THESIS

RETARDATION AND REACTION IN LOW PERMEABILITY LAYERS IN GROUNDWATER PLUMES

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ABSTRACT

RETARDATION AND REACTION IN LOW PERMEABILITY LAYERS IN GROUNDWATER PLUMES

Retardation and reaction in low permeability layers have been recognized as important factors influencing contaminant transport associated with subsurface release of chlorinated solvents and other persistent contaminants. This thesis explores retardation and reaction via analysis of a two-layer scenario with first-order reactions and a one-dimensional analysis addressing parent and decay product contaminants. Herein novel computational approaches are advanced that allow for analysis of middle to late stage chlorinated solvent releases and reaction networks in low permeability layers. Large scale analyses are relevant due to the fact that many releases are now multiple decades in age and correspondingly, large. Specifically, this thesis explores retardation and reaction in subsurface dense nonaqueous phase liquid (DNAPL) releases through three activities: (1) modeling the water quality impacts of retardation and seepage velocity in transmissive and low permeability layers in groundwater plumes; (2) modeling the water quality impacts of retardation and first-order reaction in low permeability layers; and (3) modeling a numerical solution for a network of irreversible first-order reactions in low permeability layers.

The first activity uses a two-layer model addressing retardation in transmissive and low permeability layers and groundwater seepage velocity in the transmissive layer. The two-layer system consists of a transmissive layer (e.g., sand) situated above a low permeability (low permeability) layer (e.g., clay). A source, analogous to a DNAPL, is present in the transmissive

ii

layer at the upgradient edge of the model domain immediately above the low permeability layer. Model inputs include transmissive layer seepage velocity, DNAPL pool length, DNAPL solubility, and duration of a steady source. In addition, unique values of porosity, retardation, reaction, and transverse diffusion/dispersion coefficients are provided for transmissive and low permeability layers. A hybrid approach for computations is advanced in which direct calculation and series approximations are conditionally employed to solve a complex analytical solution. The problem with direct calculations for the analytical solutions is computing exponential and error function terms with large arguments.

Sensitivity analyses were performed with respect to retardation in the transmissive and low permeability layers and transmissive layer seepage velocity. A constant source was active for 10 years and was then completely removed; the problem was studied for an additional 20 years. The entire plume domain was considered for the sensitivity analyses. Three key insights were gained from the sensitivity analyses. First, chlorinated solvent releases can evolve with space and time. Over time, the nature of the problem changes from DNAPLs in the transmissive layer to aqueous and sorbed contaminants in the transmissive and low permeability layers. As such, site conceptual models for chlorinated solvent releases need to be dynamic as opposed to static. Second, seepage velocity in the transmissive layer not only controls the plume extent, but also peak concentrations in both the transmissive and low permeability layers. The peak concentrations in an analog monitoring well at a seepage velocity of 1.0 m/day are five times lower than at a seepage velocity of 0.1 m/day. Third, 20 years after source depletion, retardation factors in the transmissive and low permeability layers control contaminant mass storage in the transmissive and low permeability layers. In the case where the transmissive layer retardation factor (R) is 1 and the low permeability layer retardation factor (R') is 1, 39% of the released

iii

contaminant mass is present in the low permeability layer. In contrast, when R=1 and R'=15, 72% of the released contaminant mass is present in the low permeability layer. Similarly, when R=1 and R'=15, 28% of the released contaminant mass is in the transmissive layer. However, with an increase to R=5 and R'=15, 48% of the released contaminant mass is present in the transmissive layer. Overall, retardation in the transmissive and low permeability layers appear to be important factors in understanding the nature of the problem posed by late stage chlorinated solvent releases.

The second activity uses the same methods and model domain as the first, with the addition of degradation in the transmissive and low permeability layers. Degradation is modeled using first-order kinetics. Critically, it is assumed that reactions only occur in the aqueous phase. Sorbed contaminants are only available for reaction after they desorb into the aqueous phase. This leads to substantial reductions in overall rates of degradation.

Three key insights were gained from the second activity. First, cross sectional plots of total contaminant concentration, versus aqueous concentrations, illuminate the challenges associated with managing contaminants in low permeability layers. Plots of total contaminant concentration can be a more rigorous basis for understanding mass distribution in heterogeneous media. Furthermore, at large time, contaminants in low permeability layers can provide a source for elevated concentrations in the transmissive layer. Second, low permeability layer reactions reduce contaminant mass available for subsequent release to the transmissive layer. Assuming only aqueous phase constituents are available for reaction, retardation dramatically reduces the benefits of reaction. Research is ongoing as to when the assumption that only aqueous phase constituents being available for reaction is appropriate. Third, fractions of contaminant mass present as nonaqueous, aqueous and sorbed phases in transmissive layers and aqueous and

iv

sorbed phases in low permeability layers evolve through time. Critically, the distribution of contaminant mass and correspondingly the age of the release are key factors that need to be recognized in the selection of remedies.

The last activity considers a one-dimensional analysis of diffusive transport in the low permeability layer that includes a network of first-order irreversible reactions (the reaction network model). The Crank-Nicolson Method was used to develop the model. Fitting the model to vertical profiles of parent and decay products in the low permeability layer provides a means of estimating first-order reaction rates for each compound in the reaction network. The half-lives calculated in this paper fell within ranges found in literature for transmissive layers under anaerobic conditions (ranging from 0.003 yr to 0.76 yr). The effects of heterogeneity in retardation factors in the low permeability layer were explored. Retardation factor heterogeneity can have a significant impact on vertical concentration profiles as well as contaminant mass flux out of the low permeability layer. A key limitation of the model is that multiple fitting parameters leads to a condition where the model can be fit to the data using non-unique inputs. Additional laboratory/field data is needed to help validate the model results and constrain the number of uncertain input parameters.

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vi

ABSTRACTii
ACKNOWLEDGEMENTS
LIST OF TABLES
LIST OF FIGURES
CHAPTER 1 1
INTRODUCTION
1.1 Problem Statement
1. 2 Research Objectives
1.2.1 Chapter 2
1.2. 2 Chapter 3
1.2. 3 Chapter 4
1. 3 Research Hypothesis
1.4 References
CHAPTER 2
WATER QUALITY IMPACTS OF RETARDATION AND SEEPAGE VELOCITY IN TRANSMISSIVE AND LOW PERMEABILITY LAYERS IN GROUNDWATER PLUMES 6
SYNOPSIS
2. 1 Introduction
2. 2 Methods
2. 2.1 Two-layer model
2. 2.2 Source zone
2.2.2.1 Source characteristic as a function of pool length
2. 2.3 Computational approach
2.2.3.1 Transmissive layer

TABLE OF CONTENTS

2.2.3.2 Low permeability layer	16
2.2.3.3 Contaminant mass flux at contact	. 17
2. 2.4 Concentrations in wells	19
2. 2.5 Total mass by compartment	19
2.2.5.1 Source zone	. 19
2.2.5.2 Transmissive layer	20
2.2.5.3 Low permeability layer	21
2. 2.6 Spatial distribution of total mass in transmissive and low permeability layers	22
2.2.6.1 Transmissive layer	. 22
2.2.6.2 Low permeability layer	. 23
2. 2.7 Modeled conditions	23
2. 3 Results	. 24
2. 3.1 Concentrations in cross sections	. 24
2. 3.2 Aqueous concentrations in downgradient wells	27
2. 3.3 Contaminant mass flux at contact	29
2. 3.4 Mass in compartments	31
2. 3.5 Spatial distribution of total mass in transmissive and low permeability layers	33
2. 3.6 Limitations	. 35
2.4 Conclusions	. 36
2. 5 References	. 38
2. 6 Appendix	. 40
CHAPTER 3	. 43
WATER QUALITY IMPACTS OF RETARDATION AND FIRST-ORDER REACTION IN LOW PERMEABILITY LAYERS	. 43
SYNOPSIS	. 43
3.1 Introduction	. 44
3.2 Methods	. 46

5.2	1. Two-layer model	. 46
3.2	2. Source zone	. 47
3	2.2.1 Source characteristic as a function of pool length	. 47
3.2	3. Computational approach	. 49
3	2.3. 1 Transmissive layer	. 49
3	2.3. 2 Low permeability layer	. 53
3	2.3. 3 Contaminant mass flux at contact	. 54
3.2	4. Concentrations in wells	. 56
3.2	5. Total mass by compartment	. 56
3	2.5.1 Source zone	. 56
3	2.5.2 Transmissive layer	. 57
3	2.5.3 Low permeability layer	. 58
3	2.5.4 Total degraded mass	. 59
3.2	6. Spatial distribution of total mass in transmissive and low permeability layers	. 60
3	2.6.1 Transmissive layer	. 60
3	2.6.2 Low permeability layer	. 60
3.2	7. Modeled conditions	. 61
3.3	Results	. 62
•	1 Concentrations in gross sections	
3.		. 62
3.	 2 Aqueous concentrations in downgradient wells	. 62 . 65
3. 3. 3.	 2 Aqueous concentrations in downgradient wells	. 62 . 65 . 67
3. 3. 3. 3.	 2 Aqueous concentrations in downgradient wells	. 62 . 65 . 67 . 69
3. 3. 3. 3. 3.	 Aqueous concentrations in downgradient wells	. 62 . 65 . 67 . 69 . 71
3. 3. 3. 3. 3. 3.	 Aqueous concentrations in downgradient wells	. 62 . 65 . 67 . 69 . 71 . 73
 3. 3. 3. 3. 3. 3.4 	 Aqueous concentrations in downgradient wells	. 62 . 65 . 67 . 69 . 71 . 73
3. 3. 3. 3. 3. 3. 3. 4 3.5	 Aqueous concentrations in downgradient wells	. 62 . 65 . 67 . 69 . 71 . 73 . 73 . 75

CHAPTER 4	80
NUMERICAL SOLUTION FOR A NETWORK OF IRREVERSIBLE FIRST-ORDER REACTIONS IN LOW PERMEABILITY LAYERS	80
SYNOPSIS	80
4.1 Introduction	80
4.2 Methods	83
4.2.1 Validation	86
4.3 Results	87
4.3.1 Use of field data to estimate parameters	87
4.3. 1.1 Pueblo Chemical Depot	88
4.3. 1.2 Takeuchi et al. (2011) silt data	91
4.3. 2 Low permeability layer reaction rates	93
4.3.3 Limitations	94
4. 4 Applications	
4.4.1 Contaminant mass flux out of the low permeability layer	95
4.4. 2 Heterogeneity in retardation in the low permeability layer	97
4. 5 Conclusions	100
4. 6 References	102
4.7 Appendix	104
CHAPTER 5	108
SUMMARY OF RESULTS AND RECOMENDATIONS FOR FUTURE WORK	108

LIST OF TABLES

Table 2.1. Input parameters of the model for the base case.	24
Table 3.1. Input parameters of the model.	61
Table 4.1. Input parameters for comparison of the analytical solution to the numerical method.	86
Table 4.2. Input parameters to the model for Pueblo Chemical Depot	89
Table 4.3. Input parameters to the model for Takeuchi et al. (2011) silt data.	92
Table 4.4. Half-lives of compounds in field data	93
Table 4.5. Input parameters to the model for considering heterogeneity in the Takeuchi et al. (2011) silt data.	98

LIST OF FIGURES

Figure 1.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008b)
Figure 1.2. 1-D reaction network model domain
Figure 2.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008b)
Figure 2.2. Analysis of contaminant concentration contours as a function of retardation and seepage velocity. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m. The x axis for 2.2e and 2.2j are different from the other plots
Figure 2.3. Analysis of concentration in wells as a function of position, retardation, seepage velocity. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m
Figure 2.4. Analysis of contaminant mass flux as a function of position, retardation, seepage velocity. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D [*] =5.75×10 ⁻¹⁰ m ² /s, L=1m. 30
Figure 2.5. Analysis of contaminant mass in each compartment as a function of retardation and seepage velocity. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m. The entire plume domain is considered for each case
Figure 2.6. Analysis of the spatial distribution of mass as a function of position, retardation, seepage velocity. Input parameters: t=30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m. The x axis is different for 2.6e
Figure 3.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008a)
Figure 3.2. Analysis of aqueous contaminant concentration contours as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m, R=1 (f _{oc} =0), k=0.023 yr ⁻¹ (30 yr half-life), v=0.27 m/day
Figure 3.3. Analysis of total contaminant concentration contours as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D [*] =5.75×10 ⁻¹⁰ m ² /s, L=1m, R=1 (f _{oc} =0), k=0.023 yr ⁻¹ (30 yr half-life), v=0.27 m/day

Figure 3.4. Analysis of concentration in wells as a function of position, retardation and degradation in the low permeability layer. Input parameters: $n=0.25$, $n'=0.45$, $\tau=10$ years, $c_o=240$ mg/L, $D_t=4.54\times10^{-9}$ m ² /s, $D^*=5.75\times10^{-10}$ m ² /s, $L=1$ m, $R=1$ ($f_{oc}=0$), $k=0.023$ yr ⁻¹ (30 yr half-life), $v=0.27$ m/day
Figure 3.5. Analysis of contamiant mass flux as a function of position, retardation and degradation in the low permeability layer. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m, R=1 (f _{oc} =0), k=0.023 yr ⁻¹ (30 yr half-life), v=0.27 m/day
Figure 3.6. Analysis of contaminant mass in each compartment as a function of retardation and degradation in the low permeability layer. Input parameters: $n=0.25$, $n'=0.45$, $\tau=10$ years, $c_o=240$ mg/L, $D_t=4.54\times10^{-9}$ m ² /s, $D^*=5.75\times10^{-10}$ m ² /s, $L=1$ m, $R=1$ ($f_{oc}=0$), $k=0.023$ yr ⁻¹ (30 yr half-life), v=0.27 m/day
Figure 3.7. Analysis of the spatial distribution of mass as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c _o = 240 mg/L, D _t = 4.54×10 ⁻⁹ m ² /s, D*=5.75×10 ⁻¹⁰ m ² /s, L=1m, R=1 (f _{oc} =0), k=0.023 yr ⁻¹ (30 yr half-life), v=0.27 m/day. 72
Figure 4.1. 1-D reaction network model domain
Figure 4.2. Comparison between parent compound analytical solution (Equation (4.8)) and the numerical model for different temporal and spatial step sizes
Figure 4.3. Model and Field Data Comparison for ESTCP 8 Boring at Pueblo Chemical Depot 90
Figure 4.4. Model and Field Data Comparison for D2M Boring at Pueblo Chemical Depot 91
Figure 4.5. Model and Field Data Comparison for MW02 Boring at Pueblo Chemical Depot 91
Figure 4.6. Model and Field Data Comparison for the silt layer from Figure 2B in Takeuchi et al. (2011)
Figure 4.7. Contaminant mass flux out of the low permeability layer for borings at Pueblo Chemical Depot
Figure 4.8. Contaminant mass flux for Takeuchi et al. (2011) silt data
Figure 4.9. Effects of heterogeneity in retardation in the low permeability silt of Takeuchi et al. (2011) on concentration profiles at t=40 years and mass flux out of the low permeability silt. The concentration profile axes (a and b) are different to better show the data

CHAPTER 1

INTRODUCTION

1.1 Problem Statement

Contaminants stored in low permeability layers can sustain adverse contaminant concentrations in transmissive layers long after removal and/or containment of dense nonaqueous phase liquid (DNAPL) sources due to slow release via diffusion and slow advection (Chapman and Parker, 2005). Building on work from Dr. Beth Parker's research group (e.g., Chapman and Parker, 2005) and others, researchers from Colorado State University developed a set of tools that allow practitioners to quantify how source zone depletion and/or containment affect downgradient groundwater quality (Sale et al., 2007). Specifically, Sale et al. (2007) advances an analytical solution for a scenario of adjacent semi-infinite transmissive and low permeability layer domains (the two-layer model). The two-layer model estimates concentrations of aqueous and sorbed contaminants in transmissive and low permeability layers as a function of space, time, and key transport parameters (Sale et al., 2008a). A source, analogous to a DNAPL, is present in the transmissive layer at the upgradient edge of the model domain immediately above the low permeability layer. Figure 1.1 shows the conceptual framework of the two-layer model. Subsequent to the publication of Sale et al. (2008a), the direct computational approach (using the original analytical equations) presented in Sale et al. (2008a) was found to be computationally impractical at large domains (generally greater than 100m for the transmissive layer and generally greater than 900m for the low permeability layer). Principle problems with a direct computational approach included solving exponential and error function terms for arguments with large values (Bolhari, 2012).

1



Figure 1.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008b)

Several attempts were made to address the limitations of the direct computational approaches. Bolhari (2012) developed a hybrid approach wherein direct computational approaches and a series approximation were conditionally applied. The hybrid approach extended the domain in which the transmissive layer solution could be used to 500m. Given the 500m constraint of Bolhari (2012), a scaling approach was attempted by the author of this work. The scaling approach involved attempts to scale results from small domains to large domains using dimensionless scaling factors. Despite initially promising results, the scaling approach failed due problems associated with diffusion occurring in two directions.

After the failure of the scaling approach, Jack Martin and Dr. David Dandy expanded the hybrid approach to include both direct calculations for small domains and up to three complex series approximations for large domains. This approach is referred to as the second generation hybrid approach. Lastly, the author of this thesis modified the source term in Sale et al. (2008a) to allow for entry of a DNAPL pool length as the characteristic describing the source strength. All of these efforts facilitated extending the domain in which Sale et al. (2008a) can be applied to the scale of kilometers (see Chapters 2 and 3 of this thesis). Results from enhancements to Sale et al. (2008a) are presented herein as two draft journal articles. The first paper does not account

for contaminant degradation in either layer (Chapter 2 of this work). The second paper considers contaminant degradation in both layers (Chapter 3 of this work).

Processes governing reactions in low permeability layers are explored further in Chapter 4 of this thesis via a one-dimensional analysis of diffusive transport in the low permeability layer that includes a network of first-order irreversible reactions. This work was wholly done by the author of this thesis. Figure 1.2 shows the one-dimensional (1-D) reaction network model domain. The Crank-Nicolson Method (Crank and Nicolson, 1947) was used to develop the model. To the author's knowledge, this is the first model (documented) that considers a reaction network in a low permeability layer as a function of depth and time.



Figure 1.2. 1-D reaction network model domain

1.2 Research Objectives

The overall objective of this thesis is to explore processes governing storage and release of contaminant in low permeability layers. The goal of this effort is to support sound decisions for releases of chlorinated solvents and other potentially persistent contaminants. Specific objectives for each chapter include:

1.2.1 Chapter 2

- Present the second generation hybrid computational approach for the two-layer model nondegradation solutions.
- Explore the sensitivity of the model output to retardation and seepage velocity.
- Document the evolution of a chlorinated solvent release through time.

1.2. 2 Chapter 3

- Present the second generation hybrid computational approach for the two-layer model degradation solutions.
- Explore the sensitivity of the model output to low permeability layer retardation and degradation.
- Document the evolution of a chlorinated solvent release through time as a function of degradation.

1.2. 3 Chapter 4

- Document a one-dimensional analysis of diffusive transport in the low permeability layer that includes a network of first-order irreversible reactions (the reaction network model).
- Use diffusion profiles to get estimates of reactions rates in the low permeability layer for energetic and chlorinated compounds.
- Apply the model to explore fluxes from the low permeability layer and the implications of heterogeneity in retardation in the low permeability layer.

1.3 Research Hypothesis

The overall hypothesis of this thesis is that advancing computational methods for the two-layer model to allow large time and space analysis will provide novel insights regarding processes concerning subsurface releases of chlorinated solvents.

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CHAPTER 2

WATER QUALITY IMPACTS OF RETARDATION AND SEEPAGE VELOCITY IN TRANSMISSIVE AND LOW PERMEABILITY LAYERS IN GROUNDWATER PLUMES SYNOPSIS

This paper presents an updated computational approach for an analytical contaminant transport model in a two-layer system to calculate concentrations at large domains. The problem with direct calculations for the analytical solutions is computing exponential and error function terms with large arguments. A hybrid approach was used wherein series approximations and direct computational methods are employed in the domains where they provide accurate results.

The two-layer system consists of a transmissive layer (e.g., sand) situated above a low permeability layer (e.g., clay). A source, analogous to a dense nonaqueous phase liquid (DNAPL), is present in the transmissive layer at the upgradient edge of the model domain immediately above the low permeability layer. Model inputs include transmissive layer seepage velocity, DNAPL pool length, DNAPL solubility, and duration for a steady source. In addition, unique values of porosity, retardation, and transverse diffusion/dispersion coefficients are provided for transmissive and low permeability layers.

