Three-Dimensional Modeling of Solute Transport with In Situ Bioremediation Based on Sequential Electron Acceptors

Dan W. Waddill

Dissertation submitted to the Faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in
Civil Engineering

Mark A. Widdowson, Chair
William E. Cox
G. V. Loganathan
Nancy G. Love
Jack C. Parker

January 29, 1998
Blacksburg, Virginia

Key words: sequential electron acceptors, contaminant transport, biodegradation, microbial growth, groundwater

Copyright 1998, Dan W. Waddill

Three-Dimensional Modeling of Solute Transport with In Situ Bioremediation Based on Sequential Electron Acceptors

Dan W. Waddill

The Charles E. Via Department of Civil Engineering

(ABSTRACT)

A numerical model for subsurface solute transport is developed and applied to a contaminated field site. The model is capable of depicting multiple species transport in a three-dimensional, anisotropic, heterogeneous domain as influenced by advection, dispersion, adsorption, and biodegradation. Various hydrocarbon contaminants are simulated as electron donors for microbial growth, with electron acceptors utilized in the following sequence: oxygen, nitrate, Mn(IV), Fe(III), sulfate, and CO_2. In addition, the model accounts for products of biodegradation such as Mn (II), Fe(II), H_2S, and CH_4. Biodegradation of each hydrocarbon substrate follows Monod kinetics, modified to include the effects of electron acceptor and nutrient availability. Inhibition functions permit any electron acceptor to inhibit utilization of all other electron acceptors that provide less Gibbs free energy to the microbes. The model assumes that Fe(III) and Mn(IV) occur as solid phase ions, while the other electron acceptors are dissolved in the aqueous phase. Microbial biomass is simulated as independent groups of heterotrophic bacteria that exist as scattered microcolonies attached to the porous medium. Diffusional limitations to microbial growth are assumed to be negligible.

In order to verify the accuracy of the computer code, the model was applied to simple, hypothetical test cases, and the results were compared to analytical solutions. In addition, a sensitivity analysis showed that variations in model inputs caused logical changes in output. Finally, the capabilities of the model were tested by comparing model output to observed concentrations of hydrocarbons, electron acceptors, and endproducts at a leaking UST site. The model was calibrated using historical site data, and predictive capabilities of the model were tested against subsequent sets of field data.

The model was used to examine the effect of porous media heterogeneities on contaminant transport and biodegradation. The turning bands method was used to produce hypothetical, yet realistic heterogeneous fields describing hydraulic conductivity, initial biomass concentration, and the maximum rate of substrate utilization. When the available electron acceptor concentrations were small compared to the hydrocarbon concentration, the overall rate of hydrocarbon mass loss increased with time, even as hydrocarbon concentrations decreased. This trend is the opposite of what would be predicted by a first order decay model.

ACKNOWLEDGEMENTS

I would like to thank Dr. Mark A. Widdowson, my major professor, for giving me the opportunity to pursue graduate studies in Civil Engineering and to carry out this research project. His support, advice, and encouragement have truly made this dissertation possible. I also appreciate his providing me with opportunities to attend meetings, make presentations, and participate in teaching.

Special thanks go to Dr. Jack Parker, who was my initial advisor in my Ph.D. work, and who introduced me to groundwater flow and transport and the intricacies of multiphase flow. I am grateful for his support and guidance in performing research and in publishing three journal articles and a book chapter. I would like to thank the other members of my committee, Dr. William E. Cox, G. V. Loganathan, and Nancy G. Love for their support and suggestions. I would also like to thank my fellow graduate students Steve Brauner and Marc Killingstad for their help with equipment, field work, and ideas. For his help and generosity in sharing the computer code MT3D, I am indebted to Chunmiao Zheng of the University of Alabama.

My experience at Virginia Tech was enriched by the opportunity I had to serve with the Graduate Honor System, and I thank Martha Johnson for her support, advice, and encouragement through many difficult cases.

I thank my wife Karen for her encouragement and hard work in taking care of Wilson, Lillian, and Evan while I was finishing this work.

I especially want to thank to the United States Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS, who sponsored this research. Additional thanks go to the Charles E. Via Endowment of the Virginia Tech Department of Civil Engineering for a supplemental doctoral fellowship.

