the simulation was slightly different in terms of proportion degraded in each redox zone: 2 to 6% for oxygen, nitrate, Fe(III), and sulfate reduction; and, 80% of TOC mass was degraded under methanogenic conditions.

Table 5.6 – Summary of TEAP-specific TOC mass degradation for Base Case.

<i>TEAP</i>	<i>Proportion of TOC Degradation</i>	
	<i>Total Simulation</i>	<i>Last Year Simulation</i>
Aerobic	0.8%	2.7%
NO ₃ -Reducing	1.7%	5.3%
Fe(III)-Reducing	11.1%	5.6%
SO ₄ -Reducing	1.5%	6.0%
Methanogenic	84.9%	80.4%
Total:	100.0%	100.0%

The significant disparity in TOC mass degradation for each TEAP is clearly the result of large Fe(III) redox buffering capacity in sediments (relative to the buffering capacity provided by the dissolved electron acceptors), and by the assumption of unlimited supply of carbon-dioxide in groundwater to support methanogenesis.

Another reason for this disparity is that total TOC mass degradation is dependent on both the first-order degradation rate and the concentration of TOC in each zone. The methanogenic zone directly below the landfill also coincides with much higher TOC concentrations than the other zones, which contributes to the significantly higher mass of TOC degraded in this zone.

The role of the Fe(III) TEAP became less significant in time (and more on par with the roles of nitrate and sulfate reduction), presumably because of a significant reduction in Fe(III) redox buffering capacity, and because Fe(III) reduction only occurred at farther distances downgradient from the landfill (where TOC concentrations were reduced). It is conceivable to expect that the relative role of a specific TEAP at a site is at least partially dependent on the ratio of the electron donor concentration(s) to the electron acceptor concentrations. At this site, the high TOC concentrations near the source, relative to background concentrations of oxygen, nitrate, and sulfate, resulted in rapid depletion of these dissolved electron acceptors.

Previously, the Fe(III) buffering capacity in sediments below the Vejen Landfill was recognized as contributing significantly to the oxidation of organic matter in leachate. However, conventional calculations of oxidation capacity do not consider the abundant oxidation likely to occur under methanogenic conditions, which is characterized by an infinite supply of electron acceptor and higher organic matter concentrations relative to the other zones. Perhaps the role of methanogenesis should be considered further when evaluating long-term capacity to support intrinsic remediation of organic matter.

5.3.2.3 Discrepancy in Vertical Extent of Redox Zonation Below Landfill

The simulated anaerobic plume directly downgradient from the landfill (Figure 5.19c) is relatively shallow compared to the 10-m depth shown for the observed redox zonation. The reason for this discrepancy is uncertain. As discussed, density effects in the field may play a role, although the reduced strength of the aged leachate is not anticipated to cause a significant density variation relative to groundwater.

5.3.2.4 Transient Redox Zone Development

Figures 5.20a through 5.20d illustrate simulated redox zones corresponding to simulation times of 1, 5, 10, and 15 years, respectively. The TOC isoconcentration contours are overlaid on the redox zone maps shown in each figure.

It is apparent from Figures 5.20a through 5.20d that the interface between the anaerobic and aerobic zone coincides with the TOC isoconcentration contour of 2 mg/L. This indicates that oxygen and nitrate are not available at this downgradient portion of the anaerobic plume, and that anaerobic (iron-reducing) biodegradation of TOC ceases when the simulated concentration of TOC decreases below the minimum threshold concentration of 2 mg/L. This confirms that BioRedox is correctly representing the effects of the minimum threshold concentration when simulating the biodegradation of the electron donor.

Figure 5.20a illustrates that amorphous Fe(III) hydroxides are rapidly depleted directly below the landfill, likely as a result of the high TOC concentrations and higher degree of reactivity of the fresh leachate (as simulated in the site model). The simulated extent of the anaerobic zone is approximately 230 m downgradient from the landfill after

Year 1 of the simulation, which is generally consistent with the approximate groundwater velocity of 150 to 200 m/y below the landfill (assuming negligible sorption of TOC).

Figure 5.20 – Transient redox zone development (from one to 15 years of the Base Case simulation).

Figure 5.20b indicates that after a simulation time of 5 years, the methanogenic zone has extended to a distance of 100 m downgradient from the landfill, and the anaerobic portion of the plume is a little more than 300 m downgradient from the landfill. The dark blue contours shown in Figure 5.20b downgradient from the leachate plume indicate that oxygen is depleted downgradient from the landfill. The colour gradations shown in the downgradient aerobic zone indicate that vertical mixing from oxygenated recharge above and below this plume are gradually increasing oxygen concentrations to background levels, which provides qualitative validation that BioRedox is correctly representing vertical mixing of dissolved electron acceptors.

The extent of the simulated anaerobic zone in Figure 5.20c (10 year simulation time) has receded slightly from the plume shown in Figure 5.20b (5 years), likely because of declining concentrations of TOC in the landfill leachate source model. Figures 5.20c and 5.20d also indicate that redox zonation does not reach a true steady-state condition because the methanogenic zone continues to expand as Fe(III) hydroxides are exhausted in the aquifer. However, the downgradient extent of the simulated anaerobic zone does reach a stable configuration, which corresponds to the general trend observed at many field sites (e.g. Wiedemeier et. al., 1999).