Sensitivity analyses were performed with respect to retardation in the transmissive and low permeability layers and seepage velocity in the transmissive layer. A constant source was active for 10 years and was then completely removed; the problem was studied for an additional 20 years. The entire plume domain was considered for the sensitivity analyses. Three key insights were gained from the sensitivity analyses. First, chlorinated solvent releases evolve in

6

space and time. Over time, the nature of the problem changes from DNAPLs in the transmissive layer to aqueous and sorbed contaminants in the transmissive and low permeability layers. As such, site conceptual models for chlorinated solvent releases need to be dynamic as opposed to static. Second, seepage velocity in the transmissive layer not only controls the plume extent, but also peak concentrations in both the transmissive and low permeability layers. The peak concentrations in an analog monitoring well at a seepage velocity of 1.0 m/day are five times lower than at a seepage velocity of 0.1 m/day. Third, 20 years after source depletion, retardation factors in the transmissive and low permeability layers control contaminant mass storage in the transmissive and low permeability layers. In the case where the transmissive layer retardation factor (R) is 1 and the low permeability layer retardation factor (R') is 1, 39% of the released contaminant mass is present in the low permeability layer. In contrast, when R=1 and R'=15, 72% of the released contaminant mass is present in the low permeability layer. Similarly, when R=1 and R'=15, 28% of the released contaminant mass is in the transmissive layer. However, with an increase to R=5 and R'=15, 48% of the released contaminant mass is present in the transmissive layer. Hence, retardation in the transmissive and low permeability layers appear to be important factors in understanding the nature of the problem posed by late stage chlorinated solvent releases.

2.1 Introduction¹

"At many sites, chlorinated solvents were historically released into subsurface settings in the form of dense nonaqueous phase liquids (DNAPLs). With time, DNAPL constituents partition into water, sorb to solids, and partition into soil gas. Following Feenstra et al. (1996) and Kueper and McWhorter (1991), DNAPLs preferentially move through the most transmissive portions of subsurface media and frequently come to rest above low permeability layers. Entry of DNAPL into low permeability layers is often precluded by insufficient capillary pressures (pool height) to displace the water from the

¹ This section is a collaborative effort with Azadeh Bolhari. Single spaced text was provided by Azadeh Bolhari's dissertation (Bolhari, 2012). She will be a coauthor on this paper when it is submitted for publication.

pore spaces in low permeability layers. As such, DNAPL is most often found in the transmissive portions of source zones. An important exception can be secondary permeability features in low permeability layers (e.g., root cast and slickenslides) that have large openings and relatively low entry pressures. With time, DNAPL constituents partition into the aqueous phase and advection carries the dissolved phase downgradient through transmissive intervals creating dissolved phase plumes. Concurrently, vapor phase plumes can form in unsaturated zones via direct evaporation of DNAPL in unsaturated zones or partitioning from aqueous phases.

A potential consequence of DNAPL dissolution and constituent advection is the formation of large concentration gradients at the contacts between transmissive and low permeability layers (Sudicky, 1986; Chapman and Parker, 2005; Parker et al., 2008; and Sale et al., 2008a). With time, large contaminant concentration gradients at contacts between transmissive and low permeability layers drive dissolved phase constituents into low permeability layers via diffusion. Processes that can enhance diffusive transport into low permeability layers (by increasing concentration gradients) include sorption (Parker et al., 1994) and degradation (Sale et al., 2008a). Dissolved phase constituents will continue to move across contacts from transmissive to low permeability layers as long as the dissolved phase constituent concentrations are greater in the transmissive layer. Conversely, given concentrations in transmissive layers, at contacts, that are less than concentrations in low permeability layers.

A number of researchers have recognized that contaminants stored in low permeability layers can sustain plumes with adverse contaminant concentrations long after mass flux from the original DNAPL source is depleted. Liu and Ball (2002) observed a slow release of chlorinated solvents from an aquitard after a source removal from an overlying sand unit. Chapman and Parker (2005) illustrated sustained releases from a low permeability unit to an overlying transmissive sand 6 years after the original DNAPL source zone was isolated from the plume using a physical barrier. Furthermore, Chapman and Parker (2005) employed high-resolution numerical modeling methods to demonstrate that releases from low permeability layers can sustain adverse concentration in a transmissive layer for 100 years after source isolation." Sale et al. (2008a) advanced an analytical solution for a two-layer system consisting of a semi-infinite transmissive layer (e.g., sand) overlying a semi-infinite low permeability layer (e.g., clay).

Recent examples of studies that employ numerical or analytical models addressing

advective-diffusive contaminant transport are Cihan and Tyner (2011), Rasa et al. (2011), Brown et al. (2012), and Chapman et al. (2012). Cihan and Tyner (2011) presented a two-dimensional analytical model using cylindrical coordinates to study advective solute transport within a macropore with simultaneous radial diffusion into a low permeability soil matrix. Rasa et al.

(2011) used two-dimensional reactive numerical transport simulations to show diffusion of solvent from a transmissive layer into adjacent low permeability layers. Brown et al. (2012) employed a one-dimensional analytical two-layer model to investigate the effects of DNAPL source zone dissolution and remediation with respect to storage and release of contaminants from a low permeability layer. Chapman et al. (2012) explored numerical modeling techniques used to depict diffusion processes. Furthermore, Chapman et al. (2012) compared numerical models to the analytical solutions from Sale et al. (2008a). Given adequate spatial and temporal discretization, the numerical models agreed with the analytical solutions.

Recognizing that many releases of chlorinated solvents and other persistent contaminants are 30, 40, or even 50 years old, research at Colorado State University has focused on transport and fate of contaminants at large space (kilometers) and time (decades). Unfortunately, direct calculation of the analytical solutions in Sale et al. (2008a) is infeasible for larges spaces and/or time (Bolhari, 2012). Specifically, problems arise with exponential and error function terms with large arguments. Bolhari (2012) proposed a hybrid approach wherein a combination of direct calculation at small space and use of a series approximation was employed for the transmissive layer. This expanded accurate calculations in the transmissive layer to roughly 500m. Unfortunately, beyond 500m, the hybrid approach was inaccurate and problems were observed with direct calculation of Sale et al. (2008a). Herein a second generation hybrid approach is developed in which direct calculations and two series approximations are employed for the transmissive layer and direct methods and a single series approximation are employed in the low permeability layer. Selection of either direct or series approximations is conditional based on the arguments of the functions. Using the second generation hybrid approach, stable solutions for concentrations have been made to distances as large as 20 km.

9

This manuscript has multiple objectives. First, the second generation hybrid computational approach for the analytical model is presented. Second, the model is used to demonstrate sensitivity to retardation in the transmissive and low permeability layers and groundwater seepage velocity in the transmissive layer. Finally, this paper documents the evolution of a chlorinated solvent release through time.

2.2 Methods

This paper employs the two-layer scenario and analytical solutions developed in Sale et al. (2008a) to estimate the distribution of DNAPL, aqueous, and sorbed phases in transmissive and low permeability layers as a function of space, time, and key transport parameters. Partitioning of contaminant between aqueous and sorbed phases is instantaneous. All calculations herein were conducted using MatlabTM. Integrals are evaluated numerically in MatlabTM using a Gaussian quadratic algorithm. The following describes the equations employed in the computational approaches adapted to large domains for the two-layer model. Furthermore, methods employed in conducting sensitivity analyses and tracking the distribution of contaminant phases are presented.

2. 2.1 Two-layer model

The two-layer model consists of a semi-infinite transmissive layer (e.g., sand) overlying a semi-infinite low permeability layer (e.g., clay). A source, analogous to a dense nonaqueous phase liquid (DNAPL), is present in the transmissive layer at the upgradient edge of the model domain immediately above the low permeability layer. Figure 2.1 presents the conceptual framework of the two-layer model. Herein, transmissive layers are conceptually defined as intervals in which advection is a primary transport process (seepage velocities > 1 m/year). Conversely, low permeability layers are conceptually defined as intervals in which advection is a

10

weak process (seepage velocities < 1 m/year). Key transport processes include longitudinal advection and transverse diffusion/dispersion in the transmissive layer and transverse diffusion in the low permeability layer.



Figure 2.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008b)

2. 2.2 Source zone

Per Sale et al. (2008a), the source is introduced in the transmissive layer at x=0m (see Figure 2.1). The concentration at the downgradient edge of the source (x=0m) is presented in Equation (2.1):

$$c_{\text{source}}(0, y, t) = c_0 e^{-by} [1 - H(t - \tau)] \qquad (y \ge 0)$$
 (2.1)

where c_0 is the concentration (M/L³) at x=0, y=0 during the DNAPL persistence time and b is the source characteristic (L⁻¹). Furthermore, τ is the DNAPL persistence time (T) and H is the Heaviside step function, such that:

$$H(t-\tau) = \begin{cases} 0 & \text{if } t \leq \tau \\ 1 & \text{if } t > \tau \end{cases}$$
(2.2)

2.2.2.1 Source characteristic as a function of pool length

The source characteristic (b) is modified from Sale et al. (2008a) to allow for entry of a DNAPL pool length as the characteristic describing the source strength. This is achieved by

equating two expressions for the mass flux from the source zone per unit width of pool. Per Sale (1998), the mass flux per unit width off the top of the source pool is calculated in Equation (2.3):

$$M_{w} = 2c_{o}n\sqrt{\frac{LvD_{t}}{\pi}}$$
(2.3)

where L is the source pool length (L), v is the groundwater seepage velocity in the transmissive layer (L/T), n is the porosity in the transmissive layer (dimensionless), and D_t, the effective transverse diffusion/dispersion coefficient of the transmissive layer (L^2/T), is estimated in Equation (2.4):

$$\mathbf{D}_{\mathrm{t}} = \mathbf{v}\boldsymbol{\alpha}_{\mathrm{t}} + \mathbf{D}_{\mathrm{e}} \tag{2.4}$$

where α_t is the transverse dispersivity (L) and D_e, the effective molecular diffusion coefficient of the contaminant in the transmissive layer (L²/T), is calculated using Equation (2.5), per Charbeneau (2000):

$$D_e = n^{\frac{1}{3}} D_{aq}$$

$$\tag{2.5}$$

where D_{aq} is the aqueous diffusion coefficient of the contaminant (L²/T).

The mass flux per unit width of pool can also be written in terms of contaminant flux above the distal end of the source, as shown in Equation (2.6):

$$M_{\rm w} = c_{\rm o,avg} hvn \tag{2.6}$$

where h is an infinite height above the source pool (L) and $c_{o,avg}$ is the average aqueous concentration (M/L³), which is defined in Equation (2.7):

$$c_{o,avg} = \frac{\int_{0}^{\infty} c_{o} e^{-by} dy}{\infty}$$
(2.7)

Taking the limit of Equation (2.7) as y goes to infinity and substitution into Equation (2.6) yields:

$$M_{w} = \frac{c_{o}}{b} vn$$
(2.8)

Equating Equations (2.3) and (2.8) and solving for b yields the source characteristic (b) as a function of source pool length, as shown in Equation (2.9):

$$b = \frac{1}{2} \sqrt{\frac{v\pi}{LD_t}}$$
(2.9)

Equation (2.9) assumes a thin source pool present in the transmissive layer. The source characteristic remains constant through time.

2. 2.3 Computational approach

Series approximations employed in the transmissive layer, low permeability layer, and flux across the contact solutions are presented in the following sections. Sale et al. (2008a) was found to be computationally impractical at large domains (generally greater than 100m for the transmissive layer and generally greater than 900m for the low permeability layer). Principle problems with a direct computational approach included solving exponential and error function terms for arguments with large values (Bolhari, 2012). Series were used to approximate functions that experience problems at large domains. Unfortunately, series are incorrect at small distances. Realization of the limitation of both the direct computational approach and the series approximation led to a strategy of using each of the approaches in the domain in which they are accurate. This approach is referred to as the second generation hybrid method.

2.2.3.1 Transmissive layer

The equation developed in Sale et al. (2008a) to calculate the contaminant concentration in the transmissive layer at a desired location and time while the source is active (for $x < v_c t$) is presented in Equation (2.10):

$$c_{\text{trans,on}}(x, y, t) = c_{o} \begin{bmatrix} \frac{1}{2} e^{\frac{b^{2}x}{\varphi^{2}}} \left(e^{by} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right) + e^{-by} \left(1 + \operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right)\right) \right) + \\ \frac{-\varphi \gamma}{\pi} e^{by} \sqrt{t - \frac{x}{v_{c}}} \int_{0}^{x} \frac{1}{\sqrt{x - \xi}} \left(\frac{e^{\frac{b^{2}\xi}{\varphi^{2}}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi} + \frac{\varphi y}{2\sqrt{\xi}}\right)}{\gamma^{2}(x - \xi) + \varphi^{2}\left(t - \frac{x}{v_{c}}\right)} \right) d\xi$$
(2.10)

where $\phi, \gamma, v_c,$ and D^* are defined as:

$$\varphi = \sqrt{\frac{\mathbf{v}}{\mathbf{D}_{\mathrm{t}}}} \tag{2.11}$$

$$\gamma = \frac{n'\sqrt{R'D^*}}{nD_t}$$
(2.12)

$$v_{c} = \frac{v}{R}$$
(2.13)

$$D^* = n^{\frac{1}{3}} D_{aq}$$
(2.14)

R and R' are the retardation factors of the transmissive and low permeability layers (dimensionless), respectively and are calculated in Equations (2.15) and (2.16):

$$R = 1 + \frac{\rho_b K_{oc} f_{oc}}{n}$$
(2.15)

$$R' = 1 + \frac{\rho_b' K_{oc} f_{oc}'}{n'}$$
(2.16)

where ρ_b , K_{oc} , f_{oc} , ρ_b ', f_{oc} ', and n' are the bulk density of the transmissive layer (M/L³), the soil organic carbon partition coefficient of the contaminant (L³/M), the fraction of organic carbon in the transmissive layer (dimensionless), the bulk density of the low permeability layer (M/L³), the fraction of organic carbon in the low permeability layer (dimensionless), and the porosity of the low permeability layer (dimensionless), respectively.

For conditions when the direct computational method fails, series were used to approximate the following functions in Equation (2.10). The conditions under which each computational approach is used is presented in the flow chart in Figure A2.1 in the Appendix. The series approximations for Equations (2.17) and (2.18) are also presented in the Appendix (Equations (A2.1) and (A2.2), respectively).

$$e^{\frac{b^2 x}{\varphi^2}} \left(e^{by} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right) + e^{-by} \left(1 + \operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right) \right) \right)$$
(2.17)

$$e^{\frac{b^{2}\xi}{\varphi^{2}}}\left(erfc\left(\frac{b}{\varphi}\sqrt{\xi}+\frac{\varphi y}{2\sqrt{\xi}}\right)\right)$$
(2.18)

Once the source is removed, the contaminant concentration in the transmissive layer at a desired location and time is calculated using the principle of superposition as shown in Equation (2.19):

$$c_{\text{trans,off}}(x, y, t, \tau) = c_{\text{trans,on}}(x, y, t) - c_{\text{trans,on}}(x, y, t - \tau)$$
(2.19)

Equations (2.10) and (2.19) calculate the aqueous concentration in the transmissive layer at a desired point in space and time. Aqueous concentrations in the transmissive layer (M/L^3) are converted to sorbed and total concentrations (M/M), as shown in Equations (2.20) and (2.21), respectively:

$$\mathbf{c}_{\text{trans, total}}(\mathbf{x}, \mathbf{y}, \mathbf{t}, \tau) = \begin{cases} \frac{Rn}{\rho_{b}} \mathbf{c}_{\text{trans, on}}(\mathbf{x}, \mathbf{y}, \mathbf{t}) & \text{if} \quad \mathbf{t} \leq \tau \\ \frac{Rn}{\rho_{b}} \mathbf{c}_{\text{trans, off}}(\mathbf{x}, \mathbf{y}, \mathbf{t}, \tau) & \text{if} \quad \mathbf{t} > \tau \end{cases}$$
(2.20)

$$c_{\text{trans,sorbed}}(x, y, t, \tau) = \begin{cases} K_{\text{oc}} f_{\text{oc}} c_{\text{trans,on}}(x, y, t) & \text{if } t \leq \tau \\ K_{\text{oc}} f_{\text{oc}} c_{\text{trans,off}}(x, y, t, \tau) & \text{if } t > \tau \end{cases}$$
(2.21)

2.2.3.2 Low permeability layer

The contaminant concentration in the low permeability layer at a desired location and time while the source is active (for x< v_ct) is calculated in Equations (2.22)-(2.23), per Sale et al. (2008a).

$$c_{lowk,on}(x, y', t) = c_o \left[\frac{1}{\sqrt{\pi}} \int_0^x \frac{I(x, y', t, \xi)}{\sqrt{x - \xi}} \left(\frac{1}{\sqrt{\pi\xi}} - \frac{b}{\varphi} e^{\frac{b^2\xi}{\varphi^2}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right) \right] d\xi \right]$$
(2.22)

where $I(x,y',t,\xi)$ is defined as:

$$I(x, y', t, \xi) = \operatorname{erfc}\left(\frac{\frac{y'}{\sqrt{\frac{D^{*}}{R'}}}}{2\sqrt{t-\frac{x}{v_{c}}}}\right) - \gamma \frac{\operatorname{erfc}\left(\frac{\frac{\sqrt{\frac{D^{*}}{R'}}}{2\left(t-\frac{x}{v_{c}}\right)\sqrt{\frac{\gamma^{2}}{t-\frac{x}{v_{c}}} + \frac{\varphi^{2}}{x-\xi}}}{\sqrt{t-\frac{x}{v_{c}}}\sqrt{\frac{\gamma^{2}}{t-\frac{x}{v_{c}}} + \frac{\varphi^{2}}{x-\xi}}}\right) (2.23)$$

$$(2.23)$$

As stated earlier, the direct computational approach for Equation (2.22) does not result in accurate values for larger plume lengths (generally greater than 900m). A series, presented in Equation (A2.3) in the Appendix, was used to approximate Equation (2.24). The conditions under which each computational approach is used is presented in the flow chart in Figure A2.2 in the Appendix.

$$e^{\frac{b^2\xi}{\varphi^2}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)$$
 (2.24)

Per Sale et al. (2008a), once the source is removed, the contaminant concentration at a desired time and location in the low permeability layer is calculated in Equation (2.25):

$$c_{\text{lowk,off}}(x, y', t, \tau) = c_{\text{lowk,on}}(x, y', t) - c_{\text{lowk,on}}(x, y', t - \tau)$$
(2.25)

Equations (2.22) and (2.25) calculate the aqueous concentration in the low permeability layer at a desired point in space and time. Aqueous concentrations in the low permeability layer (M/L^3) are converted to sorbed and total concentrations (M/M), as shown in Equations (2.26) and (2.27), respectively:

$$c_{\text{lowk,total}}(x, y', t, \tau) = \begin{cases} \frac{R'n'}{\rho_{b}'} c_{\text{lowk,on}}(x, y', t) & \text{if } t \leq \tau \\ \frac{R'n'}{\rho_{b}'} c_{\text{lowk,off}}(x, y', t, \tau) & \text{if } t > \tau \end{cases}$$
(2.26)

$$c_{\text{lowk,sorbed}}(x, y', t, \tau) = \begin{cases} K_{\text{oc}} f_{\text{oc}}' c_{\text{lowk,on}}(x, y', t) & \text{if } t \leq \tau \\ K_{\text{oc}} f_{\text{oc}}' c_{\text{lowk,off}}(x, y', t, \tau) & \text{if } t > \tau \end{cases}$$
(2.27)

2.2.3.3 Contaminant mass flux at contact

The contaminant mass flux at the contact between the transmissive and low permeability layers was obtained by taking the derivative of the concentration in the low permeability layer with respect to y' at y'=0. The contaminant mass flux across the transmissive layer-low

permeability layer boundary at a desired location and time while the source is active is calculated in Equation (2.28):

$$J_{y,on}(x,t) = -c_o n' \sqrt{\frac{vR'D^*}{D_t}} \left[\frac{b}{\pi} \int_0^x \frac{1}{\sqrt{x-\xi}} \left(\frac{\frac{b^2 \xi}{e^{\varphi^2}} \operatorname{erfd}\left(\frac{b}{\varphi}\sqrt{\xi}\right) \sqrt{t-\frac{x}{v_c}}}{\gamma^2 (x-\xi) + \varphi^2 \left(t-\frac{x}{v_c}\right)} \right) d\xi - \frac{1}{\sqrt{\pi}\sqrt{\gamma^2 x + \varphi^2 \left(t-\frac{x}{v_c}\right)}} \right]$$
(2.28)

As was the case for the low permeability direct computational approach, the direct computational approach for Equation (2.28) does not result in accurate values for larger plume lengths (generally greater than 900m). A series, presented in Equation (A2.3) in the Appendix, was used to approximate Equation (2.29). The conditions under which each computational approach is used is presented in the flow chart in Figure A2.3 in the Appendix.

$$e^{\frac{b^2\xi}{\varphi^2}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)$$
 (2.29)

Again, once the source is removed, the contaminant mass flux at the contact is calculated using the principle of superposition as shown in Equation (2.30):

$$J_{y,off}(x,t,\tau) = J_{y,on}(x,t) - J_{y,on}(x,t-\tau)$$
(2.30)

Equations (2.28) and (2.30) calculate the mass flux across the transmissive layer-low permeability layer contact. Diffusion from the transmissive layer to the low permeability layer (inward diffusion) is indicated by a positive mass flux value. Diffusion from the low permeability layer to the transmissive layer (outward diffusion) is indicated by a negative mass flux value.