TABLE OF CONTENTS

Abstract ii
Acknowledgements iii
Table of Contents iv
List of Tables vi
List of Figures viii

CHAPTER 1. INTRODUCTION
1.1 Biodegradation Modeling 1
1.2 Model Verification 2
1.3 Effect of Heterogeneities 3
1.4 Overview of SEAM3D 3
1.5 Objectives 4

CHAPTER 2. MODEL DEVELOPMENT
2.1 Conceptual Model 5
  2.1.1 Transport equations 9
  2.1.2 NAPL dissolution 11
  2.1.3 Utilization equations 12
  2.1.4 Microbial growth equations 15
2.2 Model Implementation 17

CHAPTER 3. SEAM3D CODE VERIFICATION
3.1 SEAM3D Code Verification 20
  3.1.1 Substrate Test Case 20
  3.1.2 Sulfate Test Case 24
  3.1.3 Fe(III) Test Case 27
  3.1.4 Microbial Growth Test Case 29
  3.1.5 NAPL Dissolution Test Case 31
3.2 SEAM3D Code Demonstrations 34
  3.2.1 Demonstration of Growth Limitation 34
  3.2.2 Demonstration of Microbial Growth versus Death 36
  3.2.3 Biodegradation of Five Hydrocarbons 38
3.3 Conclusions 41

CHAPTER 4. APPLICATION OF SEAM3D TO A FIELD SITE
4.1 Introduction 42
4.2 Site Description 45
  4.2.1 NAPL source history 45
  4.2.2 Field monitoring 47
  4.2.3 Hydrogeology 51

4.2.4 Laboratory investigations 51
4.3 SEAM3D Parameter Estimation 52
4.3.1 Model domain and control parameters 52
4.3.2 Flow parameters and boundary conditions 55
4.3.3 NAPL contamination 55
4.3.4 Transport parameters and boundary conditions 63
4.3.5 Biodegradation parameters 64
4.3.6 SEAM3D calibration 68
4.4 Results and Discussion 69
4.4.1 Concentrations along a transect through the center of the plume 69
4.4.2 Areal distributions 83
4.4.3 Alternative model scenarios 86
4.5 Conclusions 89

CHAPTER 5. HETEROGENEOUS SIMULATIONS

5.1 Introduction 90
5.2 Model Descriptions 91
5.2.1 Flow model 91
5.2.2 Biodegradation model 92
5.3 Methods of Analysis of Plume Behavior 92
5.3.1 Spatial Moments of the Solute Plumes 92
5.3.2 Statistical Analysis 93
5.4 Model Domain, Parameters, and Boundary Conditions 94
5.4.1 Grid spacing and control parameters 94
5.4.2 Flow parameters and boundary conditions 96
5.4.3 Transport parameters and boundary conditions 96
5.4.4 Biodegradation parameters 99
5.4.5 Generation of stochastic parameters 102
5.5 Transport Analysis 108
5.5.1 Base case plume migration 108
5.5.2 Analysis of spatial moments 112
5.5.3 Statistical Analysis 127
5.6 Sensitivity Analysis 130
5.7 Conclusions 142

REFERENCES 144

APPENDIX A. SEAM3D INPUT 153
APPENDIX B. SEAM3D OUPUT AND POST-PROCESSING 184
APPENDIX C. EXECUTING A SEAM3D SIMULATION 189

VITA 191

LIST OF TABLES

CHAPTER 2. MODEL DEVELOPMENT

Table 2.1. Electron acceptors (EAs) used by the six heterotrophic microbial populations for biodegradation of hydrocarbon substrates. The EAs are listed in order of highest to lowest Gibbs free energy provided. Utilization of each EA is inhibited by the presence of an EA that provides higher energy. 8

CHAPTER 3. SEAM3D CODE VERIFICATION

Table 3.1. Parameters for substrate half saturation coefficient ($K^{s}_{x,ls,le}$), electron acceptor half saturation coefficient ($K^{e}_{x,le}$), maximum specific rate of substrate utilization ($\nu^{max}_{x,ls,le}$), background microbial death rate ($k^{bk}_{d_x}$), yield coefficient ($Y_{x,ls,le}$), initial substrate concentration (S_{ls}), and electron acceptor use coefficient ($\gamma_{x,ls,le}$). Values of the EA index *le* were identical to the microbial population index *x*. 22