5.3.2.5 Effect of Model Dimensionality

The representation of two-dimensional cross-sectional transport ignores the effects of horizontal transverse dispersion. The trend of decreasing TOC concentrations measured along the flowpath in the aquifer (Lyngkilde and Christensen, 1992a) is due to the combined effects of dispersion and biodegradation. The half-life calculated based on

corrected NVOC concentrations (refer to Section 5.1.3) represents the true biodegradation rate, because the effects of dispersion were removed from the corrected concentration profile. The two-dimensional cross-section model underestimates the attenuation of TOC along the flowpath because it does not account for transverse dispersion into the plane of the model domain.

If transverse dispersion is underestimated, the electron donor concentration is overestimated along the flowpath, and will result in overestimation of the relative rate of electron acceptor utilization in each TEAP. For this simulation, the maximum TOC concentration observed below the landfill (after dilution from landfill recharge) was determined to be on the order of 200 mg/L, which is significantly lower than the observed range of 300 to 500 mg/L for NVOC. The measured concentration in the landfill leachate within the refuse was observed to have average and maximum values of 250 and 520 mg/L, respectively. The maximum measured leachate concentration is similar to the maximum NVOC value measured in groundwater directly adjacent to the landfill (484 mg/L). There is no clear explanation for the similarity between these values.

Although the wide landfill source area would suggest that transverse dispersion is not significant along the centreline of the leachate plume, the significant attenuation of chloride (a conservative ion) downgradient from the landfill suggests that transverse dispersion may be significant along the transect of monitoring wells. Hence the model is likely to have underestimated TOC attenuation caused by transverse dispersion. This may have been counteracted by the apparent underestimation of TOC concentrations below the landfill (compared to measured NVOC concentrations).

The limitation of using a two-dimensional cross-section model representation for simulating reactive solute transport requires important consideration. If the source of electron donors is sufficiently narrow perpendicular to groundwater flow, then neglecting transverse dispersion may result in significant overestimation of downgradient electron donor concentrations, which would result in a corresponding overestimation of the rate of depletion of available electron acceptors.

5.3.3 Validation of BioRedox TEAP Representation

Based on the general trends represented in the Vejen Landfill simulation model, the conceptual representation of long-term redox zonation in BioRedox provides a reasonable approximation to general trends observed in the field. Major differences between the simulation model and field observations, such as the sulfate-reducing zone observed downgradient from the methanogenic zone, may at least be partially explained by intuitive reasoning.

Although BioRedox provides a simplified representation of complex processes in the field, the dominant processes resulting in large-scale redox zonation appear to be represented in the BioRedox algorithm. The applicability of BioRedox for representing site-specific redox zonation must be considered at each site, based on a detailed understanding of site conditions, as well as inherent limitations in the BioRedox representation of field-scale biogeochemical processes.

5.3.4 Sensitivity to Fe(II) Mobilization and Transport

As discussed in Section 5.1.4, the analysis of samples collected along the flowpath at Vejen Landfill indicate that total iron is significantly elevated near the transition area between the iron-reducing and nitrate-reducing zones. It is also apparent from the analysis of samples that little dissolved Fe(II) was transported into the nitrate-reducing and aerobic zones. The processes responsible for the apparent attenuation of dissolved iron in the aquifer are not well understood (although ion exchange appears to have limited attenuation potential, particularly after the long duration of leachate pollution in the aquifer).

The Base Case simulation did not include representation of dissolved ferrous Fe(II) fate and transport, resulting from the reductive dissolution of Fe(III) hydroxides. Simulations A and B included representation of reductive dissolution to the Fe(II) state, downgradient transport of aqueous Fe(II), and oxidation of Fe(II) when mixed with oxygenated recharge water (assumed to be an instantaneous reaction).

Simulation A assumed a maximum solubility of Fe(II) equal to 40 mg/L (observed in the section of the flowpath between 30 and 100 m downgradient of the landfill), and simulation B assumed a maximum solubility of 20 mg/L (observed between 100 and 200 m along the flowpath). The limited solubility of Fe(II) did not limit the extent of Fe(III) reduction occurring. Placing an upper limit on Fe(II) solubility is a simplified approach for representing the complex geochemical reactions that may result in a sink for aqueous-phase Fe(II) through processes of precipitation or ion exchange.

Figure 5.21a presents the simulated TOC isoconcentration contours and redox zonation for the Base Case. Figures 5.21b and 5.21c present the simulated iron(II)

and 5.21c) indicates that the aqueous Fe(II) is scavenging oxygen from the recharge water, so that the extent of the anaerobic portion of the plume is significantly longer.

This confirms the importance of considering aqueous Fe(II) concentrations when evaluating the possibility of enhanced bioremediation alternatives that include oxygen amendments. This type of remedy will have limited success in Fe(II)-rich water because Fe(II) is such an efficient scavenger of dissolved oxygen. Representing Fe(II) transport and rapid aerobic oxidation will also have an influence on the simulated length of the anaerobic zone, which has important implications for remedies involving in-situ sequential anaerobic-aerobic treatment trains.

5.4 HYPOTHETICAL SOURCE CONTROL SIMULATIONS

Additional simulations were conducted to evaluate the influence that landfill cap permeability may have on the intrinsic remediation of a hypothetical TCE plume in the underlying aquifer. Christensen et al. (1998) suggest that intrinsic remediation of landfill leachate plumes in underlying aquifers without removing the source is an attractive approach for managing leachate plumes. However, the natural attenuation of landfill leachate is more difficult to evaluate than for a petroleum hydrocarbon or chlorinated solvent plume.