2. 2.4 Concentrations in wells

Aqueous concentrations at points were used to calculate aqueous concentrations in wells by integrating the solution (Equation (2.10)) over the vertical interval of interest (screened interval) (from 0m to 3m in the transmissive layer) shown in Equations (2.31) and (2.32):

$$c_{\text{well,on}}(x,t) = \frac{0}{3m}$$
(2.31)

$$c_{\text{well,off}}(x,t,\tau) = \frac{\frac{3m}{\int c_{\text{trans,off}}(x,y,t,\tau)dy}}{3m}$$
(2.32)

Equation (2.31) calculates the aqueous concentration in the well when the source is active and Equation (2.32) calculates the aqueous concentration in the well once the source has been removed.

2. 2.5 Total mass by compartment

Another application of the model is to predict the total contaminant mass in the DNAPL, transmissive layer, and low permeability layer. The equations used to calculate the total mass in each compartment are presented in the following sections. Each equation assumes a unit width for the solution domain.

2.2.5.1 Source zone

The total contaminant mass entering the system as a function of time is defined by integrating the influent flux of contaminant at x=0m over y and time, as calculated in Equation (2.33):

$$M_{in}(t,\tau) = \begin{cases} t \infty \\ \int \int vnc_o e^{-by} dy dt & \text{if } t \leq \tau \\ 0 0 \\ \tau \infty \\ \int \int vnc_o e^{-by} dy dt & \text{if } t > \tau \\ 0 0 \end{cases}$$
(2.33)

The mass of the DNAPL in the transmissive layer is defined in Equation (2.34):

$$M_{DNAPL}(t,\tau) = \int_{0}^{\tau \infty} \int_{0}^{\infty} vnc_o e^{-by} dy dt - M_{in}(t,\tau)$$
(2.34)

2.2.5.2 Transmissive layer

The total contaminant mass in the transmissive layer at a desired time while the source is active is calculated in Equation (2.35):

$$M_{\text{trans,on}}(t) = \operatorname{Rn} \int_{0}^{v_{c}t} \int_{0}^{2\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{\sqrt{2\sqrt{2}}} \int_{0}^{\sqrt{2\sqrt{2\sqrt{2}}}} \int_{0}^{\sqrt{2\sqrt{2}}} \int_{$$

 $v_c t$ represents the distance to the leading edge of the plume from x=0 (the source zone) and $2(D_t x/v_c)^{\frac{1}{2}}$ represents the computationally practical diffusion front into the transmissive layer. (Rigorously, the total contaminant mass in the transmissive layer would involve two semiinfinite integrals over $0 \le x < \infty$ and $0 \le y < \infty$. Those limits are not computationally practical, so the limits were set to be the bounds of where the vast majority of contaminant is located in the transmissive layer.)

Using the principle of superposition, the total contaminant mass in the transmissive layer at a desired time and over a desired area after the source is removed is calculated in Equation (2.36):

$$M_{\text{trans,off}}(t,\tau) = \operatorname{Rn} \int_{0}^{v_{c}t} \int_{0}^{2\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{1} c_{\text{trans,off}}(x, y, t, \tau) dy dx$$
(2.36)

Equations (2.35) and (2.36) can be partitioned into aqueous and sorbed phases, as shown in Equations (2.37) and (2.38), respectively.

$$M_{\text{trans, aqueous}}(t,\tau) = \begin{cases} v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \int c_{\text{trans,on}}(x,y,t) dy dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \int c_{\text{trans,off}}(x,y,t,\tau) dy dx & \text{if } t > \tau \end{cases}$$
(2.37)

$$M_{\text{trans, sorbed}}(t,\tau) = \begin{cases} v_{c}t^{2}\sqrt{\frac{D_{t}x}{v_{c}}} \\ \rho_{b}K_{oc}f_{oc}\int \int c_{\text{trans,on}}(x,y,t)dydx & \text{if} \quad t \leq \tau \\ 0 & 0 \\ v_{c}t^{2}\sqrt{\frac{D_{t}x}{v_{c}}} \\ \rho_{b}K_{oc}f_{oc}\int \int c_{\text{trans,off}}(x,y,t,\tau)dydx & \text{if} \quad t > \tau \end{cases}$$
(2.38)

2.2.5.3 Low permeability layer

The total contaminant mass in the low permeability layer at a desired time while the source is active is calculated in Equation (2.39):

$$M_{lowk, on}(t) = R' n' \int_{0}^{v_{c}t} \int_{0}^{2\sqrt{D_{t}t}} c_{lowk, on}(x, y', t) dy' dx$$
(2.39)

As was the case for the transmissive layer, $v_c t$ represents the distance to the leading edge of the plume from x=0 (the source zone) and $2(D_t t)^{1/2}$ represents the bounds of where the vast majority of the contaminant is located in the low permeability layer.

Using the principle of superposition, the total contaminant mass in the low permeability layer at a desired time and over a desired area after the source is removed is calculated in Equation (2.40):

$$M_{lowk,off}(t,\tau) = R'n' \int_{0}^{v_c} \int_{0}^{t} c_{lowk,off}(x, y', t, \tau) dy' dx$$
(2.40)

Equations (2.39) and (2.40) can be partitioned into aqueous and sorbed phases, as shown in Equations (2.41) and (2.42), respectively.

$$M_{lowk, aqueous}(t, \tau) = \begin{cases} v_c t 2\sqrt{D_t t} \\ \int & \int c_{lowk,on}(x, y', t) dy' dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t 2\sqrt{D_t t} \\ \int & \int c_{lowk,off}(x, y', t, \tau) dy' dx & \text{if } t > \tau \end{cases}$$
(2.41)

$$M_{lowk, sorbed}(t, \tau) = \begin{cases} v_c t^2 \sqrt{D_t} t \\ \rho_b' K_{oc} f_{oc}' \int \int c_{lowk,on}(x, y', t) dy' dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t^2 \sqrt{D_t} t \\ \rho_b' K_{oc} f_{oc}' \int \int c_{lowk,off}(x, y', t, \tau) dy' dx & \text{if } t > \tau \end{cases}$$
(2.42)

2. 2.6 Spatial distribution of total mass in transmissive and low permeability layers

Another application of the model is to predict the spatial distribution of the total contaminant mass in transmissive and low permeability layers. The equations used to calculate the spatial distribution of the total mass in each layer are presented in the following sections.

2.2.6.1 Transmissive layer

The spatial distribution of the total contaminant mass in the transmissive layer while the source is active is presented in Equation (2.43):
$$m_{\text{trans,on}}(x,t) = Rn \int_{0}^{2} \sqrt{\frac{D_t x}{v_c}} \int_{0}^{1} c_{\text{trans,on}}(x,y,t) dy$$
(2.43)

Using the principle of superposition, the spatial distribution of the total contaminant mass in the transmissive layer is calculated in Equation (2.44):

$$m_{\text{trans,off}}(x,t,\tau) = Rn \int_{0}^{2\sqrt{\frac{D_t x}{v_c}}} \int_{0}^{1} c_{\text{trans,off}}(x,y,t,\tau) dy$$
(2.44)

2.2.6.2 Low permeability layer

The spatial distribution of the total contaminant mass in the low permeability layer while the source is active is presented in Equation (2.45):

$$m_{lowk, on}(x, t) = R'n' \int_{0}^{2\sqrt{D_t t}} c_{lowk, on}(x, y', t) dy'$$
(2.45)

Using the principle of superposition, the spatial distribution of the total contaminant mass in the low permeability layer is calculated in Equation (2.46):

$$m_{lowk,off}(x, t, \tau) = R'n' \int_{0}^{2\sqrt{D_t t}} c_{lowk,off}(x, y', t, \tau) dy'$$
(2.46)

2. 2.7 Modeled conditions

In this study, the source is active for 10 years (τ) and then is completely removed allowing clean water to flush through the media for an additional period of 20 years. The source characteristic, b, and c_o values in this study are based on a thin, 1m long, horizontal pool of tetrachloroethene (PCE) located upgradient of the point x=0 and y=0. The parameters used in the base case are listed in Table 2.1. The sensitivity analyses presented in the following sections are variants of the base case.

Parameter	Values	Units
Average linear groundwater seepage velocity, v	0.27	m/day
Porosity of the transmissive layer, n	0.25	dimensionless
Porosity of the low permeability layer, n'	0.45	dimensionless
Mean plume loading concentration above low permeability layer during the DNAPL persistence time, c _o	240	mg/L
Bulk density of transmissive layer, ρ_b	1.99	g/mL
Bulk density of low permeability layer, ρ_b '	1.46	g/mL
Retardation factor of the transmissive layer, R	1	dimensionless
Retardation factor of the low permeability layer, R'	15	dimensionless
Effective transverse diffusion or dispersion coefficient of the transmissive layer, D_t	4.54×10 ⁻⁹	m ² /s
Effective transverse diffusion coefficient of the low permeability layer, D*	5.75×10 ⁻¹⁰	m ² /s
Source pool length, L	1	m
Source persistence time, τ	10	yr

Table 2.1. Input parameters of the model for the base case.

2.3 Results

This section presents sensitivity analyses wherein the effects of retardation and seepage velocity are evaluated with respect to aqueous and total concentrations in cross sections, aqueous concentrations in wells, mass flux at the contact between the two layers, mass in compartments, and the spatial distribution of contaminant mass in the transmissive and low permeability layers. Model limitations are also presented.

2. 3.1 Concentrations in cross sections

Equations (2.19), (2.25), (2.20), and (2.26) are used to calculate contaminant

concentrations in a cross-section, as shown in Figure 2.2. The first column of Figure 2.2 shows data plotted in terms of aqueous concentrations. This provides a basis for interpreting the y direction aqueous concentrations that control transverse diffusion. Data in the second column of

Figure 2.2 is plotted in terms of total concentration. Total concentrations provide a basis for understanding the contaminant mass that resides in transmissive and low permeability layers. The plot of total concentration is critical in that it presents the target for remediation.



Figure 2.2. Analysis of contaminant concentration contours as a function of retardation and seepage velocity. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ= 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D*=5.75×10⁻¹⁰m²/s, L=1m. The x axis for 2.2e and 2.2j are different from the other plots.

Figures 2.2a-2.2c show the effect of retardation on aqueous contaminant concentration.

Comparing Figure 2.2b and 2.2c indicates that a larger retardation value in the transmissive layer (Figure 2.2b) affects the distribution of aqueous concentration in the transmissive and low permeability layers. At R=5 and R'=15 (Figure 2.2b), there is significantly higher aqueous concentration in the transmissive layer in the first 600m than at R=1 and R'=15 (Figure 2.2c) due to slower contaminant velocity (v/R). In all cases, increasing the retardation factor in either layer leads to an increase in the total concentration in that layer (Figures 2.2f-2.2h).

Figures 2.2c-2.2e demonstrate the effect of seepage velocity on aqueous contaminant concentration. The bulk of the concentration is located closer to the source at lower seepage velocities. For example, there are considerably higher concentrations closer to the source at seepage velocities of 0.1 m/day (Figure 2.2d) and 0.27 m/day (Figure 2.2c) than at a seepage velocity of 1.0 m/day (Figure 2.2e). A similar trend occurs in the total concentration in the low permeability layer (Figures 2.2h-2.2j). In addition, when the contaminant velocity is increased, the plume travels farther downgradient. In all cases, the highest concentrations in the low permeability layer in the aqueous and total phases occur near the source zone. Moreover, for all cases, there is no longitudinal dispersion at the leading edge of the plume, thus creating a blunt nosed plume.

2. 3.2 Aqueous concentrations in downgradient wells

A primary metric for evaluating groundwater quality is aqueous concentration in wells. As was the case for Figure 2.2, the source is active for 10 years and then is completely removed. Using Equations (2.31) and (2.32), concentrations are calculated for wells located 1, 10, 100, and 500m downgradient of the source for a period of 30 years, shown in Figure 2.3.



Figure 2.3. Analysis of concentration in wells as a function of position, retardation, seepage velocity. Input parameters: n=0.25, n'= 0.45, τ= 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D*=5.75×10⁻¹⁰m²/s, L=1m

Figures 2.3a-2.3c show the effect of retardation on aqueous well concentration.

Increasing the retardation factor in the transmissive layer from 1 (Figure 2.3c) to 5 (Figure 2.3b)

delays the time at which the leading edge of the contaminant plume arrives at the well due to a lower contaminant velocity (v/R). The peak concentration in each of the wells is similar when the retardation factor in the low permeability layer is the same (Figures 2.3b-2.3c). Increasing the retardation factor in the low permeability layer from 1 (Figure 2.3a) to 15 (Figure 2.3c) decreases the peak magnitude of concentration in each well, especially at farther downgradient well locations.

The effect of seepage velocity on aqueous concentration in downgradient wells is shown in Figures 2.3c-2.3e. At a seepage velocity of 0.1 m/day (Figure 2.3e), the peak aqueous well concentrations are larger at wells located at x=1m, 10m, and 100m than at a seepage velocity of 0.27 m/day (Figure 2.3c) or at a seepage velocity of 1.0 m/day (Figure 2.3e). Another implication of decreasing seepage velocity is time at which the leading edge of the plume reaches the farther downgradient wells increases. In all cases, increasing the downgradient distance decreases the peak magnitude of aqueous well concentration. These observations indicate that greater peak magnitudes of aqueous well concentration occur closer to the source zone. The only case where well concentrations fall below the maximum contaminant level (MCL) of PCE (0.005 mg/L) in the 30 year study period is a well located at 1m where there is no retardation in either layer (Figure 2.3a).

2. 3.3 Contaminant mass flux at contact

Equations (2.28) and (2.30) are used to calculate the mass flux across the transmissivelow permeability layer contact shown in Figure 2.4. Contaminant mass flux values are calculated at points located 1, 10, 100, and 500m downgradient of the source for a period of 30 years.



Figure 2.4. Analysis of contaminant mass flux as a function of position, retardation, seepage velocity. Input parameters: n=0.25, n'= 0.45, τ= 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D*=5.75×10⁻¹⁰m²/s, L=1m.

Figures 2.4a-2.4c demonstrate the effect of retardation on mass flux. Increasing the retardation factor in the transmissive layer from 1 (Figure 2.4a) to 5 (Figure 2.4b) delays the switch from inward diffusion to outward diffusion (the asymptote) at downgradient positions due

to slower contaminant velocity in the transmissive layer. Figures 2.4c-2.4e show the effect of seepage velocity on mass flux. At a seepage velocity of 1 m/day (Figure 2.4e), the magnitude of mass flux is larger than in cases of slower seepage velocity (Figures 2.4c-2.4d). Another implication of increasing seepage velocity is that the switch from inward diffusion to outward diffusion occurs earlier in time at all downgradient positions (x=100m and x=500m). Brown et al. (2012) and others (Feenstra et al., 1996; Sale et al., 2008a ; Cihan and Tyner, 2011) have observed that contaminated site diffusion processes are hysteretic because they are gradient driven and loading occurs more rapidly than release. Regardless of retardation and seepage velocity, inward diffusion occurs more rapidly and at greater magnitudes than outward diffusion, which validates the hysteretic effect previously observed. In all cases, increasing the downgradient position decreases the magnitude of mass flux, indicating that greater magnitudes of mass flux occur in close proximity to the source zone.

2. 3.4 Mass in compartments

Figure 2.5 shows the contaminant mass in the DNAPL, aqueous and sorbed phases in the transmissive and low permeability layers. Equations (2.34), (2.37), (2.38), (2.41), and (2.42) are used to calculate the mass in the DNAPL, transmissive layer aqueous phase, transmissive sorbed phase, low permeability layer aqueous phase, and low permeability layer sorbed phase, respectively. The most critical aspect of Figure 2.5 is that it illustrates how releases of chlorinated solvent evolve from a problem of contaminants present as DNAPL to one of varied combinations of aqueous and sorbed contaminants in transmissive and low permeability layers.



Figure 2.5. Analysis of contaminant mass in each compartment as a function of retardation and seepage velocity. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ= 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D*=5.75×10⁻¹⁰m²/s, L=1m. The entire plume domain is considered for each case.

In more detail, Figures 2.5a-2.5c show the effect of retardation on contaminant mass distribution. Elevating the retardation factor in the transmissive layer from 1 (Figure 2.5c) to 5 (Figure 2.5b) increases the percentage of mass stored in the transmissive layer from 28% to 48% at t= 30 years. Increasing the retardation factor in the low permeability layer from 1 (Figure 2.5a) to 15 (Figure 2.5b) has a similar effect on the percentage of mass stored in the low permeability layer, increasing from 39% to 52% at t=30 years. Figures 2.5c-2.5e demonstrate the impact of seepage velocity on contaminant mass distribution. Increasing the seepage velocity from 0.1 m/day (Figure 2.5d) to 1.0 m/day (Figure 2.5e) does not significantly change the percentage of mass in the transmissive layer (less than 2% difference). In Figures 2.5a-2.5e, the contaminant mass is calculated across the entire plume domain and thus the plume length differs for each case due to differences in contaminant velocity. These observations indicate that the distribution of contaminant mass is largely dependent on retardation in the transmissive and low permeability layers. These figures also show that a solvent release evolves from a problem of DNAPL in the transmissive layer to aqueous and sorbed phases in the transmissive and low permeability layers.

2. 3.5 Spatial distribution of total mass in transmissive and low permeability layers

The model is used to predict the spatial distribution of the total mass in the transmissive and low permeability layers at t=30 years, shown in Figure 2.6. The purpose of this analysis is to delineate zones for remediation. Again, the source is active for 10 years and then is completely removed. Equations (2.44) and (2.46) are used to calculate the spatial distribution of contaminant mass in the transmissive and low permeability layers, respectively.



Figure 2.6. Analysis of the spatial distribution of mass as a function of position, retardation, seepage velocity. Input parameters: t=30 years, n=0.25, n'= 0.45, τ = 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m. The x axis is different for 2.6e.

Figures 2.6a-2.6c show the effect of retardation on the spatial distribution of contaminant mass. Increasing retardation in the transmissive layer (Figure 2.6b), decreases the contaminant velocity, which in turn means that the leading edge of the plume only reaches around 600 m in 30 years. The switch from greater contaminant presence in the low permeability layer to greater contaminant presence in the transmissive layer (the intersection of the two lines) occurs at a shorter distance as the retardation factor in the transmissive layer (Figure 2.6b and Figure 2.6c) increases contaminant presence in the low permeability layer (Figure 2.6b and Figure 2.6c) increases contaminant presence in the low permeability layer over the first few meters downgradient of the source zone (x=0m-10m).

The impact of seepage velocity on the spatial distribution of contaminant mass is shown in Figures 2.6c-2.6e. Decreasing the seepage velocity (Figure 2.6d) increases the distance at which the lines intersect. When the seepage velocity is increased (Figure 2.6e), a greater percentage of the mass resides in the low permeability layer throughout the model domain. In all cases, the greatest mass per area occurs in the low permeability layer near the original (DNAPL) source. This reflects that the portion of the low permeability layer located in proximity of the DNAPL source has had contact with the highest contaminant concentration for the longest period of time.

2.3.6 Limitations

The conditions addressed in this model are highly idealized. The transmissive and low permeability layers are assumed to be homogeneous and isotropic. In addition, contaminant degradation is not considered. Furthermore, stepped source reduction was not considered; instead, the source assumed to be either active or completely removed. The model does not work

for all variable combinations. Specifically, computational instability can be encountered due to the complexity of the functions that are employed.

2.4 Conclusions

Three important observations are developed from the sensitivity analyses. First, chlorinated solvent releases can evolve with space and time. Spatially, much of the contaminant mass in the low permeability layer remains in close proximity to the DNAPL source even at late time. However, at late stages in the transmissive layer, much of the contaminant mass has advected downgradient of the DNAPL source. Over time, the nature of the problem changes from DNAPL in the transmissive layer to that of aqueous and sorbed contaminants in the transmissive and low permeability layers. Critically, the age of the release and correspondingly the distribution of contaminant mass are key factors that need to be recognized in the selection of remedies.

The second major contribution of this work is a greater understanding of how seepage velocity in the transmissive layer not only controls the plume extent, but also peak concentrations in both the transmissive and low permeability layers. Higher seepage velocity coincides with lower concentrations throughout the plume domain despite more mass entering the plume. In contrast, the higher seepage velocity coincides with a larger plume domain. This leads to the observation that while higher seepage velocity may have less environmental impact in some cases due to lower peak contaminant concentrations, remediation efforts may be limited due to plume extent.

Third, the retardation factors in the transmissive and low permeability layers control contaminant mass storage in the transmissive and low permeability layers in late stage chlorinated solvent releases. In the case where R'=1, 39% of the released contaminant mass is

present in the low permeability layer after 30 years. In contrast, where R'=15, 72% of the released contaminant mass is present in the low permeability layer after 30 years. Similarly, when R=1, 28% of the released contaminant mass is in the transmissive layer after 30 years. However, with an increase to R=5, 48% of the released contaminant mass is present in the transmissive layer after 30 years. Overall, retardation in the transmissive and low permeability layers appears to be an important factor in understanding the nature of the problem posed by late stage chlorinated solvent releases.

2.5 References

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2.6 Appendix





Figure A2.1. Flow chart explaining the series approximation approach in the transmissive layer solution.