CHAPTER 4. APPLICATION OF SEAM3D TO A FIELD SITE

Table 4.1. Mass fraction of various components of gasoline, as measured or used in simulations by the researchers listed. 44

Table 4.2. Concentrations of BTEX, MTBE, electron acceptors, and products of biodegradation measured in the multilevel sampling wells on June 25, 1996. Port depth refers to depth below the 1996 water table. 50

Table 4.3. Timing and mass loading information associated with the schedule numbers in Figure 4.6 for NAPL mass loading to the model domain. 59

Table 4.4. Transport parameters representing longitudinal dispersivity (α_x), transverse dispersivity (α_y), vertical dispersivity (α_z), effective porosity (θ), and soil bulk density (ρ_b). 60

Table 4.5. Properties and composition of the NAPL phase used in the simulations. 61

Table 4.6. Biodegradation parameters representing substrate half saturation constant ($K^{s}_{x,ls,le}$), electron acceptor (EA) half saturation constant ($K^{e}_{x,le}$), yield coefficient ($Y_{x,ls,le}$), EA use coefficient ($\gamma_{x,ls,le}$), inhibition coefficient ($\kappa_{le,li}$), generation coefficient ($\zeta_{x,li}$), initial biomass concentration (M_x), and background death rate ($k^{bk}_{d_x}$) for each microbial population. Parameters apply to all substrates. 66

Table 4.7. Maximum specific rate of substrate utilization ($\nu^{max}_{x,ls,le}$) within each microbial population. 67

CHAPTER 5. HETEROGENEOUS SIMULATIONS

Table 5.1. Transport parameters representing longitudinal dispersivity (α_x), transverse dispersivity (α_y), vertical dispersivity (α_z), effective porosity (θ), and soil bulk density (ρ_b). 98

Table 5.2. Electron acceptor (EA) initial concentrations and biodegradation parameters representing maximum specific rate of substrate utilization ($\nu^{max}_{x,ls,le}$), substrate half saturation constant ($K^{s}_{x,ls,le}$), EA half saturation constant ($K^{e}_{x,le}$), yield coefficient ($Y_{x,ls,le}$), EA use coefficient ($\gamma_{x,ls,le}$), inhibition coefficient ($\kappa_{le,li}$), generation coefficient ($\zeta_{x,li}$), initial biomass concentration (M_x), and background death rate ($k^{bk}_{d_x}$) for each microbial population. These parameters represent the base case simulation. 101

Table 5.3. Geometric means and the range of values for stochastic parameters representing the horizontal hydraulic conductivity (K_h), the maximum specific rate of substrate utilization ($\nu^{max}_{x,ls,le}$), and the initial biomass concentration (M_x). In each case, $\eta_x = \eta_y$ and $\eta_z = 0.1\eta_x$. 105

Table 5.4. Parameter description and values for the sensitivity analysis. 132

LIST OF FIGURES

CHAPTER 3. SEAM3D CODE VERIFICATION

Figure 3.1. SEAM3D predicted substrate concentrations (diamonds) versus analytical solutions (lines) with parameters chosen to impose 3 rates of first order decay. . 23

Figure 3.2. SEAM3D predicted SO_4^{2-} and H_2S concentrations (diamonds) versus analytical solutions (lines). 26

Figure 3.3. SEAM3D predicted Fe(III) and Fe(II) concentrations (diamonds) versus analytical solutions (lines). Units are $\mu g\ g^{-1}$ for Fe(III) and $g\ m^{-3}$ for Fe(II). 28

Figure 3.4. SEAM3D predicted biomass concentrations (diamonds) versus analytical solutions (lines) for the microbial growth test case. 30

Figure 3.5. SEAM3D predicted NAPL and aqueous phase substrate concentrations (diamonds) versus analytical solutions (lines) for the NAPL dissolution test case. Units are kg for the NAPL and g for the aqueous phase. 33

Figure 3.6. SEAM3D predicted biomass concentrations versus time, showing the effect of the growth limitation algorithm. 35

Figure 3.7. SEAM3D predicted biomass concentrations versus time, for various values of the death rate (k_d). 37

Figure 3.8. SEAM3D predictions of the five hydrocarbon (HC) substrate concentrations, showing the effect of varying the maximum specific rate of substrate utilization ($\nu_{x,ls,le}^{max}$). Arrows indicate the termination of each electron acceptor process. 39