BioRedox may serve as a valuable tool for predicting the efficiency of integrated landfill remediation systems, including permeable caps and intrinsic remediation in underlying aquifers. The goal of these simulations was to demonstrate that BioRedox is capable of simulating the effects of landfill cap performance on plume attenuation, and to demonstrate the detrimental effect that active source control may have on downgradient

intrinsic bioremediation performance.

The Vejen Landfill Base Case simulation model was utilized for this study, and a hypothetical source of TCE with a constant concentration of 250 ug/L was added to the landfill leachate source model. The development of the TCE plume in the aquifer was simulated for the initial 15-year simulation period, over which time a permeable soil cover existed over the portion of the landfill contributing to leachate contamination in the underlying aquifer (with an average infiltration rate of 0.42 m/y).

The distribution of TOC isoconcentration contours and redox zonation at the end of the initial 15-year simulation was identical to the Base Case simulation presented in Figure 5.20d. The only additional solute included in this new simulation was TCE.

TCE was assumed to undergo first-order degradation at a uniform rate in the methanogenic, sulfate-reducing, and iron-reducing zones, with a half-life of 6 months. TCE was assumed to be recalcitrant under nitrate-reducing and aerobic conditions in the aquifer. The simulation of TCE in the landfill and underlying aquifer was completely hypothetical, and is not intended to represent the fate of actual organic pollutants measured in the Vejen Landfill.

At some sites TCE biodegradation in the Fe(III)-reducing zone may be simulated as negligible to be conservative, unless the form of Fe(III) is known to be relatively non-reactive (thus reducing the competitive inhibition of dechlorinators). However, for this demonstration TCE was assumed to undergo biodegradation in the iron-reducing zone.

Other input parameters assumed for TCE include molecular weight (131.6 g/mol) and organic carbon partitioning coefficient (126 mL/g). The fraction of organic carbon in

soil was assumed to be 0.1%. Based on these parameters and a linear isotherm, the retardation coefficient for TCE is approximately 1.6.

Landfill Cap Simulation Parameters

Two simulations were conducted to represent the effect of cap placement after the initial 15-year simulation period with uncontrolled leachate migration to the aquifer. One simulation assumed that a relatively permeable cap was placed on the landfill at the end of Year 15 (infiltration rate of 0.15 m/y), and the second simulation assumed a low-permeability cap (infiltration rate of 0.02 m/y) was placed over the landfill.

The TOC and TCE concentrations were kept constant in the landfill leachate source model (1040 mg/L and 250 ug/L, respectively) for the second fifteen year simulation (Years 15 to 30). The effect of placing an engineered cap over the landfill was to limit the migration of TOC and TCE to the underlying aquifer.

TCE Plume and Redox Zonation Prior to Cap Placement

Figure 5.22a illustrates the simulated steady-state extent of the TCE plume just prior to placement of the cap ($t=0$ for the cap simulation). The TCE contour shown in Figure 5.22a represents a concentration of 5 ug/L, which is the federal Maximum Concentration Level (MCL) for TCE based on drinking water criteria in the United States. The MCL contour for TCE was assumed to represent the extent of the TCE plume in the aquifer.

As shown in Figure 5.22a, the TCE plume occurs in the strongly reducing portion of the aquifer where TCE undergoes first-order biodegradation. The TCE plume has

reached steady-state prior to placement of the cap because the rate of mass flux of TCE from the landfill to the aquifer is equal to the total rate of mass degradation in the strongly anaerobic zone. That is, steady-state is reached when the rate of mass input for a solute equals the rate of mass output from the domain.

Figure 5.22 – Simulation of landfill cap influence on groundwater intrinsic remediation.

Effect of Low-Permeability Cap

Figure 5.22b shows the distribution of redox zones and the TCE plume one year after placement of the low-permeability cap. The reduction in leachate infiltration to the aquifer has significantly reduced the source of TOC to the aquifer, and has caused redox conditions directly downgradient of the landfill to become significantly less reducing. This is evidenced by the significant reduction in extent of the methanogenic zone, and

increasing extent of sulfate- and nitrate-reducing zones. The rate at which groundwater conditions become more oxidizing is partially dependent on groundwater velocity.

Comparison of Figures 5.22c through 5.22e indicates that the redox zonation has reached quasi-steady state within two years after cap placement. There is a small sulfate-reducing zone directly below the landfill (where Fe(III) is depleted and a reduced TOC flux continues to deplete oxygen and nitrate supplies directly below the landfill). The remainder of the aquifer is under nitrate-reducing or aerobic conditions.

TCE does not biodegrade under nitrate-reducing or aerobic conditions, and thus the portion of the TCE plume that extends beyond the extent of the sulfate-reducing zone is no longer biodegrading. The continued desorption of TCE from aquifer sediments, after the original source was contained by placement of the low-permeability cap, maintains a significant TCE plume above the MCL. Subsequent mobilization of the TCE plume occurs because TCE is not biodegrading in this portion of the aquifer.

In summary, placement of the low-permeability cap was effective in limiting contaminant flux to the aquifer. However, it also removed a significant portion of the substrate source to the aquifer, causing conditions to become significantly more oxidizing within only one to two years after cap placement. The desorption of TCE from aquifer sediments that occurred after source containment at the landfill maintained a TCE plume above the MCL which migrated downgradient from the site because TCE was no longer biodegradable in this portion of the aquifer.