Figure A2.2. Flow chart explaining the series approximation approach in the low permeability layer solution



Figure A2.3. Flow chart explaining the series approximation approach in the flux solution

Series Approximation of transmissive layer solutions

Equation (2.17) is modified by the following series approximation: μ^{2}

$$\frac{e^{\frac{b^{n}x}{\varphi^{2}}}\left(e^{by}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x}+\frac{\varphi y}{2\sqrt{x}}\right)+e^{-by}\left(1+\operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x}+\frac{\varphi y}{2\sqrt{x}}\right)\right)\right)}{\left(\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\sqrt{\pi x}}e^{-\left(\left(\frac{\varphi \frac{y}{x}}{2}\right)^{2}x\right)}\left(1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)!}{n!\left(\left(2\left(\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right)^{2}x\right)^{n}\right)}+\left(\frac{1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)!}{n!\left(\left(2\left(\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right)^{2}x\right)^{n}\right)}\right)}\right)$$
(A2.1)
$$\frac{-1}{\left(\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\sqrt{\pi x}}e^{-\left(\left(\frac{\varphi \frac{y}{x}}{2}\right)^{2}x\right)}\left(1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)!}{n!\left(\left(2\left(\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right)^{2}x\right)^{n}\right)}\right)+e^{\left(\left(\frac{b}{\varphi}\right)^{2}-bxy}\left(\frac{\left|\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right|}{\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}}\right)$$

Equation (2.18) is modified by the following series approximation:

$$\frac{e^{\frac{b^{2}\xi}{\varphi^{2}}}\left(\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}+\frac{\varphi y}{2\sqrt{\xi}}\right)\right) \cong \frac{1}{\sqrt{\pi\left(\frac{b}{\varphi}\right)^{2}\xi}} e^{-by}\left[1+\sum_{n=1}^{m}\left(\frac{(-1)^{n}\left(\frac{\varphi}{b}\right)^{2n}\left(\frac{1}{\xi}\right)^{n}}{\prod_{j=1}^{n}4j}\right)_{k=0}^{2n}\left((by)^{(2n-k)}\frac{(2n)!}{(2n-k)!}\right)\right]$$
(A2.2)

Series Approximation of low permeability layer and flux at contact solutions

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Equations (2.24) and (2.29) are modified by the following series approximation:

$$e^{\frac{b^{2}\xi}{\varphi^{2}}}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right) \cong \frac{1}{\sqrt{\pi\left(\frac{b}{\varphi}\right)^{2}\xi}} \left(1 + \sum_{n=1}^{m} \left(\frac{(-1)^{n}(2n)!}{2^{2n}n!\left(\left(\frac{b}{\varphi}\right)^{2}\xi\right)^{n}}\right)\right)$$
(A2.3)

For all cases, m is based on an empirical relationship between the height of the diffusive front and the series convergence, and is case dependent.

CHAPTER 3

WATER QUALITY IMPACTS OF RETARDATION AND FIRST-ORDER REACTION IN LOW PERMEABILITY LAYERS SYNOPSIS

Computational methods for analytical solutions for a two-layer system with reaction have been adapted to large domains wherein retardation and reaction are occurring in the low permeability layer. Calculations are conducted using a hybrid approach involving direct calculation and series approximations for exponential and error function terms.

The two-layer system consists of a transmissive layer (e.g., sand) situated above a low permeability layer (e.g., clay). A source, analogous to a dense nonaqueous phase liquid (DNAPL), is present in the transmissive layer at the upgradient edge of the model domain immediately above the low permeability layer. Model inputs include transmissive layer seepage velocity, DNAPL pool length, DNAPL solubility, and duration for a steady source. In addition, unique values of porosity, retardation, transverse diffusion/dispersion coefficients, and first-order reaction rates are provided for transmissive and low permeability layers. Critically, it is assumed that only aqueous phase constituents are available for reaction.

Three key insights are advanced. First, elevated retardation in the low permeability layer leads to high levels of contaminant concentration in the low permeability layer immediately beneath the transmissive layer. This effect is not accounted for in conventional plots of aqueous concentrations. Due to contaminant sorption, plots of total contaminant concentration can be a more rigorous basis for understanding mass distribution in heterogeneous media. Furthermore, at large time, contaminant storage in low permeability layers can provide a source for elevated concentrations in the transmissive layer. Second, low permeability layer reactions reduce contaminant mass available for subsequent release to the transmissive layer. Assuming only aqueous phase constituents are available for reaction, retardation dramatically reduces the benefits of reaction. Research is ongoing as to when the assumption that only aqueous phase constituents being available for reaction is appropriate. Third, fractions of contaminant mass present as nonaqueous, aqueous and sorbed phases in transmissive layers and aqueous and sorbed phases in low permeability layers evolve through time. Critically, the distribution of contaminant mass and correspondingly the age of the release are key factors that need to be recognized in the selection of remedies.

3.1 Introduction

A number of researchers have recognized that contaminant degradation in low permeability layers can influence contaminant transport and behavior in groundwater plumes. Starr et al. (1985) used an analytical solution of the advection-diffusion/dispersion-reaction partial differential equation to simulate the transport of a reactive solute through a transmissive layer located between two low permeability layers. Moreover, Starr et al. (1985) recognized that retardation in low permeability layers can have a significant effect on the transport of a reactive solute in an advection-diffusion controlled environment. A more recent example of an analytical solution to the advection-diffusion/dispersion-reaction partial differential equation is Sale et al. (2008a). Sale et al. (2008a) advanced an analytical solution for a two-layer system consisting of a semi-infinite transmissive layer (e.g., sand) overlying a semi-infinite low permeability layer (e.g., clay). Rasa et al. (2011) observed that aerobic degradation of MTBE/TBA in a low permeability layer over the water table significantly affected concentrations of MTBE and TBA by limiting the mass available for diffusion from the low permeability layer to the transmissive

layer. Furthermore, Rasa et al. (2011) observed that despite source removal and contaminant degradation, the MTBE/TBA plume continued to persist for an additional 15 years. Schaefer et al. (2013) performed laboratory experiments using minimally disturbed sedimentary rocks to measure coupled diffusion and abiotic degradation of trichloroethene (TCE) in rock core samples. Furthermore, Schaefer et al. (2013) used numerical and analytical models to determine effective diffusion coefficients and rate constants of TCE and its abiotic degradation products.

Recognizing that many releases of chlorinated solvents and other persistent contaminants are 30, 40, or even 50 years old, research at Colorado State University has focused on transport and fate of contaminants at large domains (kilometers) and time (decades). Unfortunately, direct calculation of the analytical solutions in Sale et al. (2008a) is infeasible for larges spaces and/or time (Bolhari, 2012). Specifically, problems arise with exponential and error function terms with large arguments. Bolhari (2012) proposed a hybrid approach wherein a combination of direct calculation at small distances and a series approximation for large distances was employed for the transmissive layer. This expanded accurate calculations in the transmissive layer to roughly 500m. Unfortunately, beyond 500m, the hybrid approach was inaccurate and problems were observed with direct calculation of Sale et al. (2008a). Herein a second generation hybrid approach is developed in which direct calculations and two series approximations are employed for the transmissive layer and direct methods and a single series approximation are employed in the low permeability layer. Selection of either direct or series approximations is conditional based on the arguments of the functions. Using the second generation hybrid approach, stable solutions for concentrations have been made to distances as large as 20 km.

This research has three objectives. First, the second generation hybrid computational approach for the two-layer analytical solution with degradation is presented. Second, the model

is used to study the implications of retardation and reaction in the low permeability layer. Third, the model is employed to explore the evolution of a chlorinated solvent release through time as a function of retardation and degradation.

3.2 Methods

This paper employs the two-layer scenario and analytical solutions developed in Sale et al. (2008a) to estimate the distribution of DNAPL, aqueous, and sorbed phases in transmissive and low permeability layers as a function of space, time, first-order contaminant degradation, and key transport parameters. First-order contaminant degradation is assumed to take place only in the aqueous phase. Partitioning of contaminant between aqueous and sorbed phases is instantaneous. All calculations herein were conducted using Matlab[™]. Integrals are evaluated numerically in Matlab[™] using a Gaussian quadratic algorithm. The following describes the methods employed in the computational approach adapted to large domains for the two-layer model with first-order contaminant degradation. Furthermore, methods employed in conducting sensitivity analyses and tracking the distribution of contaminant phases are presented.

3.2.1. Two-layer model

The two-layer model consists of a semi-infinite transmissive layer (e.g., sand) overlying a semi-infinite low permeability layer (e.g., clay). A source, analogous to a pool of dense nonaqueous phase liquid (DNAPL), is present in the transmissive layer at the upgradient edge of the model domain immediately above the low permeability layer. Figure 3.1 presents the conceptual framework of the two-layer model. Herein, transmissive layers are conceptually defined as intervals in which advection is a primary transport process (seepage velocities > 1 m/year). Conversely, low permeability layers are conceptually defined as intervals in which advection is a weak process (seepage velocities < 1 m/year).



Figure 3.1. The two-layer scenario conceptual model: A) Active source, B) Depleted Source (after Sale et al., 2008a)

3.2.2. Source zone

Per Sale et al. (2008a), the source is introduced in the transmissive layer at x=0m (see Figure 3.1). The concentration at the downgradient edge of the source (x=0m) is presented in Equation (3.1):

$$c_{\text{source}}(0, y, t) = c_0 e^{-by} [1 - H(t - \tau)] \quad (y \ge 0)$$
 (3.1)

where c_o is the mean plume loading concentration above the low permeability layer during the DNAPL persistence time (M/L³) and b is the source characteristic (L⁻¹). Furthermore, τ (T) is the DNAPL persistence time and H is the Heaviside step function, such that:

$$H(t-\tau) = \begin{cases} 0 & \text{if } t \leq \tau \\ 1 & \text{if } t > \tau \end{cases}$$
(3.2)

3.2.2.1 Source characteristic as a function of pool length

The source characteristic (b) is modified from Sale et al. (2008a) to allow for entry of a DNAPL pool length as the characteristic describing the source strength. This is achieved by equating two expressions for the mass flux from the source zone per unit width of pool. Per Sale (1998), the mass flux per unit width off the top of the source pool is calculated in Equation (3.3):

$$M_{w} = 2c_{o}n\sqrt{\frac{LvD_{t}}{\pi}}$$
(3.3)

where L is the source pool length (L), v is the groundwater seepage velocity in the transmissive layer (L/T), n is the porosity in the transmissive layer, and D_t, the effective transverse diffusion/dispersion coefficient of the transmissive layer (L^2/T), is estimated in Equation (3.4):

$$D_t = v\alpha_t + D_e \tag{3.4}$$

where α_t is the transverse dispersivity (L) and D_e, the effective molecular diffusion coefficient of the contaminant in the transmissive layer (L²/T), is calculated using Equation (3.5), per Charbeneau (2000):

$$D_e = n^{\frac{1}{3}} D_{aq}$$
(3.5)

where D_{aq} is the aqueous diffusion coefficient of the contaminant (L^2/T).

The mass flux per unit width of pool can also be written in terms of contaminant flux above the distal end of the source, as shown in Equation (3.6):

$$M_{w} = c_{o,avg} hvn$$
(3.6)

where h is an infinite height above the source pool (L) and $c_{o,avg}$ is the average source concentration (M/L³), which is defined in Equation (3.7):

$$c_{o,avg} = \frac{\int_{0}^{\infty} c_{o} e^{-by} dy}{\infty}$$
(3.7)

Taking the limit of Equation (3.7) as y goes to infinity and substituting into Equation (3.6) yields:

$$M_{w} = \frac{c_{o}}{b} vn$$
(3.8)

Equating Equations (3.3) and (3.8) and solving for b yields the source characteristic (b) as a function of source pool length (L), as shown in Equation (3.9):

$$b = \frac{1}{2} \sqrt{\frac{v\pi}{LD_t}}$$
(3.9)

Equation (3.9) assumes a thin source pool that is present in the transmissive layer. The source characteristic remains constant through time.

3.2.3. Computational approach

Series approximations employed in the transmissive layer, low permeability layer, and flux across the contact degradation solutions are presented in the following sections. Sale et al. (2008a) was found to be computationally impractical at large domains (generally greater than 100m for the transmissive layer and generally greater than 900m for the low permeability layer). Principle problems with a direct computational approach included solving exponential and error function terms for arguments with large values (Bolhari, 2012). Series were used to approximate functions that experience problems at large domains. Unfortunately, series are incorrect at small distances. Realization of the limitation of both the direct computational approach and the series approximation led to a strategy of using each of the approaches in the domain in which they are accurate. This approach is referred to as the second generation hybrid method.

3.2.3.1 Transmissive layer

The equation developed in Sale et al. (2008a) to calculate the contaminant concentration in the transmissive layer with contaminant degradation at a desired location and time while the source is active (for $x < v_c t$) is presented in Equation (3.10):

$$\mathbf{c}_{\text{trans,on}}(\mathbf{x},\mathbf{y},\mathbf{t}) = \mathbf{c}_{o} \begin{bmatrix} \frac{1}{2} e^{-k\frac{\mathbf{x}}{\mathbf{v}}} e^{\frac{\mathbf{b}^{2}\mathbf{x}}{\varphi^{2}}} \left(e^{\mathbf{b}\mathbf{y}} \operatorname{erfc}\left(\frac{\mathbf{b}}{\varphi}\sqrt{\mathbf{x}} + \frac{\varphi\mathbf{y}}{2\sqrt{\mathbf{x}}}\right) + e^{-\mathbf{b}\mathbf{y}} \left(1 + \operatorname{erf}\left(\frac{-\mathbf{b}}{\varphi}\sqrt{\mathbf{x}} + \frac{\varphi\mathbf{y}}{2\sqrt{\mathbf{x}}}\right) \right) \right) + \\ - \frac{\varphi\mathbf{y}}{\pi} e^{\mathbf{b}\mathbf{y}} e^{\frac{-k\mathbf{x}}{\mathbf{v}}} \cdot \frac{\mathbf{x}}{\mathbf{y}} \frac{e^{\frac{\mathbf{b}^{2}\xi}{\varphi^{2}}}}{\sqrt{\sqrt{\mathbf{x} - \xi}}} \operatorname{erfc}\left(\frac{\mathbf{b}}{\varphi}\sqrt{\xi} + \frac{\varphi\mathbf{y}}{2\sqrt{\xi}}\right) \cdot \begin{bmatrix} \frac{e^{-\hat{\mathbf{k}}\left(\frac{\mathbf{x}}{\mathbf{v}_{c}}\right)}\sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}}}{\sqrt{\frac{\mathbf{v}^{2}\left(\mathbf{x} - \xi\right)}{\sqrt{\mathbf{v}}}} \\ \frac{e^{-\hat{\mathbf{k}}\left(\frac{\mathbf{x}}{\mathbf{v}_{c}}\right)}\sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}}} \\ \frac{e^{-\hat{\mathbf{k}}\left(\frac{\mathbf{x}}{\mathbf{v}_{c}}\right)}\sqrt{\frac{\mathbf{v}^{2}\left(\mathbf{x} - \xi\right)}{\sqrt{\frac{\mathbf{v}^{2}\left(\mathbf{x} - \xi\right)}{\sqrt{\frac{\mathbf$$

where, I(x,t,\xi), $\phi, \gamma, v_c, D^{*}, \stackrel{_{\wedge}}{k'},$ Ei, and F are defined as:

$$I(\mathbf{x}, \mathbf{t}, \boldsymbol{\xi}) = \begin{pmatrix} \sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}} \mathrm{Ei} \left(-\mathbf{k}' \left(\left(\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}} \right) + \frac{\gamma^{2}(\mathbf{x} - \boldsymbol{\xi})}{\varphi^{2}} \right) \right) + \\ -\sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}} \left(\Gamma - 2 + \ln \mathbf{k}' \left(\left(\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}} \right) + \frac{\gamma^{2}(\mathbf{x} - \boldsymbol{\xi})}{\varphi^{2}} \right) \right) + \\ -\frac{2\gamma\sqrt{\mathbf{x} - \boldsymbol{\xi}}}{\varphi} \tan^{-1} \left(\frac{\varphi\sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}}}{\gamma\sqrt{\mathbf{x} - \boldsymbol{\xi}}} \right) + \\ -\sqrt{\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}}} \sum_{n=1}^{\infty} \frac{\left(-\mathbf{k}' \right)^{n}}{n \cdot n!} \left(\frac{\gamma}{\varphi} \right)^{2n} (\mathbf{x} - \boldsymbol{\xi})^{n} F \left(\frac{1}{2}, -n, \frac{3}{2}, -\frac{\varphi^{2} \left(\mathbf{t} - \frac{\mathbf{x}}{\mathbf{v}_{c}} \right)}{\gamma^{2} (\mathbf{x} - \boldsymbol{\xi})} \right) \end{pmatrix}$$
(3.11)

$$\varphi = \sqrt{\frac{\mathrm{v}}{\mathrm{D}_{\mathrm{t}}}} \tag{3.12}$$

$$\gamma = \frac{n'\sqrt{R'D^*}}{nD_t}$$
(3.13)

$$v_{c} = \frac{v}{R}$$
(3.14)

$$D^* = n'^{\frac{1}{3}} D_{aq}$$
(3.15)

$$\stackrel{\wedge}{\mathbf{k}'} = \frac{\mathbf{k}'}{\mathbf{R}'} \tag{3.16}$$

k and k' are the exponential decay rates for the transmissive and low permeability layers (T⁻¹), respectively.

Ei(x) and F(α,β,γ,x) are the exponential integral function and the hypergeometric function, respectively and are calculated in Equations (3.17) and (3.18):

$$Ei(x) = \Gamma + ln(-x) + \sum_{n=1}^{\infty} \frac{x^{n}}{n \cdot n!}$$
(3.17)

$$F(\alpha,\beta,\gamma,x) = 1 + \frac{\alpha\beta}{\alpha(1!)}x + \frac{\alpha(\alpha+1)\beta(\beta+1)}{\gamma(\gamma+1)(2!)}x^{2} + \frac{\alpha(\alpha+1)(\alpha+2)\beta(\beta+1)(\beta+2)}{\gamma(\gamma+1)(\gamma+2)(3!)}x^{3} + \dots$$
(3.18)

 Γ is Euler's constant (Γ =0.57721566). The hypergeometric series (Equation (3.18)) is truncated at a finite number of terms if α or β is equal to a negative integer or zero (as is the case herein). R and R' are the retardation factors of the transmissive and low permeability layers (dimensionless), respectively and are calculated in Equations (3.19) and (3.20):

$$R = 1 + \frac{\rho_b K_{oc} f_{oc}}{n}$$
(3.19)

$$R' = 1 + \frac{\rho_b' K_{oc} f_{oc}'}{n'}$$
(3.20)

where ρ_b , K_{oc} , f_{oc} , ρ_b ', f_{oc} ', and n' are the bulk density of the transmissive layer (M/L³), the soil organic carbon partition coefficient of the contaminant (L³/M), the fraction of organic carbon in the transmissive layer (dimensionless), the bulk density of the low permeability layer (M/L³), the fraction of organic carbon in the low permeability layer (dimensionless), and the porosity of the low permeability layer (dimensionless), respectively.