Figure 3.9. SEAM3D predictions of electron acceptor (EA) concentrations, showing that utilization of each EA is inhibited until the preceding EA has been depleted. 40

CHAPTER 4. APPLICATION OF SEAM3D TO A FIELD SITE

Figure 4.1. Site map of the Laurel Bay Exchange, Marine Corps Air Station, Beaufort, S.C., showing location of the leaking gasoline storage tanks and the estimated extent of non-aqueous phase contamination in 1993. 46

Figure 4.2. Location of monitoring wells and multilevel samplers at the Laurel Bay gasoline spill site. The dashed line marks the transect through the center of the plume. .. 48

Figure 4.3. Installation details of the multilevel samplers (MLS-1 to MLS-6) used to monitor the vertical distribution of contamination. The color for the sampling tubes is indicated, and the depth below land surface (LS) is given. 49

Figure 4.4. Areal view of the SEAM3D model domain used to simulate the Laurel Bay site. . 53

Figure 4.5. Vertical cross section through the SEAM3D model domain used to simulate the Laurel Bay site. 54

Figure 4.6. Location of the NAPL source within the model domain. The values of *x* and *y* indicate the distance to the center of the model blocks. Within each block, the

number refers to the schedule (see Table 4.3) for adding NAPL to the domain, while the letter refers to the mass loading rate (Table 4.3). Shading indicates those blocks in which the NAPL mass was set to zero at 1000 days to correspond to excavation of the tanks and contaminated soil. 62

Figure 4.7 (A). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for benzene. Data from the multilevel samplers are shown as triangles. 72

Figure 4.7 (B). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for toluene. Data from the multilevel samplers are shown as triangles. 73

Figure 4.7 (C). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for ethylbenzene. Data from the multilevel samplers are shown as triangles. 74

Figure 4.7 (D). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for xylene. Data from the multilevel samplers are shown as triangles. 75

Figure 4.7 (E). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for MTBE. Data from the multilevel samplers are shown as triangles. 76

Figure 4.7 (F). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for oxygen. Data from the multilevel samplers are shown as triangles. 77

Figure 4.7 (G). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for Fe(II). Data from the multilevel samplers are shown as triangles. 78

Figure 4.7 (H). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for sulfate. Data from the multilevel samplers are shown as triangles. 79

Figure 4.7 (I). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for sulfide. Data from the multilevel samplers are shown as triangles. 80

Figure 4.7 (J). Comparison of measured (symbols) and predicted (lines) concentrations along a transect through the centerline of the plume in the direction of flow for methane. Data from the multilevel samplers are shown as triangles. 81

Figure 4.7 (K). Predicted concentrations along a transect through the centerline of the plume in the direction of flow for aliphatics. 82

Figure 4.8. Areal contours of benzene (column 1), toluene (column 2), and MTBE (column 3) at 4000 days for model layers 1, 3, 5, 7, and 9. Units of the scale bar are g m^{-3} for all three constituents. 84

Figure 4.9. Areal contours of oxygen (column 1), FE(III) (column 2), and sulfate (column 3) at 4000 days for model layers 1, 3, 5, 7, and 9. Units of the scale bar are g g^{-3} for Fe(III) and g m^{-3} for oxygen and sulfate. 85

Figure 4.10. Comparison of benzene concentrations along a transect through the centerline of the plume as predicted by SEAM3D for the best estimate NAPL distribution (light solid lines), the worst case NAPL distribution (dashed lines), and entire NAPL distribution applied at initial time (heavy solid lines). 87

Figure 4.11. Comparison of sulfide concentrations along a transect through the centerline of the plume as predicted by SEAM3D using microbial growth (light lines) versus no microbial growth (heavy lines). 88

Figure 4.12. Comparison of benzene concentrations along a transect through the centerline of the plume as predicted by SEAM3D using microbial growth (light lines) versus no microbial growth (heavy lines). 89

CHAPTER 5. HETEROGENEOUS SIMULATIONS

Figure 5.1. The three-dimensional model domain in an areal view (A) and in vertical cross section (B). Vertical scale is exaggerated. 95

Figure 5.2. Autocorrelation of $\ln K_h$ in the x and z-directions for the base case. Values of the realization were produced by the turning bands method, and theoretical values were obtained from equation (5.11). 106