Organic pollutants present in older plumes that have been present for a decade or more, tend to exhibit very slow (i.e. rate-limited) desorption kinetics (Wiedemeier et al., 1999). For example, Imbrigiotta et al. (1996) measured slow TCE desorption from soils

in an aged plume. Imbrigiotta et al. (1996) determined that the TCE desorption from soil was providing a significant, long-term source of TCE to groundwater. Given that the landfill simulation assumed rapid desorption as an equilibrium process, this simulation underestimated the duration of the TCE source from desorption after cap placement. Rate-limited desorption should also be considered for aged plumes when active source control measures are being considered for implementation.

This chain of events indicates that consideration should be placed on any active source control measures that potentially remove substrates needed to maintain intrinsic bioremediation processes downgradient from the source. Reactive transport models such as BioRedox are valuable tools that may be used to explore the consequences of source control measures. Given the complex nature of biogeochemical processes, it would be difficult to predict the performance of an integrated remedy such as this without the use of a computer model.

Effect of Permeable Cap

Figure 5.22f shows the redox zonation and TCE plume distribution that was simulated to occur six years after placement of the more permeable cap. This figure indicates that the permeable cap permitted sufficient TOC migration to sustain a relatively long anaerobic plume downgradient from the landfill. This anaerobic plume maintained favourable conditions for TCE biodegradation, and therefore the existing TCE plume remained stable and within the sulfate-reducing and methanogenic conditions.

Although the permeable cap did permit pollutants to migrate from the landfill to

the aquifer, it also maintained conditions that were favourable for intrinsic remediation processes to occur downgradient from the landfill. Thus permeable caps should be considered as one component of a total landfill risk-based corrective action that includes intrinsic remediation of the groundwater pollutants.

It is particularly important to conduct long-term monitoring at landfills where natural attenuation is implemented as part of the remedy, because of uncertainty in long-term source conditions and aquifer oxidation capacity. For example, it is conceivable that sources of chlorinated solvents such as TCE in these old landfills will remain for an extended period of time, and may outlast the supply of available electron donors in the landfill and aquifer sediments. It is recommended that additional research be conducted to assess the long-term supply of electron donors that support reductive dechlorination reactions. It is also recommended that the BioRedox model be further validated to determine its applicability for predicting the performance of integrated landfill remedies involving intrinsic bioremediation.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

A comparison of empirically-determined Monod parameters and field-based estimates of first-order degradation rates for chlorinated ethenes indicated:

- the use of site-specific first-order degradation rates in a transport model is likely to be conservative (i.e. will underestimate biodegradation rates) relative to the use of Monod parameters derived from laboratory experiments; and
- first-order degradation rates are more appropriate for simulating large-scale biodegradation reactions in the field, when using site-specific rates, because they provide an implicit representation of non-ideal processes that generally inhibit the biodegradation process;

A reactive transport model (BioRedox-MT3DMS) was developed to allow for the simulation of redox-dependent biodegradation of organic pollutants, including petroleum hydrocarbons, chlorinated solvents, and organic-rich landfill leachate in groundwater. This transport model is capable of representing coupled oxidation-reduction reactions between multiple electron donors and acceptors, as well as TEAP-specific reaction mechanisms, rates, and pathways. BioRedox uses a simplified, geochemically-based algorithm to represent the preferential utilization of dominant TEAPs in groundwater. The relatively low number of input parameters required to run BioRedox facilitate its use at typical field sites with relatively sparse data and monitoring networks.

The BioRedox code was verified through manual calculations, as well as benchmark tests using analytical solutions and widely-used numerical transport models. BioRedox was also validated through a simulation of redox zonation in groundwater below the Vejen Landfill, which has been characterized in detail through scientific

publications available in the literature. The comparison of BioRedox simulations to field conditions provided validation of a number of the flexible features incorporated into BioRedox for representing coupled biodegradation and redox reactions.

Other findings from the simulation of leachate attenuation at the Vejen Landfill site include:

- methanogenic degradation plays a significantly larger role than iron reduction in landfill leachate TOC attenuation;
- the extent of TEAP zones is strongly dependent on the relative concentrations of electron donors and electron acceptors; high electron donor concentrations relative to the electron acceptor concentrations will result in rapid depletion of the electron acceptors; mineral-phase electron acceptors are typically present in much higher abundance than dissolved electron acceptors, and thus provide a significantly greater contribution to the overall redox buffering capacity of a system;
- BioRedox may be applicable for representing sequential TEAP utilization, even if concomitant TEAPs are occurring, provided that proper consideration is given to the effect of concomitant TEAPs on substrate utilization behaviour.

BioRedox may serve as a valuable tool for predicting the efficiency of integrated landfill remediation systems, including permeable caps and intrinsic remediation in underlying aquifers. Landfill cap simulations indicated that important consideration should be placed on any active source control measures, which potentially remove substrates needed to maintain intrinsic bioremediation processes downgradient from the source. Reactive transport models such as BioRedox are valuable tools that may be used to explore the consequences of source control measures. Given the complex nature of biogeochemical processes, it would be difficult to predict the performance of an integrated remedy such as this without the use of a computer model.