For conditions when the direct computational method fails, series were used to approximate the following functions in Equation (3.10). The conditions under which each computational approach is used is presented in the flow chart in Figure A3.1 in the Appendix. The series approximations for Equations (3.21) and (3.22)) are also presented in the Appendix (Equations (A3.1) and (A3.2), respectively).

$$e^{\frac{b^2x}{\varphi^2}} \left(e^{by} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right) + e^{-by} \left(1 + \operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x} + \frac{\varphi y}{2\sqrt{x}}\right)\right) \right)$$
(3.21)

$$e^{\frac{b^{2}\xi}{\varphi^{2}}}\left(\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}+\frac{\varphi y}{2\sqrt{\xi}}\right)\right)$$
(3.22)

Once the source is removed, the contaminant concentration in the transmissive layer with contaminant degradation at a desired location and time is calculated using the principle of superposition as shown in Equation (3.23):

$$c_{\text{trans,off}}(x, y, t, \tau) = c_{\text{trans,on}}(x, y, t) - c_{\text{trans,on}}(x, y, t - \tau)$$
(3.23)

Equations (3.10) and (3.23) calculate the aqueous concentration in the transmissive layer at a desired point in space and time. Aqueous concentrations in the transmissive layer (M/L^3) are converted to sorbed and total concentrations (M/M), as shown in Equations (3.24) and (3.25), respectively:

$$c_{\text{trans,total}}(x, y, t, \tau) = \begin{cases} \frac{Rn}{\rho_b} c_{\text{trans,on}}(x, y, t) & \text{if } t \leq \tau \\ \frac{Rn}{\rho_b} c_{\text{trans,off}}(x, y, t, \tau) & \text{if } t > \tau \end{cases}$$
(3.24)

$$\mathbf{c}_{\text{trans,sorbed}}(\mathbf{x}, \mathbf{y}, \mathbf{t}, \tau) = \begin{cases} \mathbf{K}_{\text{oc}} \mathbf{f}_{\text{oc}} \mathbf{c}_{\text{trans,on}}(\mathbf{x}, \mathbf{y}, \mathbf{t}) & \text{if } \mathbf{t} \leq \tau \\ \mathbf{K}_{\text{oc}} \mathbf{f}_{\text{oc}} \mathbf{c}_{\text{trans,off}}(\mathbf{x}, \mathbf{y}, \mathbf{t}, \tau) & \text{if } \mathbf{t} > \tau \end{cases}$$
(3.25)

3.2.3. 2 Low permeability layer

The contaminant concentration in the low permeability layer with degradation at a desired location and time while the source is active (for $x < v_c t$) is calculated in Equations (3.26)-(3.28), per Sale et al. (2008a).

$$\mathbf{c}_{\text{lowk,on}}(\mathbf{x},\mathbf{y}',\mathbf{t}) = \mathbf{c}_{o} \frac{\varphi^{2}}{2\pi} e^{\frac{-\mathbf{k}\mathbf{x}}{\mathbf{v}}} \int_{0}^{\mathbf{t}-\frac{\mathbf{x}}{\mathbf{v}_{c}}} \int_{0}^{\frac{2}{\mathbf{v}} - \frac{\mathbf{x}}{\mathbf{v}_{c}}} \int_{0}^{\frac{2}{\mathbf{v}} - \frac{\mathbf{x}}{\mathbf{v}_{c}}} \int_{0}^{\mathbf{v}-\frac{\mathbf{v}}{\mathbf{v}_{c}}} \int_{0}^{\frac{2}{\mathbf{v}} - \frac{\mathbf{v}}{\mathbf{v}_{c}}} \int_{0}^{\frac{2}{\mathbf{v}} - \frac{\mathbf{v}^{2}B^{2}}{\mathbf{v}_{c}}} \left(\frac{\frac{-\mathbf{Y}^{2}B^{2}}{(\gamma^{2} + 4B^{2}u)}}{(\gamma^{2} + 4B^{2}u)} \left(\frac{4\mathbf{Y}B^{2}ue^{\frac{-\mathbf{Y}^{2}\gamma^{2}}{4u(\gamma^{2} + 4B^{2}u)}}}{(\sqrt{\gamma^{2} + 4B^{2}u})^{2}} \left(\frac{4\mathbf{Y}B^{2}ue^{\frac{-\mathbf{Y}^{2}\gamma^{2}}{4u(\gamma^{2} + 4B^{2}u)}}}{\sqrt{\frac{1}{\gamma^{2} + 4B^{2}u}}} e^{\operatorname{erfc}\left(\frac{\mathbf{Y}\gamma}{2u}\sqrt{\frac{u}{\gamma^{2} + 4B^{2}u}}\right)} \right) \right) dud\xi$$
(3.26)

where Y and B are defined as:

$$Y = -\frac{y'}{\sqrt{D^*}}$$
(3.27)

$$B = \frac{\varphi^2}{4(x - \xi)}$$
(3.28)

where $\overset{\wedge}{D^*}$ is defined as:

$$\overset{\wedge}{\mathrm{D}^{*}} = \frac{\mathrm{D}^{*}}{\mathrm{R}^{'}} \tag{3.29}$$

As stated earlier, the direct computational approach for Equation (3.26) does not result in accurate values for larger plume lengths (generally greater than 900m). A series, presented in Equation (A3.3) in the Appendix, was used to approximate the following function presented in

Equation (3.30). The conditions under which each computational approach is used is presented in the flow chart in Figure A3.2 in the Appendix.

$$e^{\frac{b^2\xi}{\varphi^2}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)$$
 (3.30)

Per Sale et al. (2008a), once the source is removed, the contaminant concentration at a desired time and location in the low permeability layer is calculated in Equation (3.31):

$$c_{\text{lowk,off}}(x, y', t, \tau) = c_{\text{lowk,on}}(x, y', t) - c_{\text{lowk,on}}(x, y', t - \tau)$$
 (3.31)

Equations (3.26) and (3.31) calculate the aqueous concentration in the low permeability layer at a desired point in space and time. Aqueous concentrations in the low permeability layer (M/L^3) are converted to sorbed and total concentrations (M/M), as shown in Equations (3.32) and (3.33), respectively:

$$c_{\text{lowk,total}}(x, y', t, \tau) = \begin{cases} \frac{R'n'}{\rho_b} c_{\text{lowk,on}}(x, y', t) & \text{if } t \leq \tau \\ \frac{R'n'}{\rho_b} c_{\text{lowk,off}}(x, y', t, \tau) & \text{if } t > \tau \end{cases}$$
(3.32)

$$c_{\text{lowk,sorbed}}(x, y', t, \tau) = \begin{cases} K_{\text{oc}} f_{\text{oc}}' c_{\text{lowk,on}}(x, y', t) & \text{if } t \leq \tau \\ K_{\text{oc}} f_{\text{oc}}' c_{\text{lowk,off}}(x, y', t, \tau) & \text{if } t > \tau \end{cases}$$
(3.33)

3.2.3. 3 Contaminant mass flux at contact

The contaminant mass flux at the contact between the transmissive and low permeability layers with degradation was obtained by taking the derivative of the concentration in the low permeability layer with respect to y' at y'=0. The contaminant mass flux across the transmissive layer-low permeability layer boundary at a desired location and time while the source is active is calculated in Equation (3.34):

$$J_{y,on}(x,t) = -c_{o}n'\sqrt{\frac{vR'D^{*}}{D_{t}}}e^{\frac{-kx}{v}}\left[\frac{\frac{b^{2}\xi}{\sigma^{2}}}{\sqrt{x-\xi}}e^{rfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)\left(\frac{\sqrt{t-\frac{x}{v_{c}}}e^{-\hat{k}\left(t-\frac{x}{v_{c}}\right)}}{\gamma^{2}(x-\xi)+\varphi^{2}\left(t-\frac{x}{v_{c}}\right)}+\right)\right]d\xi$$

$$\left(-\frac{e^{-\hat{k}\left(t-\frac{x}{v_{c}}\right)}}{\sqrt{\pi}\sqrt{\gamma^{2}x+\varphi^{2}\left(t-\frac{x}{v_{c}}\right)}}-\frac{\hat{k}'}{\varphi\pi^{\frac{3}{2}}0}\left(\frac{e^{\frac{\hat{k}'\gamma^{2}(x-\xi)}{\varphi^{2}}}(I(x,t,\xi))}{\sqrt{\xi(x-\xi)}I(x,t,\xi)}\right)d\xi\right]$$

$$(3.34)$$

As was the case for the low permeability direct computational approach, the direct computational approach for Equation (3.34) does not result in accurate values for larger plume lengths (greater than 900m). A series, presented in Equation (A3.3) in the Appendix, was used to approximate Equation (3.35). The conditions under which each computational approach is used is presented in the flow chart in Figure A3.3 in the Appendix.

$$e^{\frac{b^2\xi}{\varphi^2}} \operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right)$$
(3.35)

Once the source is removed, the contaminant mass flux at the contact is calculated using the principle of superposition as shown in Equation (3.36):

$$J_{y,off}(x,t,\tau) = J_{y,on}(x,t) - J_{y,on}(x,t-\tau)$$
(3.36)

Equations (3.34) and (3.36) calculate the mass flux across the transmissive layer-low permeability layer contact. These equations can be used to show if diffusion into or out of the low permeability layer is occurring. Diffusion from the transmissive layer to the low permeability layer (inward diffusion) is indicated by a positive mass flux value. Diffusion from the low permeability layer to the transmissive layer (outward diffusion) is indicated by a negative mass flux value.

3.2.4. Concentrations in wells

Aqueous concentrations at points were used to calculate aqueous concentrations in wells by integrating the solution (Equation (3.10)) over the vertical interval of interest (screened interval) (from 0m to 3m in the transmissive layer) shown in Equations (3.37) and (3.38):

$$c_{\text{well,on}}(x,t) = \frac{0}{3m}$$
(3.37)

$$c_{\text{well,off}}(x,t,\tau) = \frac{\frac{3m}{\int c_{\text{trans,off}}(x,y,t,\tau)dy}}{3m}$$
(3.38)

Equation (3.37) calculates the aqueous concentration in the well when the source is active and Equation (3.38) calculates the aqueous concentration in the well once the source has been removed.

3.2.5. Total mass by compartment

Another application of the model is to predict the total contaminant mass in the DNAPL, transmissive layer, low permeability layer, and the total mass degraded. The equations used to calculate the total mass in each compartment are presented in the following sections. Each equation assumes a unit width for the solution domain.

3.2.5.1 Source zone

The total contaminant mass entering the system as a function of time is defined by integrating the influent flux of contaminant at x=0m over y and time, as calculated in Equation (3.39):

$$M_{in}(t,\tau) = \begin{cases} t \infty \\ \int \int vnc_o e^{-by} dy dt & \text{if } t \leq \tau \\ 0 0 \\ \tau \infty \\ \int \int vnc_o e^{-by} dy dt & \text{if } t > \tau \\ 0 0 \end{cases}$$
(3.39)

The mass of the DNAPL in the system is calculated in Equation (3.40).

$$M_{DNAPL}(t,\tau) = \int_{0}^{\tau \infty} \int_{0}^{\infty} vnc_o e^{-by} dy dt - M_{in}(t,\tau)$$
(3.40)

3.2.5.2 Transmissive layer

The total contaminant mass in the transmissive layer at a desired time while the source is active is calculated in Equation (3.41):

$$M_{\text{trans,on}}(t) = \operatorname{Rn} \int_{0}^{v_{c}t} \int_{0}^{2\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}}} \int_{0}^{\sqrt{D_{t}x}} \int_{0}^{\sqrt{D_{t}x}$$

 $v_c t$ represents the distance to the leading edge of the plume from x=0 (the source zone) and $2(D_t x/v_c)^{\frac{1}{2}}$ represents the computationally practical diffusion front into the transmissive layer. (Rigorously, the total contaminant mass in the transmissive layer would involve two semiinfinite integrals over $0 \le x < \infty$ and $0 \le y < \infty$. Those limits are not computationally practical, so the limits were set to be the bounds of where the vast majority of contaminant is located in the transmissive layer.)

Using the principle of superposition, the total contaminant mass in the transmissive layer at a desired time and over a desired area after the source is removed is calculated in Equation (3.42):

$$M_{\text{trans,off}}(t,\tau) = \operatorname{Rn} \int_{0}^{v_{c}t} \int_{0}^{2\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{z_{c}} c_{\text{trans,off}}(x, y, t, \tau) dy dx$$
(3.42)

Equations (3.41) and (3.42) can be partitioned into aqueous and sorbed phases, as shown in Equations (3.43) and (3.44), respectively.

$$M_{\text{trans, aqueous}}(t,\tau) = \begin{cases} v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \int c_{\text{trans,on}}(x, y, t) dy dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \int c_{\text{trans,off}}(x, y, t, \tau) dy dx & \text{if } t > \tau \end{cases}$$
(3.43)

$$M_{\text{trans, sorbed}}(t,\tau) = \begin{cases} v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \rho_b K_{oc} f_{oc} \int c_{\text{trans, on}}(x, y, t) dy dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t^2 \sqrt{\frac{D_t x}{v_c}} \\ \rho_b K_{oc} f_{oc} \int c_{\text{trans, off}}(x, y, t, \tau) dy dx & \text{if } t > \tau \end{cases}$$
(3.44)

3.2.5.3 Low permeability layer

The total contaminant mass in the low permeability layer at a desired time while the source is active is calculated in Equation (3.45):

$$M_{lowk, on}(t) = R'n' \int_{0}^{v_c t} \int_{0}^{2\sqrt{D_t t}} \int_{0}^{t} c_{lowk, on}(x, y', t) dy' dx$$
(3.45)

As was the case in the transmissive layer, $v_c t$ represents the distance to the leading edge of the plume from x=0 (the source zone) and $2(D_t t)^{1/2}$ represents bounds of where the vast majority of contaminant is located in the low permeability layer.
Using the principle of superposition, the total contaminant mass in the low permeability layer at a desired time and over a desired area after the source is removed is calculated in Equation (3.46):

$$M_{lowk,off}(t,\tau) = R'n' \int_{0}^{v_c} \int_{0}^{t} c_{lowk,off}(x, y', t, \tau) dy' dx$$
(3.46)

Equations (3.45) and (3.46) can be partitioned into aqueous and sorbed phases, as shown in Equations (3.47) and (3.48), respectively.

$$M_{lowk, aqueous}(t, \tau) = \begin{cases} v_c t 2\sqrt{D_t t} \\ \int & \int c_{lowk,on}(x, y', t) dy' dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t 2\sqrt{D_t t} \\ \int & \int c_{lowk,off}(x, y', t, \tau) dy' dx & \text{if } t > \tau \end{cases}$$
(3.47)

$$M_{lowk, sorbed}(t, \tau) = \begin{cases} v_c t 2\sqrt{D_t t} \\ \rho_b' K_{oc} f_{oc}' \int \int c_{lowk,on}(x, y', t) dy' dx & \text{if } t \leq \tau \\ 0 & 0 \\ v_c t 2\sqrt{D_t t} \\ \rho_b' K_{oc} f_{oc}' \int \int c_{lowk,off}(x, y', t, \tau) dy' dx & \text{if } t > \tau \end{cases}$$
(3.48)

3.2.5.4 Total degraded mass

The total degraded mass in the system (includes degradation in the transmissive and low permeability layers) while the source is active is found by using a mass balance, as shown in Equation (3.49):

$$M_{\text{degraded,on}}(t,\tau) = M_{\text{in}}(t,\tau) - M_{\text{DNAPL}}(t,\tau) - M_{\text{trans,on}}(t) - M_{\text{lowk,on}}(t)$$
(3.49)

The total degraded mass in the system after the source is removed is calculated using a mass balance in Equation (3.50):

$$M_{\text{degraded,off}}(t,\tau) = M_{\text{in}}(t,\tau) - M_{\text{trans,off}}(t,\tau) - M_{\text{lowk,off}}(t,\tau)$$
(3.50)

3.2.6. Spatial distribution of total mass in transmissive and low permeability layers

Another application of the model is to predict the spatial distribution of the total contaminant mass in the transmissive and low permeability layers. The equations used to calculate the spatial distribution of the total mass in each layer are presented in the following sections.

3.2.6.1 Transmissive layer

The spatial distribution of the total contaminant mass in the transmissive layer while the source is active is presented in Equation (3.51):

$$m_{\text{trans,on}}(x,t) = Rn \int_{0}^{2\sqrt{\frac{D_{t}x}{v_{c}}}} \int_{0}^{1} c_{\text{trans,on}}(x,y,t) dy$$
(3.51)

Using the principle of superposition, the spatial distribution of the total contaminant mass in the transmissive layer is calculated in Equation (3.52):

$$m_{\text{trans,off}}(x,t,\tau) = Rn \int_{0}^{2\sqrt{\frac{D_t x}{v_c}}} \int_{0}^{1} c_{\text{trans,off}}(x,y,t,\tau) dy$$
(3.52)

3.2.6.2 Low permeability layer

The spatial distribution of the total contaminant mass in the low permeability layer while the source is active is presented in Equation (3.53):

$$m_{lowk, on}(x, t) = R' n' \int_{0}^{2\sqrt{D_t t}} c_{lowk, on}(x, y', t) dy'$$
(3.53)

Using the principle of superposition, the spatial distribution of the total contaminant mass in the low permeability layer is calculated in Equation (3.54):

$$m_{\text{lowk,off}}(x, t, \tau) = R'n' \int_{0}^{2\sqrt{D_t t}} c_{\text{lowk,off}}(x, y', t, \tau) dy'$$
(3.54)

3.2.7. Modeled conditions

In this study, the source is active for 10 years (τ) and then is completely removed allowing clean water to flush through the media for an additional 20 years. The source characteristic, b, and c_o values in this study are based on a thin, 1m long, horizontal pool of tetrachloroethene (PCE) located upgradient of the point x=0 and y=0. The parameters used in the model are listed in Table 3.1.

Parameter	Values	Units
Average linear groundwater seepage velocity, v	0.27	m/day
Porosity of the transmissive layer, n	0.25	dimensionless
Porosity of the low permeability layer, n'	0.45	dimensionless
Mean plume loading concentration above low permeability layer during DNAPL persistence time, c _o	240	mg/L
Bulk density of transmissive layer, ρ_b	1.99	g/mL
Bulk density of low permeability layer, ρ_b '	1.46	g/mL
Retardation factor of the transmissive layer, R	1	dimensionless
¹ Retardation factor of the low permeability layer, R'	1, 5, 15	dimensionless
Exponential decay rate for the transmissive layer, k	0.023	yr ⁻¹
² Exponential decay rate for the low permeability layer, k'	0.023, 0.069, 0.231	yr ⁻¹
Effective transverse diffusion coefficient of the transmissive layer, D _t	4.54×10 ⁻⁹	m ² /s
Effective transverse diffusion coefficient of the low permeability layer, D*	5.75×10 ⁻¹⁰	m ² /s
Source pool length, L	1	m
Source persistence time, τ	10	yr

Table 3.1. Input parameters of the model.

¹Retardation factors of the low permeability layer are varied from 1 to 5 to 15.

²Decay rates for the low permeability layer are varied from 0.023 yr⁻¹ to 0.069 yr⁻¹ to 0.231 yr⁻¹.

3.3 Results

The results of the sensitivity analyses are presented with respect to aqueous and total concentrations in cross sections, aqueous concentrations in wells, flux at the contact between the two layers, mass in compartments, and the spatial distribution of contaminant mass in the transmissive and low permeability layers. Model limitations are also presented.

3. 3.1 Concentrations in cross sections

Equations (3.23), (3.24), (3.31), and (3.32) are used to calculate contaminant concentrations in a cross-section shown in Figure 3.2. Figure 3.2 shows data plotted in terms of aqueous concentrations. This provides a basis for interpreting the y direction aqueous concentrations that control transverse diffusion/dispersion. Data in Figure 3.3 is plotted in terms of total concentration. Total concentrations provide a basis for understanding the contaminant mass that resides in transmissive and low permeability layers.



Figure 3.2. Analysis of aqueous contaminant concentration contours as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ= 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.



Figure 3.3. Analysis of total contaminant concentration contours as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.

Figure 3.2 shows aqueous concentration contours with varying levels of retardation and degradation in the low permeability layer. When the degradation rate in the low permeability layer (k') is held constant, increasing the retardation factor in the low permeability layer (R') decreases the depth into the low permeability layer (y') in which there is significant aqueous concentration due to an increase in the fraction of mass sorbed. When R' is held constant, increasing the degradation rate in the low permeability layer decreases the aqueous concentration in the low permeability layer due to an increase in degraded aqueous mass in the low permeability layer. Increasing k' also decreases the peak aqueous concentration because less mass is diffusing from the low permeability layer to the transmissive layer (see Figure 3.5). For each case, the greatest concentration in the low permeability layer occurs close to the source zone (x=0, y'=0). However, the peak concentration in the transmissive layer is located downgradient of the source zone due to contaminant advection and source removal.

Similar conclusions can be drawn from Figure 3.3, which shows total concentration contours as a function of retardation and degradation in the low permeability layer. Figure 3.3 provides a more rigorous basis for understanding mass distribution in heterogeneous media. For example, when retardation is elevated in the low permeability layer, high levels of contaminant concentration occur in the low permeability layer immediately beneath the transmissive layer, but this effect is missed in conventional plots of aqueous concentrations (Figure 3.2).

3. 3.2 Aqueous concentrations in downgradient wells

A primary metric for evaluating groundwater quality is aqueous concentration in wells. Using Equations (3.37) and (3.38), concentrations are calculated for wells located 1, 10, 100, and 500m downgradient of the source for a period of 30 years, shown in Figure 3.4.

65



Figure 3.4. Analysis of concentration in wells as a function of position, retardation and degradation in the low permeability layer. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.

Figure 3.4 shows the effects of both retardation and degradation in the low permeability layer on aqueous concentration in wells. As the retardation factor increases with a constant degradation rate, the concentration in the wells increases. For the case of R'=15 (Figure 3.4c, 3.4f and 3.4i), increasing the degradation rate in the low permeability layer does not reduce the well concentration as significantly at each well location as for the cases where R'=1 and R'=5. A reduction of contaminant in the aqueous phase (i.e., increasing retardation) means that less contaminant is available for degradation.

There are several cases where the well concentration falls below the maximum contaminant level (MCL) of PCE (0.005 mg/L). For R'=1 (Figure 3.4a, Figure 3.4d, and Figure 3.4g), the well concentration drops below the MCL at well locations 1m downgradient of the source for each of the three degradation rates. The well concentration at x=10m falls below the MCL when k'=0.069 yr⁻¹(10 year half-life) (Figure 3.4d) and when k'=0.231 yr⁻¹ (3 year half-life) (Figure 3.4g). For all well locations in Figure 3.4g, the well concentration falls below the MCL. For retardation factors of 5 and 15, there is only one case where the well concentration in the low permeability layer is low or nonexistent, even modest degradation rates will allow well concentrations close to the source zone to decrease below the MCL during the 30 year study period.

3. 3.3 Contaminant mass flux at contact

Equations (3.34) and (3.36) are used to calculate the mass flux across the transmissivelow permeability layer contact shown in Figure 3.5. Contaminant mass flux values are calculated at points located 1, 10, 100, and 500m downgradient of the source for a period of 30 years.



Figure 3.5. Analysis of contamiant mass flux as a function of position, retardation and degradation in the low permeability layer. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.