Figure 5.3. Filled contour intervals for the base case heterogeneous distribution of K_h in model layer 1, layer 3, and layer 30. Dimensions of the scale bar are m day^{-1}. 107

Figure 5.4. Distribution of biodegradable hydrocarbon and nondegradable tracer in a horizontal slice (layer 30) and a vertical slice (row 21) through the center of the model domain at 2000 days. The scale bar applies to all four figures, with dimensions of g m^{-3}. Vertical (z-direction) scale is exaggerated. 109

Figure 5.5. Distribution of the electron acceptors oxygen and sulfate in a horizontal slice (layer 30) and a vertical slice (row 21) through the center of the model domain at 2000 days. Each scale bar also applies to the figure below, with dimensions of g m^{-3}. Vertical (z-direction) scale is exaggerated. 110

Figure 5.6. Distribution of the product H_2S in a horizontal slice (layer 30) and a vertical slice (row 21) through the center of the model domain at 500, 1000, and 1500 days. The scale bar applies to all six figures, with dimensions of g m^{-3}. Vertical (z-direction) scale is exaggerated. 111

Figure 5.7. Total mass of hydrocarbon remaining in the model domain versus time for the base case and the case where oxygen (O_2) only was simulated. 114

Figure 5.8. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case ($\sigma_{\ln K_h}$ = 1.0) versus case 2a with low sigma $\ln K_h$ ($\sigma_{\ln K_h}$ = 0.5) and Case 2b with high sigma $\ln K_h$ ($\sigma_{\ln K_h}$ = 1.25). 115

Figure 5.9. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case (η = 1.5 m) versus Case 3a with low correlation scale (η = 0.5 m) and Case 3b with high correlation scale (η = 3.0 m). 116

Figure 5.10. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 4a with stochastic, correlated K_h, $\nu^{max}_{x,ls,le}$ and M_x and Case 4b with stochastic, uncorrelated K_h, $\nu^{max}_{x,ls,le}$ and M_x. 117

Figure 5.11. Location of the center of mass in the x-direction (A), the y-direction (B), and the z-direction (B) of the solute plumes versus time for the base case. 119

Figure 5.12. Maximum values of the location of the center of mass (x_c) for the hydrocarbon and tracer in the base case, the “oxygen only” case, and Cases 2 through 4. 120

Figure 5.13. Velocity of the center of mass in the x-direction (A), the y-direction (B), and the z-direction (C) of the solute plumes versus time for the base case. The average x-velocity as calculated for a homogeneous porous medium is also depicted. 123

Figure 5.14. Minimum and maximum values of the x-velocity of the hydrocarbon and tracer in the base case, the “oxygen only” case, and Cases 2 through 4. 124

Figure 5.15. Spatial standard deviations (σ_{ii}) of the solute plumes in the x-direction (A), the y-direction (B), and the z-direction (C) versus time for the base case. 125

Figure 5.16. Maximum values of the spatial standard deviations (σ_{ii}) of the solute plumes in the x-direction (A), the y-direction (B), and the z-direction (C) for the base case, the “oxygen only” case, and Cases 2 through 4. 126

Figure 5.17. Comparison of the mean (A) and the coefficients of variation (B) of the resident and flux hydrocarbon concentrations over time. Values were obtained by averaging over a vertical slice through the center of the model domain, perpendicular to the direction of flow (i.e., column 40). 128

Figure 5.18. Maximum values of the resident and flux-averaged concentrations of hydrocarbon in the base case, the “oxygen only” case, and Cases 2 through 4. 129

Figure 5.19. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 5a with low EA available and Case 5b with high EA. 133

Figure 5.20. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 6a with low initial microbial populations (M_x) and Case 6b with high initial M_x. 134

Figure 5.21. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 7a with low maximum specific rate of substrate utilization ($\nu^{max}_{x,ls,le}$) and Case 7b with high $\nu^{max}_{x,ls,le}$. 135

Figure 5.22. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 8a with low half saturation constants ($K^e_{x,le}$ and $K^s_{x,ls,le}$) and Case 8b with high $K^e_{x,le}$ and $K^s_{x,ls,le}$. 136

Figure 5.23. Total mass of hydrocarbon (A) and total mass of H_2S (B) remaining in the model domain versus time for the base case versus Case 9a with low inhibition coefficient ($\kappa_{le,li}$) and Case 9b with $\kappa_{le,li}$ high enough to eliminate inhibition. 137