6.2 RECOMMENDATIONS

The following are general recommendations arising from this study:

- attention should be paid to the potential for hydrogen sulfide to react directly with iron(III) minerals; this reaction may reduce the oxidation capacity for organic matter biodegradation, although it is difficult to quantify the significance of this reaction;
- more research is required to determine the extent to which halorespiration may occur during iron(III) reduction;
- better delineation of iron(III) and iron(II) speciation in sediments is recommended when using reactive transport models that represent iron(III) background concentrations for evaluating redox zonation in aquifers
- slow rate-limited desorption should be considered for aged plumes when active source control measures are being considered for implementation; it is recommended that rate-limited desorption kinetics be incorporated into the BioRedox code;
- it is recommended that additional research be conducted to assess the long-term supply of electron donors that support reductive dechlorination reactions. It is also recommended that the BioRedox model be further validated to determine its applicability for predicting the performance of integrated landfill remedies involving intrinsic bioremediation;

REFERENCES

- Abrams, R.H., and K. Loague, 2000, A Compartmentalized Solute Transport Model for Redox Zones in Contaminated Aquifers 1 (Theory and Development), *Water Resources Research*, 36(8): 2001-2013.
- Abrams, R.H., and K. Loague, 2000, A Compartmentalized Solute Transport Model for Redox Zones in Contaminated Aquifers 2 (Field-Scale Simulations), *Water Resources Research*, 36(8): 2015-2029.
- Abrams, R.H., K. Loague and D.B. Kent, 1998, Development and Testing of a Compartmentalized Reaction Network Model for Redox Zones in Contaminated Aquifers, *Water Resources Research*, 34(6): 1531-1541.
- Appelo, C.A.J., and D. Postma, 1993, *Geochemistry, Groundwater and Pollution*, A.A. Balkema, Rotterdam, Netherlands.
- Baedecker, M.J., and W. Back, 1979a, Modern Marine Sediments as a Natural Analog to the Chemically Stressed Environment of a Landfill, *Journal of Hydrology*, 43: 393-414.
- Baedecker M.J., and W. Back, 1979b, Hydrogeological Processes and Chemical Reactions at a Landfill, *Ground Water*, 17(5): 429-437.
- Bekins, B.A., E.M. Godsy and E. Warren, 1999, *Microb. Ecol.*, 37: 263-275.
- Bekins, B.A., E. Warren and E.M. Godsy, 1998, A Comparison of Zero-Order, First-Order, and Monod Biotransformation Models, *Ground Water*, 36(2): 261-268.
- Bjerg, P.L., K. Rügge, J. Cortsen, P.H. Nielsen and T.H. Christensen, 1999, Degradation of Aromatic and Chlorinated Aliphatic Hydrocarbons in the Anaerobic Part of the Grindsted Landfill Leachate Plume: In Situ Microcosm and Laboratory Batch Experiments, *Ground Water*, 37(1): 113-121.
- Bjerg, P.L., and T.H. Christensen, 1992, Spatial and Temporal Small-Scale Variation in Groundwater Quality of a Shallow Sandy Aquifer, *Journal of Hydrology*, 131: 133-149.
- Bradley P.M. and F.H. Chapelle, 1996, Anaerobic Mineralization of Vinyl Chloride in Fe(III)-Reducing Aquifer Sediments, *Environmental Science & Technology*, Vol. 30, pp. 2084-2086.

- Chapelle, F.H., D.A. Vroblesky, J.C. Woodward, and D.R. Lovley, 1997, Practical Considerations for Measuring Hydrogen Concentrations in Groundwater, *Environmental Science & Technology*, 31(10): 2873-2877.
- Chapelle, F.H., P.B. McMahon, N.M. Dubrovsky, R.F. Fujii, E.T. Oaksford and D.A. Vroblesky, 1995, Deducing the Distribution of Terminal Electron-Accepting Processes in Hydrologically Diverse Groundwater Systems, *Water Resources Research*, 31(2): 359-371.
- Cho, C.M., 1971, Convective Transport of Ammonium with Nitrification in Soil, *Canadian Journal of Soil Science*, Vol. 51, No. 3, pp. 339-350.
- Christensen T.H., P.L. Bjerg and P. Kjeldsen, 2000, Natural Attenuation: A Feasible Approach to Remediation of Ground Water Pollution at Landfills, *Ground Water Monitoring & Remediation*, 20(1): 69-77.
- Christensen T.H., P. Kjeldsen, H. Albrechtsen, G. Heron, P.H. Nielsen, P.L. Bjerg and P.E. Holm, 1994, Attenuation of Landfill Leachate Pollutants in Aquifers, *Critical Reviews in Environmental Science and Technology*, 24(2): 119-202.
- Clement, T.P., Y. Sun, B.S. Hooker and J.N. Petersen, 1998, Modeling Multispecies Reactive Transport in Ground Water, *Ground Water Monitoring & Remediation*, 18(2): 79-92.
- Cozzarelli, I.M., J.S. Herman, M.J. Baedecker and J.M. Fischer, 1999, *Journal of Contaminant Hydrology*, 40: 261-284.
- Cozzarelli, I.M., J.M. Suflita, G.A. Ulrich, S.M. Harris, M.A. Scholl, J.L. Schlottmann, and S. Christenson, 2000, Geochemical and Microbiological Methods for Evaluating Anaerobic Processes in an Aquifer Contaminated by Landfill Leachate, *Environmental Science and Technology*, 34(18): 4025-4033.
- Deutsch, W.J., 1997, *Groundwater Geochemistry: Fundamentals and Applications to Contamination*, Lewis Publishers, New York.
- Dragun, J., 1988, *The Soil Chemistry of Hazardous Materials*, The Hazardous Materials Control Research Institute, Silver Spring, Maryland.
- Duynisveld, W.H.M., O. Strebel and J. Boettcher, 1990, Modeling of Multicomponent Transport With Microbial Transformation in Groundwater: The Fuhrberg Case, *Water Resources Research*, 26(8): 1707-1719.
- Ehrlich, H.L., 1996, *Geomicrobiology*, Marcel Dekker, New York, NY.