Figure 3.5 shows the effects of varying levels of retardation and degradation in the low permeability layer on the contaminant mass flux across the transmissive-low permeability layer contact. In general, increasing the retardation factor in the low permeability layer delays the switch from inward diffusion to outward diffusion (the asymptote). In addition, for a constant retardation factor in the low permeability layer increases the rate at which outward diffusion approaches zero (10⁻⁴ mg/m²/day is assumed to be approximately zero). Therefore, for a low retardation factor in the low permeability layer, increasing the degradation factor in the low permeability layer, increasing the degradation factor in the low for a constant retardation factor in the low permeability layer increases the rate at which outward diffusion approaches zero (10⁻⁴ mg/m²/day is assumed to be approximately zero). Therefore, for a low retardation factor in the low permeability layer, increasing the degradation rate lessens the impacts of outward diffusion. As observed by others (Feenstra et al., 1996; Sale et al., 2008a ; Parker et al., 2008; Cihan and Tyner, 2011; and Brown et al., 2012), contaminated site diffusion processes are hysteretic because they are gradient driven and loading occurs much more rapidly than release. The mass flux plots in Figure 3.5 agree with these observations.

3. 3.4 Mass in compartments

Figure 3.6 shows the contaminant mass in the DNAPL, aqueous and sorbed phases in the transmissive and low permeability layers. Equations (3.40), (3.43), (3.44), (3.47), and (3.48) are used to calculate the contaminant mass in the DNAPL, transmissive layer aqueous phase, transmissive layer sorbed phase, low permeability layer aqueous phase, and low permeability layer sorbed phase, respectively. The total degraded mass is calculated using Equations (3.49) and (3.50) for situations when the source is active and after the source is completely removed, respectively. The most critical aspect of Figure 3.6 is that it illustrates how releases of chlorinated solvents evolve from a problem of contaminants present as DNAPL to one of varied combinations of aqueous and sorbed contaminants in transmissive and low permeability layers.



Figure 3.6. Analysis of contaminant mass in each compartment as a function of retardation and degradation in the low permeability layer. Input parameters: n=0.25, n'= 0.45, τ = 10 years, c_o= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.

In more detail, Figure 3.6 shows the contaminant mass in each compartment as a function of retardation and degradation in the low permeability layer. As retardation in the low permeability layer increases, the contaminant mass in the low permeability layer aqueous phase decreases. Consequently, the percentage of the total mass that is degraded declines. As the degradation rate in the low permeability layer increases, so does the percentage of the total mass that is degraded, regardless of the retardation factor in the low permeability layer. However, there is a more significant increase in the total mass degraded when the retardation factor in the low permeability layer is low (i.e., there is a greater percentage of mass degraded when R'=1 than for R'=5 or R'=15). The greatest percentage of mass is degraded when R'=1 and k'=0.231 yr^{-1} (Figure 3.6g) since this is the case in which the most contaminant mass is present in the aqueous phase of the low permeability layer with the highest degradation rate. Even when R'=15 and k'=0.023 yr⁻¹ (Figure 3.6c, the worst-case scenario in this paper), 18% of the total mass is degraded by year 30. This leads to the observation that even with modest degradation rates in the low permeability layer, a significant percentage of the mass can be degraded. 3. 3.5 Spatial distribution of total mass in transmissive and low permeability layers

The model is used to predict the spatial distribution of the total mass in the transmissive and low permeability layers at t=30 years, shown in Figure 3.7. The purpose of this analysis is to delineate zones for remediation. Again, the source is active for 10 years and then is completely removed. Equations (3.52) and (3.54) are used to calculate the spatial distribution of the contaminant mass in the transmissive and low permeability layers, respectively.



Figure 3.7. Analysis of the spatial distribution of mass as a function of retardation and degradation in the low permeability layer. Input parameters: t= 30 years, n=0.25, n'= 0.45, τ = 10 years, c₀= 240 mg/L, D_t= 4.54×10⁻⁹m²/s, D^{*}=5.75×10⁻¹⁰m²/s, L=1m, R=1 (f_{oc}=0), k=0.023 yr⁻¹ (30 yr half-life), v=0.27 m/day.

Figure 3.7 shows the effects of retardation and degradation in the low permeability layer with respect to total mass per area in each layer. Increasing retardation in the low permeability layer increases the mass per area in the low permeability layer in the first 1000m. In addition, increasing the degradation rate in the low permeability layer decreases the mass per area in the low permeability layer decreases the mass per area in the low permeability layer decreases the mass per area in the low permeability layer. A key example is when $k'=0.231 \text{ yr}^{-1}$ (3 year half-life) and R'=1 (Figure 3.7g). There is a more significant decrease in the mass per area for this situation than for any other case examined herein. Since there is no retardation in the low permeability layer, all the mass in that layer is present in the aqueous phase and therefore available for degradation.

3. 3.6 Limitations

The analytical model relies on simplifying assumptions. The transmissive and low permeability layers are assumed to be homogeneous and isotropic. In addition, any degradation reactions were assumed to be irreversible and may be described by first-order rate equations. Reaction was assumed to occur only in the aqueous phase. This is a standard assumption in many reactive contaminant transport models. Nevertheless, the validity of this assumption needs to be further explored. Furthermore, the source is either considered to be active or completely removed, so a step-off source was not studied. Moreover, reaction networks in the low permeability layer were not considered. The model does not work for all variable combinations. Specifically, computational instability can be encountered due to the complexity of the functions that are employed.

3.4 Conclusions

Three key observations are developed from the sensitivity analyses. First, elevating the retardation factor in the low permeability layer limits the benefits of degradation. When the retardation factor is elevated less contaminant mass is present in the aqueous phase, where

73

degradation is assumed to occur. When the retardation factor in the low permeability layer is equal to 1 and the half-life of PCE in the low permeability layer is 3 years, 79% of the total mass is degraded by year 30. Whereas when the retardation factor in the low permeability layer is elevated to 15 for the same degradation rate, only 37% of the total mass is degraded by year 30.

Second, even with modest degradation rates in the low permeability layer, a significant percentage of the contaminant mass can be degraded. In the scenario with the highest low permeability layer retardation (R'=15, k'=0.023 yr⁻¹), 18% of the total mass is degraded by year 30. Similarly, when the retardation factor in the low permeability layer is 1 and the half-life in the low permeability layer is 3 years, enough mass degrades to allow for the well concentration close to the source to fall below the MCL in the 30 year study period.

Finally, even with degradation, water quality improvements associated with source removal diminish significantly with increasing downgradient distance from the source. The concentrations at the more downgradient well locations remain above the MCL for PCE for longer periods of time than the concentration at locations closer to the source, even where there is no retardation in the low permeability layer and a 3 year half-life.

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3.6 Appendix





Figure A3.1. Flow chart explaining the series approximation approach in the transmissive layer solution.



Figure A3.2. Flow chart explaining the series approximation approach in the low permeability layer solution



Figure A3.3. Flow chart explaining the series approximation approach in the flux solution

Equation (3.21) is modified by the following series approximation:

$$\frac{e^{\frac{b^{2}x}{\varphi^{2}}}\left(e^{by}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{x}+\frac{\varphi y}{2\sqrt{x}}\right)+e^{-by}\left(1+\operatorname{erf}\left(\frac{-b}{\varphi}\sqrt{x}+\frac{\varphi y}{2\sqrt{x}}\right)\right)\right)}{\left[\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right]\sqrt{\pi x}}e^{-\left[\left(\frac{\varphi \frac{y}{x}}{2}\right)^{2}x\right)}\left[1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)}{n!\left(\left[2\left(\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right]^{2}x\right)^{n}}\right]+\left(\frac{1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)}{n!\left(\left[2\left(\frac{b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right]^{2}x\right)^{n}}\right)\right]}\right]+\left(A3.1\right)$$

$$\frac{-1}{\left[\left(\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\sqrt{\pi x}}e^{-\left[\left(\frac{\varphi \frac{y}{x}}{2}\right)^{2}x\right)\left(1+\sum_{n=1}^{m}\frac{(-1)^{n}(2n)}{n!\left(\left[2\left(\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right)\right)^{2}x\right)^{n}}\right)\right]}\right]+e^{\left(\left(\frac{b}{\varphi}\right)^{2}-bxy}\left(\frac{\left|\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}\right|}{\frac{-b}{\varphi}+\frac{\varphi \frac{y}{x}}{2}}\right)$$

Equation (3.22) is modified by the following series approximation:

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$$\frac{e^{\frac{b^{2}\xi}{\varphi^{2}}}\left(\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}+\frac{\varphi y}{2\sqrt{\xi}}\right)\right) \cong \frac{1}{\sqrt{\pi\left(\frac{b}{\varphi}\right)^{2}\xi}} e^{-by}\left[1+\sum_{n=1}^{m}\left(\frac{(-1)^{n}\left(\frac{\varphi}{b}\right)^{2n}\left(\frac{1}{\xi}\right)^{n}}{\prod_{j=1}^{n}4j}\right)_{k=0}^{2n}\left((by)^{(2n-k)}\frac{(2n)}{(2n-k)!}\right)\right]$$
(A3.2)

Series Approximation of low permeability layer and flux at contact solutions

Equations (3.30) and (3.35) are modified by the following series approximation:

$$e^{\frac{b^{2}\xi}{\varphi^{2}}}\operatorname{erfc}\left(\frac{b}{\varphi}\sqrt{\xi}\right) \cong \frac{1}{\sqrt{\pi\left(\frac{b}{\varphi}\right)^{2}\xi}} \left(1 + \sum_{n=1}^{m} \left(\frac{(-1)^{n}(2n)}{2^{2n} n!\left(\left(\frac{b}{\varphi}\right)^{2}\xi\right)^{n}}\right)\right)$$
(A3.3)

For all cases, m is based on an empirical relationship between the height of the diffusive front and the series convergence, and is case dependent.

CHAPTER 4

NUMERICAL SOLUTION FOR A NETWORK OF IRREVERSIBLE FIRST-ORDER REACTIONS IN LOW PERMEABILITY LAYERS

SYNOPSIS

An emerging issue in the field of contaminant hydrology is reaction rates for contaminants in low permeability layers. Herein a one-dimensional model is advanced that includes a network of irreversible first-order reactions. The Crank-Nicolson Method was used to create the model. Fitting the model to vertical profiles of parent and decay products in the low permeability layer provides a means of estimating reaction rates for each compound in a reaction network of irreversible first-order reactions. Half-lives calculated in this paper fall within ranges found in literature for transmissive layers under anaerobic conditions (ranging from 0.003 yr to 0.76 yr). The effects of heterogeneity in retardation factors in the low permeability layer were explored. Retardation factor heterogeneity can have a significant impact on vertical concentration profiles as well as contaminant mass flux out of the low permeability layer. A key limitation of the model is that multiple fitting parameters leads to a condition where the model can be fit to the data using non-unique inputs. Additional laboratory/field data is needed to help validate the model results and constrain the number of uncertain input parameters.

4.1 Introduction

Reaction in low permeability layers is emerging as an important process in the natural attenuation of plumes (Sale et al., 2008; Rasa et al., 2011). Unfortunately, there is little basis for anticipating reaction rates in low permeability layers. Furthermore, little attention has been

given to networks of reactions. Important developments to date include Scheutz et al. (2010), Takeuchi et al. (2011), and Schaefer et al. (2013). Scheutz et al. (2010) showed that a bioactive zone in a sand filled fracture in a low permeability layer could expand to the adjacent low permeability media and enable mass transfer from the low permeability matrix to the bioactive zone in the fracture. In addition, a one-dimensional (1-D) model was used to simulate chlorinated ethene diffusion profiles in the clay. Takeuchi et al. (2011) provides early documentation that low permeability layers, as well as transmissive layers, can be habitats for dechlorinating microbial communities that naturally attenuate chlorinated ethenes through biodegradation. Schaefer et al. (2013) performed laboratory experiments using minimally disturbed sedimentary rocks to measure coupled diffusion and abiotic reaction of trichloroethene (TCE) through rock core samples. Furthermore, Schaefer et al. (2013) used numerical and analytical models to determine effective diffusion coefficients and rate constants of TCE and the abiotic degradation products.

The most common approach to degradation in low permeability layers has been to assume first-order decay of the parent compound (e.g., Sale et al., 2008). In those models that do address reaction pathways, reactions are only a function of time and not depth in the low permeability layer (Eykholt, 1999) or the model only addresses reaction pathways in a fracture – clay matrix system (Chambon et al., 2010; Scheutz et al., 2010). In this paper, a 1-D model that addresses reaction pathways as a function of both time and depth in a low permeability layer is presented. Mechanism for reaction can be either biotic or abiotic. To the authors' knowledge, this is the first model that considers reaction networks in a low permeability layer as a function of depth and time under the condition of diffusive transport.

81

The model domain is a 1-D system consisting of a semi-infinite low permeability layer (e.g., clay) bounded by a source. The source is a time varied concentration boundary. Conceptually, the source can be analogous to a pool of dense nonaqueous phase liquids (DNAPLs) or concentrations in a plume downgradient of a source. Figure 4.1 presents the conceptual framework of the model. The model computes simultaneous contaminant transport and first-order irreversible degradation as a function of depth and time while considering a degradation pathway. The model relies on finite difference methods, specifically the Crank-Nicolson Method.



Figure 4.1. 1-D reaction network model domain

Objectives for this paper are threefold. First, governing equations and computational methods are introduced. Second, estimates of reaction rates in the low permeability layer are developed for energetic (2,4,6-TNT (2,4,6-trinitrotoluene) and 2,4-DNT (2,4-dinitrotoluene)) and chlorinated (PCE (tetrachloroethene), TCE (trichloroethene), cis-DCE (cis-dichloroethene), and VC (vinyl chloride)) compounds by fitting the model to field data. Finally, the model is applied to explore fluxes from the low permeability layer and the implications of heterogeneity in retardation in the low permeability layer.

4.2 Methods

Herein, a numerical model has been developed to predict concentrations of parent and decay products in a 1-D system with diffusion (Figure 4.1) as a function of space and time. Per Figure 4.1, the position z=0 corresponds to the location of the source. Key assumptions include: (1) the domain is assumed to be infinite in extent in the low permeability layer ($z\rightarrow\infty$); (2) transport in the low permeability layer occurs solely by molecular diffusion; (3) any degradation reactions in the low permeability layer are irreversible and may be described by first-order rate equations; (4) sorption is instantaneous and linear; and (5) rates of contaminant transformations are solely dependent on concentrations of contaminants in the aqueous phase.

The partial differential equation governing solute transport in the low permeability layer for the parent compound is presented in Equation (4.1).

$$\frac{dC}{dt} = \frac{D_e}{R} \frac{d^2 C}{dz^2} - \frac{k}{R} C \qquad 0 \le z < \infty$$
(4.1)

where C(z,t) is the solute concentration of the parent compound in the low permeability layer aqueous phase (M/L³), D_e is the effective diffusion coefficient of the parent compound (L²/T), k is the first-order degradation rate of the parent compound (T⁻¹), and R, the retardation in the low permeability layer (dimensionless), is defined as

$$R = 1 + \frac{\rho_b K_{oc} f_{oc}}{n'}$$
(4.2)

where ρ_b is the bulk density of the low permeability layer (M/L³), K_{oc} is the soil organic carbon partition coefficient of the parent compound (L³/M), f_{oc} is the fraction of organic carbon in the low permeability layer (dimensionless), and n' is the porosity in the low permeability layer (dimensionless). The parent compound in the model is subject to the following initial and boundary conditions shown in Equations (4.3)-(4.5).

$$C(z,0) = 0$$
 (4.3)

$$\mathbf{C}(\mathbf{0},\mathbf{t}) = \mathbf{C}_{\mathbf{0}} \tag{4.4}$$

$$C(\infty, t) = 0 \tag{4.5}$$

where C_o is the aqueous concentration of the parent compound (M/L³) present at z=0. Initially it is assumed that no solute is present in the low permeability layer (Equation (4.3)). In addition, since a numerical model is being used, the boundary conditions can change with relative ease compared with an analytical model. The source can be removed at the contact between the transmissive and low permeability layers by modifying Equation (4.4).

Using the Crank-Nicolson Method (Crank and Nicolson, 1947), the partial differential equation for the parent compound is re-written as shown in Equation (4.6).

$$\frac{r}{2}C_{i-1,j} + (1-r)C_{i,j} + \frac{r}{2}C_{i+1,j} = -\frac{r}{2}C_{i+1,j+1} + \left(1+r+\frac{k}{R}\Delta t\right)C_{i,j+1} - \frac{r}{2}C_{i-1,j+1}$$
(4.6)

where r is defined as

$$r = \frac{D_e \Delta t}{R \Delta z^2}$$
(4.7)

 Δt and Δz are the time (T) and spatial (L) step sizes, respectively. A program loop was written in Mathcad 15TM to solve for the aqueous concentration of the parent compound at a certain time and space, $C_{i,j+1}$ (where i is a counter for z and j is a counter for t), using the LDU decomposition method (Fausett, 2002).

To validate the numerical model for the parent compound, the Crank-Nicolson Method was compared to the analytical solution for the partial differential equation (Equation (4.1)) and boundary conditions (Equations (4.3)-(4.5)) (Crank, 1975), presented in Equation (4.8).

$$C(z,t) = C_{o}\left(\frac{1}{2}exp\left(-z\sqrt{\frac{k}{\frac{D_{e}}{R}}}\right)erfd\left(\frac{z}{\sqrt{4\frac{D_{e}}{R}t}} - \sqrt{\frac{k}{R}t}\right) + \frac{1}{2}exp\left(z\sqrt{\frac{k}{\frac{D_{e}}{R}}}\right)erfd\left(\frac{z}{\sqrt{4\frac{D_{e}}{R}t}} + \sqrt{\frac{k}{R}t}\right)\right)$$
(4.8)

The same method was used for subsequent decay compounds, except the boundary conditions changed and the Crank-Nicolson equation for the first time step changes. The new boundary conditions for decay products are presented in Equations (4.9)-(4.11).

$$C_{decayl}(z,0) = 0 \tag{4.9}$$

$$C_{\text{decayl}}(0,t) = 0 \tag{4.10}$$

$$C_{\text{decayl}}(\infty, t) = 0 \tag{4.11}$$

where C_{decay1} is the aqueous concentration of the first decay product. The source is assumed to contain only the parent compound. In addition, the boundary conditions for the parent compound still apply.

The equation for the first spatial step (z=0m) for the first decay product is shown in Equation (4.12).

$$cc_{0} = C_{0,j} - \frac{r}{2}C_{decayl_{0,j+1}} + (1-r)C_{decayl_{1,j}} + \frac{r}{2}C_{decayl_{2,j}} - C_{i,j}$$
(4.12)

where cc_0 is a spatial vector of concentrations through the low permeability layer. The source concentration at z=0 for the parent compound ($C_{0,j}$) is in the spatial vector equation (Equation (4.12)). For subsequent decay products, the concentration present in the previous compounds, in this case the parent compound ($C_{i,j}$), is subtracted from the right hand side of Equation (4.12). The concentration is calculated in mmol/L and converted to kg/m³ once the program loop has completed. Heterogeneity in retardation was incorporated into the model using if statements within the program loop. The program is presented in the Appendix for two compounds.

4.2.1 Validation

The validity of the numerical approach is demonstrated by comparing the numerical solution to the exact analytical solution for a single compound. The input parameters are presented in Table 4.1. The Crank-Nicolson Method is unconditionally stable, but not necessarily unconditionally accurate. With that in mind, the comparison of the model to the parent compound analytical solution is shown in Figure 4.2 with respect to several time and space step sizes (Δt and Δz , respectively). The R² values in Figure 4.2 were calculated using the correlation function in Microsoft ExcelTM (correl).

Table 4.1. Input parameters for comparison of the analytical solution to the numerical method.

Parameter	Value	Units
¹ Molecular weight of PCE, MW _{PCE}	165.83	g/mol
¹ Effective diffusion coefficient of PCE, D _{ePCE}	5.00×10 ⁻⁵	m ² /day
Decay rate of PCE, k _{PCE}	0.0745	day ⁻¹
² Porosity of the low k media, n'	0.4	dimensionless
² Bulk density of low k media, ρ_b	1.59	g/cm ³
² Retardation factor of PCE, R _{PCE}	33.56	dimensionless
³ Concentration of PCE at $z=0m$ while the PCE source is active,	1.2	mmol/L
Co		
Time of output for model, t	40	yr
Amount of time source is active, τ	30	yr

¹From Literature. ²Based on typical silt media. ³The aqueous solubility of PCE (Pankow and Cherry, 2006).

All of the temporal and spatial steps compare well to the analytical solution (Figure 4.2). However, when the time step is decreased from 2 days to 1 day with the same spatial step, the computation time almost doubles. In addition, increasing the spatial step size from 0.001m to 0.01 m increased the error between the analytical solution (Equation (4.8)) and the Crank-Nicolson numerical approximation. There is the greatest amount of error for a spatial step size of 0.1m, since the 1m low permeability domain is only divided into 10 sections. To minimize the error and computing time, a time step of 2 days and a space step of 0.001m were chosen.



Figure 4.2. Comparison between parent compound analytical solution (Equation (4.8)) and the numerical model for different temporal and spatial step sizes.

4.3 Results

The model is applied to field data to estimate parameters. From the parameter results, the

reaction rates of parent and decay products are obtained.

4.3. 1 Use of field data to estimate parameters

The model is applied to data from low permeability layers collected at two field sites.