Figure 5.24. Maximum values of the location of the center of mass (x_c) for the hydrocarbon and tracer in Cases 5 through 9. 138

Figure 5.25. Minimum and maximum values of the x-velocity of the hydrocarbon and tracer in Cases 5 through 9. 139

Figure 5.26. Maximum values of the spatial standard deviations (σ_{ii}) of the solute plumes in the x-direction (A), the y-direction (B), and the z-direction (C) for Cases 5 through 9. 140

Figure 5.27. Maximum values of the resident and flux-averaged concentrations of hydrocarbon for Cases 5 through 9. 141

Chapter 1. Introduction

1.1 Biodegradation Modeling

During recent decades, leaking storage tanks and pipelines have allowed petroleum-derived hydrocarbons to contaminate soil and groundwater at thousands of sites. Microbes degrade many hydrocarbons in aerobic groundwater with molecular oxygen serving as a terminal electron acceptor (EA). Generally, oxygen is rapidly depleted, but hydrocarbons may continue to degrade under anaerobic conditions if alternate EAs are available. Research has shown that a variety of hydrocarbons will degrade using the following EAs: nitrate (e.g. Arcangeli and Arvin, 1994), oxidized manganese (e.g. Baedecker et al., 1993; Lovley, 1991), ferric iron (e.g. Lovley and Lonergan, 1990), sulfate (e.g. Reuter et al., 1994), and carbon dioxide under methanogenic conditions (e.g. Grbic-Galic and Vogel, 1987).

In certain cases, natural (or intrinsic) *in situ* bioremediation may provide a low cost alternative to other methods of site restoration. However, the effectiveness of intrinsic bioremediation depends on the relationship between the contaminant biodecay rate and the groundwater velocity (Chapelle, 1995). Biodecay rate is affected by many factors, including the geochemical environment, contaminant type and concentration, EA availability, and the dominant terminal EA process (TEAP). Since these factors are often site dependent and vary with time and space, prediction of the biodecay rate is difficult. Nevertheless, in order to design successful and cost effective strategies to clean up a site, the potential for bioremediation should be assessed. Due to variability in the biological processes, evidence suggests that bioremediation potential must be evaluated on a site-by-site basis (Atlas and Cerniglia, 1995), and mathematical solute transport models can assist in such evaluations.

Various models (see Bedient et al., 1994; de Blanc et al. 1995) have been developed to predict movement and biodecay of contaminants. Biodegradation of organic compounds may be based on the instantaneous reaction assumption (Borden and Bedient, 1986) or pseudo first order kinetics coupled to geochemical interactions with inorganic constituents (McNab and Narasimhan, 1995). Most commonly, Monod kinetics are used to describe rates of microbial growth (e.g. Molz et al., 1986) or substrate utilization (e.g. Chen et al., 1992). Biodegradation models often consider oxygen alone or in combination with one alternate EA such as nitrate (Widdowson et al., 1988). Field evidence suggests that up to five EAs may be active in bioremediation at a single site (e.g. Baedecker et al., 1993; Borden et al., 1995; Ludvigsen et al., 1995); thus accurate predictions of biodegradation may require simulation of multiple alternate EAs.

When a biodegradation model is limited to one or two spatial dimensions, its application to a field site requires averaging over the vertical dimension. This practice may lead to errors in predicting contaminant transport, especially in highly stratified aquifers. Using a vertical profile model, Molz and Widdowson (1988) showed that minimal vertical mixing was required to replicate geochemical data trends in a stratified aquifer, and that increased vertical dispersion resulted in an exaggerated rate of biodegradation. In unconfined aquifers, biodegradation rates may vary over the vertical dimension as redox conditions near the water table differ from conditions at lower depths. For example, Vroblesky and Chapelle (1994) found that variable recharge caused the predominant TEAP at the water table to shift among Fe(III) reduction, sulfate reduction, and methanogenesis; while the dominant TEAP at the aquifer bottom remained methanogenesis. Moreover, recharge brings oxygenated water to the upper boundary of a plume, and field evidence indicates that the elevation of a plume's center of mass may decrease with time (Borden et al., 1995). Due to the lack of adequate data, modeling in three dimensions is not always justified; however, the 3-D approach may be beneficial for sites where sampling is rigorous.