- Engesgaard, P., and R. Traberg, 1996, Contaminant Transport at a Waste Residue Deposit 2 (Geochemical Transport Modeling), *Water Resources Research*, 32(4): 939-951.
- Ellis D.E., 1996, Intrinsic Remediation in the Industrial Marketplace, In: *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, EPA/540/R-96/509, pp. 120-123.
- Essaid, H.I., B.A. Bekins, E.M. Godsy, E. Warren, M.J. Baedeker and I.M. Cozzarelli, 1995, Simulation of Aerobic and Anaerobic Biodegradation Processes at a Crude Oil Spill Site, *Water Resources Research*, 31(12): 3309-3327.
- Fennell, D.E., and J.M. Gossett, 1998, Modeling the Production of and Competition for Hydrogen in a Dechlorinating Culture, *Environmental Science & Technology*, 32(16): 2450-2460.
- Friedly, J.C., J.A. Davis and D.B. Kent, 1995, Modeling Hexavalent Chromium Reduction in Groundwater in Field-Scale Transport and Laboratory Batch Experiments, *Water Resources Research*, 31(11): 2783-2794.
- Fryar, A.E., and F.W. Schwartz, 1994, Modeling the Removal of Metals from Groundwater by a Reactive Barrier: Experimental Results, *Water Resources Research*, 30(12): 3455-3469.
- Gossett, J.M., and S.H. Zinder, 1996, Microbiological Aspects Relevant to Natural Attenuation of Chlorinated Ethenes, In: *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, EPA/540/R-96/509, pp. 10-13.
- Gouy, J., P. Bergé and L. Labroue, 1984, *Gallionella ferruginea*, facteur de dénitrification dans les eaux pauvre en matière organique. *C.R. Acad. Sc. Paris* 298: 153-156.
- Haston, Z.C., and P.L. McCarty, 1999, Chlorinated Ethene Half-Velocity Coefficients (K_d) for Reductive Dehalogenation, *Environmental Science & Technology*, 33(2): 223-226.
- Hem, J.D., 1985, Study and Interpretation of the Chemical Characteristics of Natural Water, Third Edition, U.S. Geological Survey Water - Supply Paper 2254.
- Heron, G., and T.H. Christensen, 1995, Impact of Sediment-Bound Iron on Redox Buffering in a Landfill Leachate Polluted Aquifer (Vejen, Denmark), *Environmental Science & Technology*, 29(1): 187-192.

- Heron, G., C. Crouzet, A.C.M. Bourg and T.H. Christensen, 1994a, Speciation of Fe(II) and Fe(III) in Contaminated Aquifer Sediments Using Chemical Extraction Techniques, *Environmental Science & Technology*, 28: 1698-1705.
- Heron, G., T.H. Christensen and J.C. Tjell, 1994b, Oxidation Capacity of Aquifer Sediments, *Environmental Science & Technology*, 28(1): 153-158.
- Hossain, A., and M.Y. Corapcioglu, 1996, Modeling Primary Substrate Controlled Biotransformation and Transport of Halogenated Aliphatics in Porous Media, *Transport in Porous Media*, 24: 203-220.
- Huyakorn, P.S. and G.F. Pinder, 1983, Computational Methods in Subsurface Flow, Academic Press, San Diego, 473 pp.
- Imbrigiotta, T.E., T.A. Ehlke, B.H. Wilson, and J.T. Wilson, 1996, Case Study: Natural Attenuation of a Trichloroethene Plume at Picatinny Arsenal, New Jersey, *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, United States Environmental Protection Agency, Report EPA/540/R-96/509, pp. 83-89.
- Iversen, N., and B.B. Jørgensen, 1985, Anaerobic Methane Oxidation Rates at the Sulfate-Methane Transition in Marine Sediments from Kattegat and Skagerrak (Denmark), *Limnol. Oceanogr.*, 30: 944-955.
- Jakobsen, R., H.J. Albrechtsen, M. Rasmussen, H. Bay, P.L. Bjerg and T.H. Christensen, 1998, H₂ Concentrations in a Landfill Leachate Plume (Grindsted, Denmark): In Situ Energetics of Terminal Electron Acceptor Processes, *Environmental Science & Technology*, 32(14): 2142-2148.
- Kennedy, L.G., J.W. Everett, K.J. Ware, R. Parsons and V. Green, 1998, Iron and Sulfur Mineral Analysis Methods for Natural Attenuation Assessments, *Bioremediation Journal*, 2(3&4): 259-276.
- Kimball, J.W., 1983, *Biology, Fifth Edition*, Addison-Wesley Publishing Company, USA.
- Kjeldsen, P., 1993, Groundwater Pollution Source Characterization of an Old Landfill, *Journal of Hydrology*, 142: 349-371.
- Larsen, T., T.H. Christensen, F.M. Pfeffer and C.G. Enfield, 1992, Landfill Leachate Effects on Sorption of Organic Micropollutants onto Aquifer Materials, *Journal of Contaminant Hydrology*, 9: 307-324.
- Lensing, H.J., M. Vogt and B. Herrling, 1994, Modeling of Biologically Mediated Redox Processes in the Subsurface, *Journal of Hydrology*, 159: 125-143.