The first field site is Pueblo Chemical Depot near Pueblo, CO. At Pueblo Chemical Depot,

coarse fluvial deposits overlie the Pierre Shale. Locally the Pierre Shale contained energetic

compounds (2,4,6-TNT and 2,4-DNT). More information on this site can be found in Sale et al.

(2009). Total contaminant concentrations obtained from soil core samples collected at three borings were compared to the model. The second field site is a PCE spill from a dry cleaning factory located on the east side of the Yonezawa Basin in Yamagata Prefecture, Japan (from Takeuchi et al., 2011). Soil from this site contained chlorinated compounds (PCE, TCE, cis-DCE, and VC). More information on this site can be found in Takeuchi et al. (2011).

4.3. 1.1 Pueblo Chemical Depot

Table 4.2 shows the input parameters for each boring at Pueblo Chemical Depot. A spatial step size of 1 mm was chosen to provide agreement with both the analytical solution for the parent compound, 2.4.6-TNT, (Equation (4.8)) and to minimize numerical dispersion (Chapman et al., 2012). The degradation pathway of 2,4,6-TNT varies depending upon the bacteria and/or fungi present and whether degradation occurs under aerobic or anaerobic conditions (Esteve-Núñez et al., 2001). At Pueblo Chemical Depot, the low permeability layer (Pierre Shale) was under anaerobic conditions and contained 2% organic carbon (Sale et al., 2009). The presence of 2,4-DNT could indicate that the anaerobic degradation of 2,4,6-TNT to 2,4-DNT takes place due to the bacteria *Pseudomonas* sp. strain JLR11 (Esteve-Núñez et al., 2001). Differences in source concentration and decay rates for each compound at different boring locations can be attributed to heterogeneity in the site over space. For all cases, only a fraction of each decay rate (k/R) contributes to the degradation of the compounds. Heterogeneity in retardation is taken into account in the model for ESTCP 8 Boring and MW02 Boring at Pueblo Chemical Depot. In addition, the R² values in the following figures were calculated using the correlation function in Microsoft ExcelTM (correl).

Parameter	Value	Units
Molecular weight of 2,4,6-TNT, MW _{2,4,6-TNT}	227.113	g/mol
Molecular weight of 2,4-DNT, MW _{2,4-DNT}	182.14	g/mol
¹ Effective diffusion coefficient of 2,4,6-	1.76×10 ⁻⁶	m ² /day
¹ Effective diffusion coefficient of 2.4 DNT		
$D_{e2,4-DNT}$	5.0×10 ⁻⁷	m ² /day
¹ Decay rate of 2,4,6-TNT, $k_{2,4,6-TNT}$	0.65, 0.7, 0.24	day ⁻¹
¹ Decay rate of 2,4-DNT, $k_{2,4-DNT}$	0.076, 0.1525, 0.05	day ⁻¹
Thickness of the no f_{oc} layer at ESTCP 8 Boring and MW02 Boring, y	0.003, 0.01	m
Porosity of the low k media, n'	0.25	dimensionless
Bulk density of low k media, ρ_b	1.987	g/cm ³
³ Retardation factor for 2,4,6-TNT at ESTCP	1.0	1 1
8 Boring and MW02 Boring in first y m, $R_{12.4.6-TNT}$	1.0	dimensionless
⁴ Retardation factor for 2,4,6-TNT in low k, $R_{2,4,6-TNT}$	292.6	dimensionless
³ Retardation factor for 2,4-DNT at ESTCP 8 Boring and MW02 Boring in first y m, R ₁₂ 4DNT	1.0	dimensionless
⁴ Retardation factor for 2,4-DNT in low k, $R_{2,4-DNT}$	58.8	dimensionless
² Concentration of 2,4,6-TNT at $z=0m$ while the 2,4,6-TNT source is active, C_0	0.5, 0.315, 0.5	mmol/L
Time of output for model, t	45	yr
Amount of time source is active, τ	36	yr
Spatial step size, Δz	0.001	m
Temporal step size, Δt	2	days

Table 4.2. Input parameters to the model for Pueblo Chemical Depot.

¹These parameters were used to fit the data for each boring. The effective diffusion coefficients were chosen to optimize the fit for the three borings. ²Based on the aqueous solubility of 2,4,6-TNT (Ro et al., 1996). The first number is for ESTCP 8 Boring, the second number is for D2M Boring, and the third number is for MW02 Boring. All other parameters were measured per the experiments in Sale et al. (2009). ⁴Corresponds to $f_{oc1}=0.0$. ⁴Corresponds to $f_{oc}=0.02$.

Figure 4.3 shows the model comparison for 2,4,6-TNT and 2,4-DNT in the soil cores from ESTCP 8 Boring. The model compares well to the data, but at larger depths the model over predicts the total concentration for 2,4,6-TNT and 2,4-DNT. Heterogeneity is taken into account in the low permeability layer. Based on visual logs of the soil for ESTCP 8 Boring, a different

fraction of organic carbon is assumed for the first 0.003 m. In addition, degradation rates may not be constant throughout the low permeability layer.



Figure 4.3. Model and Field Data Comparison for ESTCP 8 Boring at Pueblo Chemical Depot

Figure 4.4 shows the model comparison for 2,4,6-TNT and 2,4-DNT in the soil cores from D2M Boring. The model compares well to the data. The most prominent limitation of the model is that the total concentration of 2,4-DNT in the shale at shallow depths is overestimated. Conversely, the model underestimates the total concentration of 2,4,6-TNT in the shale at larger depths. These differences could be due to heterogeneity in the distribution of microorganisms in the shale. For this boring, the source was not considered to be completely removed after the source zone was removed at a time of 36 years (τ). Instead, the source was considered to be 99.999% removed.



Figure 4.4. Model and Field Data Comparison for D2M Boring at Pueblo Chemical Depot Figure 4.5 shows the model comparison for 2,4,6-TNT and 2,4-DNT in the soil cores from MW02 Boring. The model compares well to the data for 2,4-DNT. The model over predicts the total concentration of 2,4,6-TNT and 2,4-DNT at larger depths. Heterogeneity is taken into account in the low permeability layer. Based on visual logs of the soil for MW02 Boring, a different fraction of organic carbon is assumed for the first 0.01 m. The differences between the model and the field data could be due to different degradation rates within the shale.





4.3. 1.2 Takeuchi et al. (2011) silt data

Table 4.3 shows the input parameters for the silt layer from Figure 2B in Takeuchi et al.

(2011). A spatial step size of 1 mm was chosen to provide agreement with both the analytical

solution for the parent compound, PCE, (Equation (4.8)) and to minimize numerical dispersion (Chapman et al., 2012). The biological degradation pathway of PCE is well established (Takeuchi et al., 2011). For all cases, only a fraction of each decay rate (k/R) contributes to the degradation of the compounds. In addition, the R^2 values in the following figure were calculated using the correlation function in Microsoft ExcelTM (correl).

Parameter	Value	Units
¹ Molecular weight of PCE, MW _{PCE}	165.83	g/mol
¹ Molecular weight of TCE, MW _{TCE}	131.4	g/mol
¹ Molecular weight of cis-DCE, MW _{cis-DCE}	96.95	g/mol
¹ Molecular weight of VC, MW _{VC}	62.498	g/mol
² Effective diffusion coefficient of PCE, D _{ePCE}	5.00×10 ⁻⁵	m ² /day
² Effective diffusion coefficient of TCE, D _{eTCE}	2.00×10^{-5}	m ² /day
² Effective diffusion coefficient of cis-DCE, D _{ecis-DCE}	1.00×10^{-5}	m ² /day
² Effective diffusion coefficient of VC, D _{eVC}	3.00×10 ⁻⁶	m ² /day
² Decay rate of PCE, k_{PCE}	0.0745	day ⁻¹
² Decay rate of TCE, k_{TCE}	0.0205	day ⁻¹
² Decay rate of cis-DCE, $k_{cis-DCE}$	0.00955	day ⁻¹
² Decay rate of VC, k_{VC}	0.0025	day ⁻¹
³ Porosity of the low k media, n'	0.4	dimensionless
³ Bulk density of low k media, ρ_b	1.59	g/cm ³
⁵ Retardation factor of PCE, R _{PCE}	33.56	dimensionless
⁵ Retardation factor of TCE, R _{TCE}	12.27	dimensionless
⁵ Retardation factor of cis-DCE, R _{cis-DCE}	8.69	dimensionless
⁵ Retardation factor of VC, R _{VC}	1.98	dimensionless
⁴ Concentration of PCE at z=0m while the PCE source is active,	1.2	mmol/I
Co	1.2	IIIIII0I/L
⁶ Time of output for model, t	40	yr
⁶ Amount of time source is active, τ	30	yr
Spatial step size, Δz	0.001	m
Temporal step size, Δt	2	days

Table 4.3. Input parameters to the model for Takeuchi et al. (2011) silt data.

¹From Literature. ²Parameters used to fit the data for the silt. ³Based on typical silt media. ⁴The aqueous solubility of PCE (Pankow and Cherry, 2006). ⁵From Takeuchi et al. (2011) (Given as soil organic matter (SOM) therein). SOM typically consists of 52-58% carbon (Sparks, 2002); in this case, 50% of the SOM in the silt was assumed to be organic carbon. The retardation factors given correspond to f_{oc} =0.0225 ⁶Based on typical source history of chlorinated solvent releases worldwide (PCE production peaked in the 1960s-1970s and declined thereafter) (Moran, 2006).

Figure 4.6 shows the model comparison for PCE, TCE, cis-DCE, and VC in the silt layer

from Figure 2B in Takeuchi et al. (2011). The model compares well to the data. However, the

model underestimates the total concentration in the silt for all compounds for data taken at depths of 0.25 m and 0.5 m. This may be due to differences in the number of microorganisms in the silt layer. Another reason for the discrepancy is that the model assumes that the low permeability layer is infinite in depth, which is untrue for this data set (a fine sand underlies the silt).





4.3. 2 Low permeability layer reaction rates

Using the degradation rates for each of the compounds at each field data site, the half-life

for each compound was calculated, as shown in Table 4.4.

Compound	Half-life (yr)	Site
2,4,6-TNT	0.003	ESTCP 8 Boring Pueblo Chemical Depot
2,4-DNT	0.025	ESTCP 8 Boring Pueblo Chemical Depot
2,4,6-TNT	0.003	D2M Boring Pueblo Chemical Depot
2,4-DNT	0.012	D2M Boring Pueblo Chemical Depot
2,4,6-TNT	0.008	MW02 Boring Pueblo Chemical Depot
2,4-DNT	0.038	MW02 Boring Pueblo Chemical Depot
PCE	0.025	Takeuchi et al. (2011) silt
TCE	0.093	Takeuchi et al. (2011) silt
cis-DCE	0.20	Takeuchi et al. (2011) silt
VC	0.76	Takeuchi et al. (2011) silt

Table 4.4. Half-lives of compounds in field data

The half-lives of each of the compounds, shown in the second column of Table 4.4, suggest that the compounds would be completely degraded by the time the soil samples were collected from each field site (on the order of 40 years). Retardation limits the effects of the degradation due to the assumption that contaminant degradation takes place only in the aqueous phase. Therefore, effective degradation rates (k/R) should be used to quantify the degree to which contaminant degradation is occurring at each site. Furthermore, historical persistence of these contaminants seems to be due to retardation. The half-lives for the energetic compounds at Pueblo Chemical Depot and the chlorinated compounds in Takeuchi et al. (2011) fall within ranges for biodegradation in transmissive layers under anaerobic conditions found in literature (Howard et al., 1991; US EPA, 1999) and for abiotic degradation in low permeability layers for the chlorinated compounds (Schaefer et al., 2013).

4.3. 3 Limitations

The numerical model relies on simplifying assumptions. The degradation reactions were assumed to be irreversible and undergo first-order kinetics only in the aqueous phase. In addition, the source was considered to contain only the parent compound (i.e., reaction networks in the transmissive layer were not considered). Furthermore, a gradually declining source was not considered. Therefore, the model may not be applicable to more complex situations. Moreover, the model is limited by over parameterization. Good fits for the field data from ESTCP 8 Boring at Pueblo Chemical Depot were obtained for several different parameter values. For example, the parent compound concentration at the contact while the 2,4,6-TNT source was active for ESTCP 8 Boring at Pueblo Chemical Depot was changed from 0.5 mmol/L 2,4,6-TNT to 5.0 mmol/L 2,4,6-TNT, keeping all other variables constant except the degradation rates of 2,4,6-TNT and 2,4-DNT. The half-life of 2,4,6-TNT changed from 0.003 years to 0.002 years.

94
Similarly, the half-life of 2,4-DNT changed from 0.025 years to 0.018 years. These results indicate the effect of the parent compound concentration at the contact while the source is active. These results indicate that the calculated half-lives may not be unique due to uncertainty in the source history and boundary conditions at field sites.

4.4 Applications

Model applications can provide further insights into contaminant behavior at field sites in low permeability layers. The model was used to calculate the flux of contaminants out of the low permeability layer and was used to evaluate heterogeneity in retardation factors throughout the low permeability layer.

4.4.1 Contaminant mass flux out of the low permeability layer

Using Fick's First Law, the mass flux out of the low permeability layer was calculated as a function of time for each of the field sites. The concentration gradient was calculated by taking the difference in concentration at 1 mm into the low permeability layer and the concentration at z=0. Diffusion into the low permeability layer (inward diffusion) is indicated by a positive mass flux value. Diffusion out of low permeability layer (outward diffusion) is indicated by a negative mass flux value.

Figure 4.7 shows the flux out of the low permeability layer for the borings at Pueblo Chemical Depot. Since the source is assumed to contain only 2,4,6-TNT, 2,4-DNT is always undergoing outward diffusion. While the source is active, the 2,4,6-TNT undergoes inward diffusion. After the source is depleted at 36 years, the 2,4,6-TNT undergoes outward diffusion. The fluxes for ESTCP 8 Boring and MW02 Boring are similar due to heterogeneity being taken into account, specifically near z=0m. Even though the concentrations in ESTCP 8 Boring and D2M Boring are similar, the flux into the transmissive layer for 2,4-DNT is different because of

the differences in the degradation rate of 2,4-DNT for the two locations and because of the heterogeneity in the shale at ESTCP 8 Boring.



Figure 4.7. Contaminant mass flux out of the low permeability layer for borings at Pueblo Chemical Depot

Figure 4.8 shows the flux out of the low permeability layer for Takeuchi et al. (2011) silt data. Since the source is assumed to contain only PCE (the parent compound), TCE, cis-DCE, and VC are always undergoing outward diffusion. While the source is active, PCE undergoes inward diffusion. After the source is depleted at 30 years, the PCE undergoes outward diffusion. Outward diffusion for TCE, cis-DCE, and VC seem to be important processes while the PCE source is active. However, the effect of outward diffusion for these compounds diminishes once the source is removed.



Figure 4.8. Contaminant mass flux for Takeuchi et al. (2011) silt data

4.4. 2 Heterogeneity in retardation in the low permeability layer

Heterogeneity in retardation in the low permeability layer is addressed by changing the fractions of organic carbon in the low permeability layer for the Takeuchi et al. (2011) silt data. Four different fractions of organic carbon were used in the model domain. Input parameters for the data are shown in Table 4.5.

Parameter	Value	Units
Molecular weight of PCE, MW _{PCE}	165.83	g/mol
Molecular weight of TCE, MW _{TCE}	131.4	g/mol
Molecular weight of cis-DCE, MW _{cis-DCE}	96.95	g/mol
Molecular weight of VC, MW _{VC}	62.498	g/mol
Effective diffusion coefficient of PCE, D _{ePCE}	5.00×10 ⁻⁵	m ² /day
Effective diffusion coefficient of TCE, D _{eTCE}	2.00×10^{-5}	m ² /day
Effective diffusion coefficient of cis-DCE, D _{ecis-DCE}	1.00×10^{-5}	m ² /day
Effective diffusion coefficient of VC, D _{eVC}	3.00×10^{-6}	m ² /day
Decay rate of PCE, k _{PCE}	0.0745	day ⁻¹
Decay rate of TCE, k _{TCE}	0.0205	day ⁻¹
Decay rate of cis-DCE, k _{cis-DCE}	0.00955	day ⁻¹
Decay rate of VC, k _{VC}	0.0025	day ⁻¹
Porosity of the low k media, n'	0.4	dimensionless
Bulk density of low k media, p _b	1.59	g/cm ³
¹ Retardation factor for PCE in first 0.03m, R _{PCE}	1.00	dimensionless
² Retardation factor for PCE from 0.03m to 0.1m, R_{PCE1}	33.56	dimensionless
³ Retardation factor for PCE from 0.1m to 0.2m, R _{PCE2}	15.47	dimensionless
⁴ Retardation factor for PCE in remaining domain, R _{PCE3}	29.94	dimensionless
¹ Retardation factor for TCE in first 0.03m, R _{TCE}	1.00	dimensionless
² Retardation factor for TCE from 0.03m to 0.1m, R_{TCE1}	12.27	dimensionless
³ Retardation factor for TCE from 0.1m to 0.2m, R _{TCE2}	6.01	dimensionless
⁴ Retardation factor for TCE in remaining domain, R _{TCE3}	11.02	dimensionless
¹ Retardation factor for cis-DCE in first 0.03m, R _{cis-DCE}	1.00	dimensionless
² Retardation factor for cis-DCE from 0.03m to 0.1m, $R_{cis-DCE1}$	8.69	dimensionless
³ Retardation factor for cis-DCE from 0.1m to 0.2m, R _{cis-DCE2}	4.42	dimensionless
⁴ Retardation factor for cis-DCE in remaining domain, R _{cis-DCE3}	7.84	dimensionless
¹ Retardation factor for VC in first 0.03m, R _{VC}	1.00	dimensionless
² Retardation factor for VC from 0.03m to 0.1m, R _{VC1}	1.98	dimensionless
³ Retardation factor for VC from 0.1m to 0.2m, R _{VC2}	1.44	dimensionless
⁴ Retardation factor for VC in remaining domain, R _{VC3}	1.87	dimensionless
Concentration of PCE at z=0m while the PCE source is active, C_o	1.2	mmol/L
Time of output for model, t	40	yr
Amount of time source is active, τ	30	yr
Spatial step size, Δz	0.001	m
Temporal step size, Δt	2	days

Table 4.5. Input parameters to the model for considering heterogeneity in the Takeuchi et al. (2011) silt data.

¹Corresponds to $f_{oc}=0.0$. ²Corresponds to $f_{oc1}=0.0225$. ³Corresponds to $f_{oc2}=0.01$. ⁴Corresponds to $f_{oc3}=0.02$. All other parameters were previously fitted in Table 4.3.

The effects of heterogeneity in retardation in the low permeability layer are shown in

Figure 4.9. The two concentration profiles (Figures 4.9a and 4.9b) show the profound

differences between no heterogeneity and considering 4 different fractions of orgainc carbon (and therefore retardation factors) in the low permeability silt. For example, the peak total concentration is significantly lower for all the compounds when heterogeneity is considered (Figure 4.9b). There are also significant differences when comparing the two mass flux plots (Figures 4.9c and 4.9d). For instance, the mass flux out of the low permeability layer reaches approximately zero (10^{-10} mmol/m²/day) earlier in time when heterogeneity is considered in the low permeability layer probably due to the low retardation factor in the first 0.03m (R=1 for all compounds). Both the concentration profiles and mass flux plots indicate that when the maximum fraction of organic carbon is assumed to be constant throughout the low permeability layer and degradation is assumed to only take place in the aqueous phase, the benefits of contaminant degradation are reduced.



Figure 4.9. Effects of heterogeneity in retardation in the low permeability silt of Takeuchi et al. (2011) on concentration profiles at t=40 years and mass flux out of the low permeability silt. The concentration profile axes (a and b) are different to better show the data.

4.5 Conclusions

Two key observations can be gleaned from the results and model applications. First, contaminant half-lives calculated in this paper fell within ranges found in literature for transmissive layers under anaerobic conditions. Due to model over parameterization and uncertainty in source history, these results could be inaccurate. Second, retardation factor heterogeneity in the low permeability layer can have a significant impact on vertical

concentration profiles as well as contaminant mass flux out of the low permeability layer. This indicates the importance of incorporating heterogeneity in retardation into models. However, additional laboratory/field data is needed to help validate the model results.