1.2 Model Verification

Researchers have recognized that costly decisions may be based on the results of modeling studies (van der Heijde and Elnawawy, 1992). Thus, models must be validated in order to establish not only their credibility but also their limitations (Beljin and van der Heijde, 1989). In order to validate a model, van der Heijde et al. (1984) recommend a three level testing procedure. Level 1 involves verification of the model's computer code. During level 2, the model is tested under a variety of hypothetical conditions, and model performance may be evaluated through code intercomparison. Level 3 involves validating the model against independent field or laboratory data, and includes post-audits. Since it is impossible to test all conditions for which a model may be applied, model validity cannot be established absolutely. Instead, each validation scenario confirms a degree of accuracy that applies to the specific conditions of the scenario.

1.3 Effect of Heterogeneities

Since soils exhibit a large degree of spatial variability, a complete mathematical description of the subsurface is impossible to produce. Therefore, modeling of flow and transport in large-scale field problems is often simplified through the use of averaged or "effective" soil parameters. As a result, essential information may be lost, and the model may no longer represent the field situation. In order to capture the effects of soil heterogeneity, researchers have focused on placing soil variability in a probabilistic framework, and the emphasis in modeling has shifted from a deterministic to a stochastic approach.

The theory of stochastic flow and transport in the subsurface has been developed and reviewed by numerous authors (e.g. Gelhar, 1986; Jury et al., 1987; Dagan, 1990; Russo, 1991). Stochastic theory is based on the assumption that a heterogeneous soil property can be treated as a single sample, or realization, taken from a random field. A complete statistical description of this field is impractical, so the quantification of spatial variability is generally limited to estimating the first and second spatial moments (i.e., the mean and variance) of the field variable. If the mean and variance are constant throughout the spatial domain, the field variable is said to be second order stationary or statistically homogeneous. In general, only one measurement of the field variable is available at a given point in space; nevertheless, estimates of the mean and variance may still be obtained under the ergodic hypothesis (Lumley and Panofsky, 1964; Sposito et al., 1986). Numerous studies have focused on stochastic flow and transport of nonbiodegradable solutes in the water phase for saturated and unsaturated soils (e.g., Yeh et al., 1985; Russo, 1991; Chen et al., 1994; Russo et al., 1994). However, limited research has focused on the effect of soil and microbial heterogeneity on biodegradation in the subsurface.

1.4 Overview of SEAM3D

This dissertation describes the development, verification, and application of SEAM3D (<u>s</u>equential <u>e</u>lectron <u>a</u>cceptor <u>m</u>odel, 3 <u>d</u>imensional), a numerical model for subsurface solute transport with aerobic and sequential anaerobic biodegradation. The model can depict multiple constituents in a three-dimensional, anisotropic, heterogeneous domain. Hydrocarbon contaminants are simulated as electron donors (i.e., substrates) for microbial growth, with available electron acceptors (EAs) utilized in the following sequence: O_2, NO_3^-, Mn(IV), Fe(III),

SO_4^{2-}, and CO_2. SEAM3D can account for Mn(II), Fe(II), H_2S, CH_4, and a user defined nitrogenous compound as products of biodegradation. In addition, each hydrocarbon substrate can produce a single daughter product. Biodegradation of each substrate follows Monod kinetics, modified to include the effects of EA and nutrient availability. Inhibition functions allow any EA to inhibit utilization of all other EAs that provide less energy to the microbes. Microbial biomass is simulated as scattered microcolonies attached to the porous medium. The model assumes that interphase diffusional limitations to microbial growth are negligible, and no geometrical parameters are assigned to the colonies.

1.5 Objectives

The overall goal of this research was to develop a model that will aid in quantifying the potential for *in situ* bioremediation at sites contaminated by hydrocarbons. Specific objectives of the research were as follows: 1) to describe SEAM3D, a three-dimensional numerical model for calculation of subsurface transport and biodegradation of multiple aqueous phase solutes utilizing multiple EAs and nutrients in a fully saturated porous medium; 2) to present scenarios for verification of the SEAM3D computer code; 3) to present results of a field scale application of SEAM3D to an unconfined aquifer contaminated by gasoline, 4) to analyze the effect of heterogeneities in soil and microbial population parameters on transport and biodegradation, and 5) to provide detailed information on model input, output, and execution.