- Lindberg, R.D., and D.D. Runnells, 1984, Ground water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling, *Science*, 225: 925-927.
- Lovley, D.R., and F.H. Chapelle, 1995, Deep Subsurface Microbial Processes, *Rev. Geophys.*, 33: 365-381.
- Lovley, D.R., F.H. Chapelle and J.C. Woodward, 1994, Use of Dissolved H₂ Concentrations To Determine Distribution of Microbially Catalyzed Redox Reactions in Anoxic Groundwater, *Environmental Science & Technology*, 28(7): 1205-1210.
- Lovley, D.R., E.J.P. Phillips and D.J. Lonergan, 1991, Enzymatic Versus Nonenzymatic Mechanisms for Fe(III) Reduction in Aquatic Sediments, *Environmental Science & Technology*, 25: 1062-1067.
- Lovley, D.R., and S. Goodwin, 1988, Hydrogen Concentrations as an Indicator of the Predominant Terminal Electron-Accepting Reactions in Aquatic Sediments, *Geochimica et Cosmochimica Acta*, 52: 2993-3003.
- Lovley, D.R., D.F. Dwyer and M.J. Klug, 1982, Kinetic Analysis of Competition Between Sulfate Reducers and Methanogens for Hydrogen in Sediments, *Applied and Environmental Microbiology*, 43(6): 1373-1379.
- Lu, G., T.P. Clement, C. Zheng and T.H. Wiedemeier, 1999, Natural Attenuation of BTEX Compounds: Model Development and Field-Scale Application, *Ground Water*, 37(5): 707-717.
- Lu, J.C.S., R.D. Morrison, and R.J. Stearns, 1981, Leachate Production and Management From Municipal Landfills: Summary and Assessment, In: *In-Land Disposal Municipal Solid Waste Proc. Seventh Ann. Res. Symp.*, EPA/600/9-81-002a.
- Lyngkilde J., and T.H. Christensen, 1992, Redox Zones of a Landfill Leachate Pollution Plume (Vejen, Denmark), *Journal of Contaminant Hydrology*, 10: 273-289.
- Lyngkilde J., and T.H. Christensen, 1992, Fate of Organic Contaminants in the Redox Zones of a Landfill Leachate Pollution Plume (Vejen, Denmark), *Journal of Contaminant Hydrology*, 10: 291-307.
- MacKay, D., W.Y. Shiu, A. Maijanen, and S. Feenstra, 1991, Dissolution of Non-aqueous Phase Liquids in Groundwater, *Journal of Contaminant Hydrology*, 8: 23-42.
- MacNab, W.W. and T.N. Narasimhan, 1993, A Multiple Species Transport Model with Sequential Decay Chain Interactions in Heterogeneous Subsurface Environments, *Water Resources Research*, Vol. 29, No. 8, pp. 2737-2746.

- Magar, V.S., H.D. Stensel, J.A. Puhakka and J.F. Ferguson, 1999, Sequential Anaerobic Dechlorination of Pentachlorophenol: Competitive Inhibition Effects and a Kinetic Model, *Environmental Science & Technology*, 33(10): 1604-1611.
- McCarty P.L., 1996, Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water, In: *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, EPA/540/R-96/509, pp. 5-9.
- McNab Jr., W.W., and T.N. Narasimhan, 1995, Reactive Transport of Petroleum Hydrocarbon Constituents in a Shallow Aquifer: Modeling Geochemical Interactions Between Organic and Inorganic Species, *Water Resources Research*, 31(8): 2027-2033.
- McNab Jr., W.W., and T.N. Narasimhan, 1994, Modeling Reactive Transport of Organic Compounds in Groundwater Using a Partial Redox Disequilibrium Approach, *Water Resources Research*, 30(9): 2619-2635.
- Metcalf and Eddy, Inc., 1979, *Wastewater Engineering: Treatment/Disposal/Reuse (Second Edition)*, Revised by G. Tchobanoglous, McGraw-Hill, Inc., USA
- Miller, R.N., 1990, A Field-Scale Investigation of Enhanced Petroleum Hydrocarbon Biodegradation in the Vadose Zone at Tyndall Air Force Base, Florida, in *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Restoration Conference*, NWWA/API, pp. 339-351.
- Monod, J., 1949, The growth of Bacterial Cultures, *Annual Review of Microbiology*, 3: 371-394.
- Munch, J.C., and J.C.G. Ottow, 1983, Reductive Transformation Mechanism of Ferric Oxides in Hydromorphic Soils, *Environ. Biogeochem.*, 35: 383-394.
- Munch, J.C., and J.C.G. Ottow, 1980, Preferential Reduction of Amorphous to Crystalline Iron Oxides by Bacterial Activity, *Soil Sci.*, 129(1): 15-21.
- Nielsen, P.H., H.J. Albrechtsen, G. Heron and T.H. Christensen, 1995, In Situ and Laboratory Studies on the Fate of Specific Organic Compounds in an Anaerobic Landfill Leachate Plume, 2 (Experimental Conditions and Fate of Phenolic Compounds), *Journal of Contaminant Hydrology*, 20: 27-50.
- Nielsen, P.H., H. Bjarnadóttir, P.L. Winter and T.H. Christensen, 1995, In Situ and Laboratory Studies on the Fate of Specific Organic Compounds in an Anaerobic Landfill Leachate Plume, 2 (Fate of Aromatic and Chlorinated Aliphatic Compounds), *Journal of Contaminant Hydrology*, 20: 51-66.