4.6 References

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4.7 Appendix

(Copied from one continuous Mathcad 15TM worksheet)

Inputs to Model

MW _{TNT} :=227.113	Molecular weight of 2,4,6-TNT in g/mol
MW _{DNT} :=182.14	Molecular weight of 2,4-DNT in g/mol
$D_{eTNT} := 1.76 \cdot 10^{-6}$	Effective diffusion coefficient in water for 2,4,6-TNT in m^2/day
$D_{eDNT} := 5.0 \cdot 10^{-7}$	Effective diffusion coefficient in water for 2,4-DNT in m^2/day
k _{TNT} :=0.65	Decay coefficient for 2,4,6-TNT in day ⁻¹
k _{DNT} :=0.076	Decay coefficient for 2,4-DNT in day ⁻¹
n':=0.25	Porosity of the low k media
$\rho_b := 1.987$	Bulk density of low k media in g/cm ³
R _{TNT} :=1	Retardation factor of 2,4,6-TNT in the top y m
$R_{TNT1} := 292.606$	Retardation factor of 2,4,6-TNT in bottom (a-y) m
R _{DNT} :=1	Retardation factor of 2,4-DNT in the top y m
R _{DNT1} :=58.844	Retardation factor of 2,4-DNT in bottom (a-y) m
y :=0.003	Depth in m at which the fraction of organic carbon changes
f(z) :=0	Initial condition
g1p(t) :=0.5	Boundary condition for 2,4,6-TNT at z=0 (based on the aqueous solubility of 2,4,6-TNT)
g1t(t) :=0	Boundary condition for 2,4-DNT at z=0 in mmol/L
g2(t) :=0	Boundary condition for 2,4,6-TNT and TCE at z=a m in mmol/L
a :=1.0	Length of z domain in m
T :=25550	Length of time domain in days
n :=1000	Number of z grids where $\Delta z=a/n$
m :=12775	Number of t grids where $\Delta t=T/m$
tau :=6570	Time in which source is active divided by Δt in days

LDU Solver (after Fausett, 2002)

$$LU_factor_T(a,d,b) := \begin{cases} n \leftarrow length(d) \\ bb_0 \leftarrow 0 \\ dd_0 \leftarrow d_0 \\ for \quad i \in 1.. n - 1 \\ \\ bb_i \leftarrow \frac{b_i}{dd_{i-1}} \\ dd_i \leftarrow d_i - bb_i \cdot a_{i-1} \\ z \leftarrow augment(bb, dd) \\ z \end{cases}$$

$$LU_solve_T(a,d,b,r) := \begin{cases} n \leftarrow rows(a) \\ x_0 \leftarrow r_0 \\ \text{for } i \in 1..n - 1 \\ x_i \leftarrow r_i - b_i \cdot x_{i-1} \\ z_{n-1} \leftarrow \frac{x_{n-1}}{d_{n-1}} \\ \text{for } i \in n - 2, n - 3..0 \\ z_i \leftarrow \frac{\left(x_i - a_i \cdot z_{i+1}\right)}{d_i} \\ z \end{cases}$$

Program Loop of Parent Compound (modified from Fausett, 2002)

$$\begin{split} \mathbf{C}_{\text{implicitCNran}}\left(\mathbf{f}, g|\mathbf{p}, g|\mathbf{2}, \mathbf{a}, \mathbf{T}, \mathbf{n}, \mathbf{m}, \mathbf{D}_{q}, \mathbf{R}, \mathbf{R}_{(\mathrm{TMT}}, \mathbf{k}, \mathbf{y}) := & \Delta \mathbf{x} \leftarrow \frac{\pi}{n} \\ \Delta \mathbf{x} \leftarrow \frac{\pi}{n} \\ \mathbf{r} \leftarrow \frac{\mathbf{D}_{q}, \Delta \mathbf{x}}{\mathbf{R}_{n, \mathrm{TMT}} - \Delta \mathbf{x}^{2}} \\ \mathbf{r}_{1} \leftarrow \frac{\mathbf{D}_{q}, \Delta \mathbf{x}}{\mathbf{R}_{1, \mathrm{TMT}} - \Delta \mathbf{x}^{2}} \\ \mathbf{r}_{2} \leftarrow \frac{\mathbf{D}_{q}, \Delta \mathbf{x}}{\mathbf{R}_{1, \mathrm{TMT}} - \Delta \mathbf{x}^{2}} \\ \mathbf{r}_{2} \leftarrow \mathbf{x} < \mathbf{x} < \mathbf{x} < \mathbf{x} \\ \mathbf{w} \leftarrow \mathbf{f}(t) \\ \mathbf{for} \quad \mathbf{i} = \mathbf{0}, \mathbf{m} \\ \mathbf{x}_{1} \leftarrow 2\mathbf{p}(1) \quad \mathbf{f} \quad \mathbf{i} \leq \mathbf{u} \\ \mathbf{w}_{0, 1} \leftarrow 2\mathbf{p}(1) = \mathbf{p}(\mathbf{p}_{1, \mathrm{run}}) \quad \mathbf{f} \quad \mathbf{i} > \mathbf{u} \\ \mathbf{w}_{0, 1} \leftarrow 2\mathbf{p}(1) = \mathbf{p}(\mathbf{p}_{1, \mathrm{run}}) \quad \mathbf{f} \quad \mathbf{i} > \mathbf{u} \\ \mathbf{w}_{0, 1} \leftarrow 2\mathbf{p}(1) = \mathbf{p}(\mathbf{p}_{1, \mathrm{run}}) \quad \mathbf{f} \quad \mathbf{i} > \mathbf{u} \\ \mathbf{w}_{0, 1} \leftarrow 2\mathbf{p}(1) = \mathbf{p}(\mathbf{p}_{1, \mathrm{run}}) \quad \mathbf{f} \quad \mathbf{i} > \mathbf{u} \\ \mathbf{w}_{0, 1} \leftarrow 2\mathbf{p}(1) = \mathbf{x} \\ \mathbf{d}_{1} \leftarrow \mathbf{1} + \mathbf{r} + \frac{\mathbf{k}}{\mathbf{R}} \wedge \mathbf{x} \quad \mathbf{f} \quad \mathbf{f} \leq \frac{\mathbf{y}}{\Delta \mathbf{x}} \\ \mathbf{d}_{1} \leftarrow \mathbf{1} + \mathbf{r} + \frac{\mathbf{k}}{\mathbf{R}} \wedge \mathbf{x} \quad \mathbf{f} \quad \mathbf{f} \leq \frac{\mathbf{y}}{\Delta \mathbf{x}} \\ \mathbf{d}_{1} \leftarrow \mathbf{1} + \mathbf{r} + \frac{\mathbf{k}}{\mathbf{R}} \wedge \mathbf{x} \quad \mathbf{f} \quad \mathbf{f} \leq \frac{\mathbf{y}}{\Delta \mathbf{x}} \\ \mathbf{u}_{1} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{x} \\ \mathbf{u}_{2} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{f} \\ \mathbf{u}_{1} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{f} \\ \mathbf{u}_{2} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{f} \\ \mathbf{u}_{2} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{f} \\ \mathbf{u}_{2} \leftarrow \mathbf{0} \leq \mathbf{n}_{1} \quad \mathbf{f} \quad \mathbf{f} \\ \mathbf{u}_{2} \leftarrow \mathbf{0} \\ \mathbf{u}_{2} = \mathbf{0} \\ \mathbf{u}_{2} = \mathbf{0} \\ \mathbf{u}_{2} = \mathbf{0} \\ \mathbf{u}_{1} + (1 - \mathbf{n}) \cdot \mathbf{w}_{1,1} + \mathbf{0} \\ \mathbf{u}_{1,1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} = \mathbf{0} \\ \mathbf{u}_{1} = \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} = \mathbf{u}_{2} + \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{1} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} = \mathbf{u}_{2} + \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{2} \\ \mathbf{u}_{2} \\ \mathbf{u}_{2} \\ \mathbf{u}_{2} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\ \mathbf{u}_{1} \\ \mathbf{u}_{2} \\$$

 $C_{\text{TNT}} \coloneqq C_{\text{implicit}CNrx} \left(f, g1p, g2, a, T, n, m, D_e, R, R_{1\text{TNT}}, k, y \right)$

Program Loop of Decay Product (modified from Fausett, 2002)

 $C_{\text{implicitCNDNT}}\left(f,glp,glt,g2,a,T,n,m,D_{el},R_{1},R_{1}DNT,k_{1},y\right) \coloneqq \Delta z \leftarrow \Delta z$

$$\begin{cases} \Delta x \leftarrow \frac{a}{n} \\ \Delta t \leftarrow \frac{\pi}{m} \\ \pi \leftarrow \frac{D_{el} \cdot \Delta t}{R_{1} \cdot \Delta x^{2}} \\ \pi_{1} \leftarrow \frac{D_{el} \cdot \Delta t}{R_{1} \cdot \Delta x^{2}} \\ \pi_{1} \leftarrow \frac{D_{el} \cdot \Delta t}{R_{1} \cdot \Delta x^{2}} \\ r_{1} \leftarrow \frac{D_{el} \cdot \Delta t}{R_{1} \cdot \Delta x^{2}} \\ r_{1} \leftarrow \frac{D_{el} \cdot \Delta t}{R_{1} \cdot \Delta x^{2}} \\ r_{2} \leftarrow \Delta x \cdot i \\ w \leftarrow f(2) \\ for \ i \in 0...n \\ t_{i} \leftarrow \Delta x \cdot i \\ w = p_{0,i} \leftarrow glp(t_{i}) - glp(t_{i-tau}) \quad if \ i > tau \\ w_{0,i} \leftarrow glp(t_{i}) - glp(t_{i-tau}) \quad if \ i > tau \\ w_{0,i} \leftarrow glp(t_{i}) - glp(t_{i-tau}) \quad if \ i > tau \\ w_{0,i} \leftarrow glp(t_{i}) - glp(t_{i-tau}) \quad if \ i > tau \\ w_{0,i} \leftarrow glp(t_{i}) - glp(t_{i-tau}) \quad if \ i > tau \\ w_{n,i} \leftarrow gl(t_{i}) \\ d_{i} \leftarrow 1 + \pi + \frac{k_{1}}{R_{1}} \Delta t \quad if \ i \le \frac{y}{\Delta z} \\ d_{i} \leftarrow 1 + \pi + \frac{k_{1}}{R_{1}DNT} \Delta t \quad if \ i > \frac{y}{\Delta z} \\ a_{i} \leftarrow -0.5 \cdot \pi \cdot if \ i \le \frac{y}{\Delta z} \\ b_{i} \leftarrow -(0.5 \cdot \pi) \quad if \ i \le \frac{y}{\Delta z} \\ b_{i} \leftarrow -(0.5 \cdot \pi) \quad if \ i \le \frac{y}{\Delta z} \\ b_{i} \leftarrow -(0.5 \cdot \pi) \quad if \ i > \frac{y}{\Delta z} \\ b_{i} \leftarrow -(0.5 \cdot \pi) \quad if \ i > \frac{y}{\Delta z} \\ b_{i} \leftarrow 0 - a_{i} \\ a_{n-2} \leftarrow 0 \\ B \leftarrow LU_{n} tator_{T} \quad (a, d, b) \\ bb \leftarrow B^{(0)} \\ dd \leftarrow B^{(1)} \\ for \ i \ e \ 0.5 \cdot \pi \cdot w_{0,j} + (0.5 \cdot \pi \cdot w_{0,j+1} + (1 - \pi) \cdot w_{1,j} + 0.5 \cdot \pi \cdot w_{2,j} - C_{TNT} \\ c_{i} \leftarrow (c \ 5 \cdot \pi_{1} \cdot w_{i,j} + (1 - \pi_{1}) \cdot w_{i+1,j} + 0.5 \cdot \pi_{1} \cdot w_{1,j} + 1 \\ c_{i} \leftarrow 0.5 \cdot \pi_{1} \cdot w_{i,j} + (1 - \pi_{1}) \cdot w_{i+1,j} + 0.5 \cdot \pi_{1} \cdot w_{n,j+1} \\ c_{i} \leftarrow 0.5 \cdot \pi_{1} \cdot w_{n,j} + (0 - \pi_{1}) \cdot w_{n-2,j} + (1 - \pi_{1}) \cdot w_{n-1,j} + 0.5 \cdot \pi_{1} \cdot w_{n,j+1} \\ z \leftarrow LU_{2} olve_{T} \quad (aa, d, bb, cc) \\ for \ i \ i \ 1...n - 1 \\ w_{i,j+1} \leftarrow z_{i-1} \\ w \end{aligned}$$

 $C_{\text{DNT}} \coloneqq C_{\text{implicit}CNDNT} \left(f, g1p, g1t, g2, a, T, n, m, D_{e1}, R_1, R_{1DNT}, k_1, y \right)$

CHAPTER 5

SUMMARY OF RESULTS AND RECOMENDATIONS FOR FUTURE WORK

The primary objective of this research was to explore processes governing storage and release of contaminant in low permeability layers. The goal of this effort was to support sound decisions for releases of chlorinated solvents and other potentially persistent contaminants. Three studies were undertaken including:

- Modeling the water quality impacts of retardation and seepage velocity in transmissive and low permeability layers in groundwater plumes (Chapter 2)
- Modeling the water quality impacts of retardation and first-order reaction in low permeability layers (Chapter 3)
- Modeling a numerical solution for a network of irreversible first order reactions in low permeability layers (Chapter 4)

The two-layer models presented in Chapters 2 and 3 were done in conjunction with Jack Martin, Dr. Azadeh Bolhari, Dr. Tom Sale, and Dr. David Dandy. Chapter 4 was wholly done by the author of this thesis with support from Dr. Sale. The following presents a summary of each chapter and suggestions for future work of each activity.

Chapter 2: Modeling the water quality impacts of retardation and seepage velocity in transmissive and low permeability layers in groundwater plumes

Objectives: There were several objectives for this activity. First, this chapter presented the second generation hybrid computational approach for the analytical model. Second, the model was applied to demonstrate sensitivity to retardation in the transmissive and low

permeability layers and groundwater seepage velocity in the transmissive layer. Finally, this chapter documented the evolution of a chlorinated solvent release through time.

Methods: This study addressed a two-layer system involving semi-infinite transmissive and low permeability layers using analytical solutions without degradation developed in Sale et al. (2008). The study addressed tetrachloroethene (PCE) contaminant mass present in transmissive and low permeability layers. All calculations were carried out using MatlabTM. The direct computational approach for the non-degradation solutions presented in Sale et al. (2008) are limited to plume lengths less than 100m in the transmissive layer (Bolhari, 2012) and less than 900m in the low permeability layer. To expand these solutions to larger domains, series approximations were used. However, since series approximations are inaccurate at small domains, a second generation hybrid approach was developed wherein series approximations were used for the portions of the domain where the direct computational approach presented in Sale et al. (2008) is inaccurate.

Results: The objective that chlorinated solvent releases can evolve through time was met through the sensitivity analyses. Over time, the nature of the problem changed from DNAPL in the transmissive layer to that of aqueous and sorbed contaminants in the transmissive and low permeability layers. Another contribution of this activity is an understanding of how contaminant mass and concentration in the transmissive and low permeability layers varies spatially with time. Observed contaminant distributions in the low permeability layer suggest that even at late stages much of the contaminant concentration in the transmissive and low permeability layers remain in close proximity to the DNAPL source. However, at late stages in the transmissive layer, much of the contaminant concentration has advected downgradient of the DNAPL source. Another major result of this work is a greater understanding of how seepage

velocity in the transmissive layer not only controls the plume extent, but also peak concentrations in both the transmissive and low permeability layers. Higher seepage velocity leads to lower concentrations throughout the plume domain despite more mass entering the plume. In contrast, the higher seepage velocity leads to a larger plume domain. This leads to the observation that while higher seepage velocity may have less environmental impact in some cases due to lower peak contaminant concentrations, remediation efforts may be limited due to plume extent. An additional result is retardation factors in the transmissive and low permeability layers control contaminant mass stored in the transmissive and low permeability layers at late time. Overall, retardation in the transmissive and low permeability layers appear to be important factors in understanding the nature of the problem posed by late stage chlorinated solvent releases.

Limitations: The conditions addressed in this model are highly idealized. The transmissive and low permeability layers are assumed to be homogeneous and isotropic. In addition, contaminant degradation is not considered. Furthermore, stepped source reduction was not considered; instead, the source assumed to be either active or completely removed. The model does not work for all variable combinations. Specifically, computational instability can be encountered due to the complexity of the functions that are employed.

Suggestions for future work: A similar study could consider a time variant source. In addition, a model that addresses a multiple layer scenario could be investigated.

Chapter 3: Modeling the water quality impacts of retardation and first-order reaction in low permeability layers

Objectives: There were three objectives for this activity. First, the second generation hybrid computational approach for the two-layer analytical solution with degradation was presented.

Second, the model was used to study the implications of retardation and reaction in the low permeability layer. Third, the model was employed to explore the evolution of a chlorinated solvent release through time as a function of retardation and degradation.

Methods: This study addressed a two-layer system involving semi-infinite transmissive and low permeability layers using analytical solutions with degradation developed in Sale et al. (2008). The study addressed tetrachloroethene (PCE) contaminant mass present in transmissive and low permeability layers. All calculations were carried out using MatlabTM. The direct computational approach for the degradation solutions presented in Sale et al. (2008) are limited to plume lengths less than 100m in the transmissive layer (Bolhari, 2012) and less than 900m in the low permeability layer. To overcome these challenges, a hybrid approach was developed wherein series approximations were used for the portions of the domain where the direct computational approach for the degradation equations presented in Sale et al. (2008) are inaccurate.

Results: Three key observations are developed from the sensitivity analyses. First, elevating the retardation in the low permeability layer limits the benefits of degradation. Less contaminant mass is present in the aqueous phase, where degradation is assumed to occur, when the retardation factor is elevated. For example, when the retardation factor in the low permeability layer is equal to 1 and the half-life of PCE in the low permeability layer is 3 years, 79% of the total mass was degraded by year 30. Whereas when the retardation factor in the low permeability layer was elevated to 15 for the same degradation rate, only 37% of the total mass was degraded by year 30. Second, even with modest degradation rates in the low permeability layer, a significant percentage of the contaminant mass can be degraded. In the scenario with the highest low permeability layer retardation (R'=15, k'= 0.023 yr⁻¹), 18% of the total mass was

degraded by year 30. Similarly, when the retardation factor in the low permeability layer is 1 and the half-life in the low permeability layer is 3 years, enough mass degrades to allow for the well concentration close to the source to fall below the MCL in the 30 year study period. Finally, even with degradation, water quality improvements associated with source removal diminish significantly with increasing downgradient distance from the source. For example, the concentrations at the more downgradient well locations remain above the MCL for PCE for longer periods of time than the concentration at locations closer to the source, even where there was no retardation in the low permeability layer and a 3 year half-life.

Limitations: The analytical model relies on simplifying assumptions. The transmissive and low permeability layers are assumed to be homogeneous and isotropic. In addition, any degradation reactions were assumed to be irreversible and may be described by first-order rate equations. Reaction was assumed to occur only in the aqueous phase. This is a standard assumption in many reactive contaminant transport models. Nevertheless, the validity of this assumption needs to be further explored. Furthermore, the source is either considered to be active or completely removed, so a step-off source was not studied. Moreover, reaction networks in the low permeability layer were not considered. The model does not work for all variable combinations. Specifically, computational instability can be encountered due to the complexity of the functions that are employed.

Suggestions for future work: A similar study could consider a time variant source. In addition, a model that addresses a multiple layer scenario could be investigated. Research is ongoing as to when the assumption that only aqueous phase constituents being available for reaction is appropriate.

Chapter 4: Modeling a numerical solution for a network of irreversible first order reactions in low permeability layers

Objectives: The objectives for this study were three fold. First, a one-dimensional analysis of diffusive transport in the low permeability layer that includes a network of first-order irreversible reactions (the reaction network model) was documented. Second, estimates of reaction rates in the low permeability layer were developed for energetic (2,4,6-TNT (2,4,6-trinitrotoluene) and 2,4-DNT (2,4-dinitrotoluene)) and chlorinated (PCE (tetrachloroethene), TCE (trichloroethene), cis-DCE (cis-dichloroethene), and VC (vinyl chloride)) compounds by fitting the model to field data. Finally, the model was applied to explore fluxes from the low permeability layer.

Methods: This study addresses a one-dimensional system involving a semi-infinite low permeability layer bounded by a source. The model computes simultaneous contaminant transport and first-order irreversible degradation as a function of depth and time while considering a degradation pathway. The model relies on finite difference methods, specifically the Crank-Nicolson Method (Crank and Nicolson, 1947) to calculate the concentration of each compound as a function of time and depth into the low permeability layer. All calculations were carried out using Mathcad 15TM. The model was fitted to field data using the effective diffusion coefficients, original source concentration, and degradation rates for each compound.

Results: Two key observations can be gleaned from the results and model applications. First, contaminant half-lives calculated in this paper fell within ranges found in literature for transmissive layers under anaerobic conditions. Due to model over parameterization and uncertainty in source history, these results could be inaccurate. Second, retardation factor

heterogeneity in the low permeability layer can have a significant impact on vertical concentration profiles as well as contaminant mass flux out of the low permeability layer. This indicates the importance of incorporating heterogeneity in retardation into models. However, additional laboratory/field data is needed to help validate the model results.

Limitations: The numerical model relies on simplifying assumptions. The degradation reactions were assumed to be irreversible and undergo first-order kinetics only in the aqueous phase. In addition, the source was considered to contain only the parent compound (i.e., reaction networks in the transmissive layer were not considered). Furthermore, a gradually declining source was not considered. Therefore, the model may not be applicable to more complex situations. Moreover, the half-lives calculated for each field site may not be unique since more than one set of input parameters could be used to match the concentration profiles.

Suggestions for future work: The model should be compared to additional field and/or laboratory data. In addition, parallel degradation pathways (e.g., biotic and abiotic pathways) should be investigated with respect to this model. To better represent field conditions, more complex sources (e.g., exponentially decaying source or a source consisting of a parent compound and decay product(s)) should be considered.

References

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