- Park, S.S., and P.R. Jaffé, 1996, Development of a Sediment Redox Potential Model for the Assessment of Postdepositional Metal Mobility, *Ecological Modelling*, 91: 169-181.
- Pavlostathis, S.G., and M.T. Prytula, 2000, Kinetics of the Sequential Microbial Reductive Dechlorination of Hexachlorobenzene, *Environmental Science & Technology*, 34(18): 4001-4009.
- Postma, D., and R. Jakobsen, 1996, Redox Zonation: Equilibrium Constraints on the Fe(III)/SO₄-Reduction Interface, *Geochimica et Cosmochimica Acta*, 60(17): 3169-3175.
- Roden, E.E., and J.M. Zachara, 1996, The Reduction of Fe Iron(III) Oxides: Measure of Oxide Surface Area and Potential for Cell Growth, *Environmental Science & Technology*, 30(5): 1618-1628.
- Rifai, H.S., C.J. Newell, J.R. Gonzales, S. Dendrou, L. Kennedy, and J. Wilson, *BIOPLUME III - Natural Attenuation Decision Support System: Version 1.0 User's Manual*, Air Force Center for Environmental Excellence, San Antonio, TX.
- Smith, R.L., B.L. Howes and J.H. Duff, 1991, Denitrification in Nitrate-Contaminated Groundwater: Occurrence in Steep Vertical Geochemical Gradients, *Geochem. Cosmochim. Acta*, 55: 1815-1825.
- Smith, S.L., and P.R. Jaffé, 1998, Modeling the Transport and Reaction of Trace Metals in Water-Saturated Soils and Sediments, *Water Resources Research*, 34(11): 3135-3147.
- Schäfer, W., and W.K.H. Kinzelbach, 1996, Transport of Reactive Species in Heterogeneous Porous Media, *Journal of Hydrology*, 183: 151-168.
- Semprini L., P.K. Kitanidis, D.H. Kampbell, and J.T. Wilson, 1995, Anaerobic Transformation of Chlorinated Aliphatic Hydrocarbons in a Sand Aquifer Based on Spatial Chemical Distributions, *Water Resources Research*, Vol. 31, pp. 1051-1062.
- Swindoll, M.C., C.M. Aelion and F.K. Pfaender, 1988, Influence of Inorganic and Organic Nutrients on Aerobic Biodegradation and on the Adaptation Response of Subsurface Microbial Communities, *Appl. Environ. Microbiol.*, 54(1): 221-217.
- U.S. Environmental Protection Agency, 1999, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*, Office of Solid Waste and Emergency Response Directive 9200. 4-17p, April 1999.

- van der Heijde, P.K.M. and D.A. Kanzer, 1997, Ground-Water Model Testing: Systematic Evaluation and Testing of Code Functionality and Performance, United States Environmental Protection Agency, EPA/600/R-97/007.
- van Genuchten, M.Th., 1985, Convective-Dispersive Transport of Solutes Involved in Sequential First-Order Decay Reactions, *Computers & Geosciences*, Vol. 11, No. 2, pp. 129-147.
- Vroblesky, D.A., P.M. Bradley and F.H. Chapelle, 1996, Influence of Electron Donor on the Minimum Sulfate Concentration Required for Sulfate Reduction in a Petroleum Hydrocarbon-Contaminated Aquifer, *Environmental Science & Technology*, 30(4): 1377-1381.
- Vogel T.M., T.M. Criddle, and P.L. McCarty, 1987, Transformations of Halogenated Aliphatic Compounds, *Environmental Science & Technology*, Vol. 21, pp. 723-736.
- Waddill, D.W., and M.A. Widdowson, 1998, Three-Dimensional Model for Subsurface Transport and Biodegradation, *Journal of Environmental Engineering*, 124(4): 336-344.
- Walter, A.L., E.O. Frind, D.W. Blowes, C.J. Ptacek and J.W. Molson, 1994, Modeling of Multicomponent Reactive Transport in Groundwater 1 (Model Development and Evaluation), *Water Resources Research*, 30(11): 3137-3148.
- Wiedemeier, T.H., H.S. Rifai, C.J. Newell and J.T. Wilson, 1999, *Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface*, John Wiley & Sons, Inc., New York.
- Wiedemeier, T.H., M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, P.E. Haas, R.N. Miller, J.E. Hansen and F.H. Chapelle, 1998, *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, United States Environmental Protection Agency, Report No. EPA/600/R-98/128, Washington, DC.
- Wilson J.T., D.H. Kampbell, and J.W. Weaver, 1996, Environmental Chemistry and the Kinetics of Biotransformation of Chlorinated Organic Compounds in Ground Water, In: *Symposium on Natural Attenuation of Chlorinated Organics in Ground Water*, EPA/540/R-96/509, pp. 124-127.
- Zhender, A.J.B., (ed), 1988, *Biology of Anaerobic Microorganisms*, Wiley & Sons, New York, pp 872.

- Zheng, C. and P.P. Wang, 1998, *MT3DMS: A Modular Three-Dimensional Multispecies Transport Model*, U.S. Army Corps. Of Engineers, Vicksburg, Mississippi.
- Zheng, C. and G.B. Bennett, 1995, *Applied Contaminant Transport Modeling*, Van Nostrand Reinhold, New York, USA, 440 pp.
- Zheng, C., 1990, *MT3D: A Modular Three-Dimensional Transport Model for Simulation of Advection, Dispersion and Chemical Reaction of Contaminants in Groundwater Systems*, S.S. Papadopoulos & Associates, Inc., Rockville, Maryland.
- Zysset, A., F. Stauffer and T. Dracos, 1994, Modeling of Chemically Reactive Groundwater Transport, *Water Resources Research*, 30(7): 2217-2228.
- Zysset, A., F. Stauffer and T. Dracos, 1994, Modeling of Reactive Groundwater Transport Governed by Biodegradation, *Water Resources Research*, 30(8): 2423-2434.