NAPL (Non Aqueous Phase Liquid) Source Characterization Based on Dissolved Contaminant Concentrations

by

Freddi-Jo Eisenberg

Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of

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Abstract

Subsurface contamination frequently originates from spatially distributed sources of Non-Aqueous Phase Liquids (NAPLs). Such chemicals are typically persistent sources of groundwater contamination that are difficult to characterize. This work addresses the feasibility of using dissolved concentration measurements to estimate the spatial distribution of an immobile (or residual) NAPL mixture in a saturated field-scale system.

We first developed a state estimation algorithm for a one-dimensional point source problem. (Bennett 1992, McLaughlin 1995). The spatially and temporally varying states (i.e., the dissolved contaminant concentrations and the NAPL saturations) were estimated by taking advantage of the time-dependence of solute concentrations originating from competitive dissolution of a NAPL mixture. We applied the estimator to a point source problem using sixteen measurement strategies with dissolved concentration measurements placed at different points in space and time. The estimation results assessed the uncertainty reduction associated with each strategy, highlighting the importance of capturing a characteristic scale of the problem with the sampling design. The characteristic scale for a given problem is either a temporal or spatial spread of measurements large enough to capture the temporal change in the NAPL source. At least for the sample problem, sampling strategies that utilized multiple measurements at the same location were as effective as those that sampled over a wider spatial domain.

In the second part of this research we developed a two-dimensional coupled flow/dissolution/transport model for a spatially distributed residual NAPL source. We modeled the distributed NAPL as a first order gradient driven source term of the dissolved phase transport equation. Since this model was specifically designed to describe a residual NAPL source, it is a useful tool for analyzing the sensitivity of dissolved measurements under various source regimes.

Based on the results of the one-dimensional estimator as well as the analyses we performed with the two-dimensional model, we concluded that dissolved concentration measurements are sufficiently sensitive to NAPL source composition and location to make source estimation feasible. However, this analysis assumed that both the prior statistics of the NAPL saturation and the field scale mass transfer coefficient for NAPL dissolution were known, an unlikely assumption in practical/applied estimation.

Thesis Supervisor: Dennis B. McLaughlin
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Chapter 1

Introduction

In the beginning, the idea behind this project was the creation of a methodology for 'mapping' NAPL contamination; determining the location and strength of a distributed source with an eye to aiding remediation. The work that followed has developed into this thesis—an examination of the relationship between a NAPL source and the resulting dissolved phase contamination. It provides a sound basis for further NAPL source modeling and estimation work as well as insights into these processes.

Non-aqueous phase liquids (NAPLs) are a class of environmental contaminants that exist as a separate phase in the subsurface due to their low solubility in water. Pools or even pore scale droplets of NAPL in the subsurface behave as long-term sources of dissolved contamination to groundwater. These chemicals are among the most common groundwater contaminants in North America as a result of decades of production, use, and subsequent release into the environment (Cohen and Mercer 1993). Furthermore, NAPL contaminants are frequently considered toxic at dissolved concentrations far lower than their aqueous solubility (Pankow and Cherry 1996). Our current understanding of NAPL behavior in the subsurface relies primarily on complex multiphase physical models that are most easily applied at the pore scale and in glass-bead laboratory experiments. The heterogeneities encountered in the field combined with difficulties in directly observing NAPLs in the field make accurate determination of NAPL location very difficult (Bedient 1994). Ambiguities in the NAPL source location complicate remediation efforts. To effectively remove, treat, or contain the source of subsurface contamination, spatial characterization of NAPL distributions is essential.
NAPLs are usually divided into two categories: D(dense)NAPLs and L(light)NAPLs. The density or lightness of the NAPL is evaluated relative to water. This distinction is made because of the difference in their behavior in the subsurface. LNAPLs tend to “float” on the water table and thus exist primarily in the unsaturated zone while DNAPLs sink to the bottom of the aquifer and thus exist primarily in the saturated zone. LNAPLs are usually petroleum products or by-products. Typical LNAPL chemical constituents are benzene, toluene, ethyl benzene, and xylenes.

The primary types of DNAPLs found in the environment are halogenated solvents, coal tar and creosote, PCB oils, and complex DNAPL mixtures. Of these, the most widespread contamination is associated with halogenated solvents (Cohen and Mercer 1993), especially chlorinated solvents. These chemicals, most notably trichloroethene, trichloroethane, and carbon tetrachloride are used in chemical production, degreasing, dry cleaning, and many other manufacturing processes. In 1990, twenty-nine billion pounds of chlorinated solvents were produced in the United States (U.S. International Trade Commission 1991). It is estimated that these DNAPL constituents contaminate literally thousands of sites in the US (NRC 1990).

Other types of DNAPLs are also important sources of contamination in some areas. Coal tar is a byproduct of coal gassification and steel industry coking operations. In 1990, 158 million gallons of crude coal tar were produced in the United States (U.S. International Trade Commission 1991). Creosotes, made up of coal tar distillates, are primarily used in wood treating operations. Although current use of creosotes in wood preserving is decreasing, in the first half of this century creosote was the only available preservative. Because waste management practices at the time involved direct release into the environment, most wood-treating sites have DNAPL contamination (Cohen and Mercer 1993). Although PCB use is now severely restricted, in the past PCBs were commonly used in transformer oil production. Of the 1.25 billion pounds of PCBs produced from 1929 to 1977, 440 million pounds were either placed in land disposal sites or directly released to the environment (Lavigne 1990). Of the top 20 contaminants detected in any medium at hazardous waste sites, 10 are considered DNAPL constituents (U.S. Environmental Protection Agency 1991). These statistics help to illustrate the significance of DNAPLs as environmental contaminants in the United States.

Compounding the detrimental effect of widespread NAPL contamination are the low toxicity levels associated with most NAPL constituents. Many NAPL chemicals are considered harmful to humans at part per billion levels. Thus small amounts of NAPL phase contamination may result
in large amounts of dissolved contamination. For example, the aqueous solubility of pure phase trichloroethene (TCE) is 1100 mg/L. To produce a dissolved phase contaminant plume of TCE of 25 thousand cubic meters at 0.01 mg/L requires only 5.3 liters of TCE (Cohen and Mercer 1993). Note that this is still twice the Maximum Contaminant Level (MCL) set for TCE by the USEPA. Actual plumes tend to be much bigger than this. For example, at the Massachusetts Military Reservation on Cape Cod, a plume of TCE and trichloroethane (TCA) from the sewage treatment area comprises 40 million cubic meters of groundwater. The estimated volume of NAPL that contributed to this contamination was only 1.5 cubic meters, or approximately seven 55-gallon drums (Mackay and Cherry 1989). In general, the MCLs for NAPL chemicals are very low, making even very small amounts of NAPL cause for concern.

This research addresses NAPL characterization by focusing on a subset of the problem: The case of a NAPL present as part of a chemical mixture in the saturated zone at residual saturation. Residual saturation is defined as the pore volume fraction of NAPL that is held in place by capillary forces (i.e., it is not flowing). The pore volume fraction of NAPL, the NAPL saturation, is defined as:

\[ S_n = \frac{V_n}{V_p} \]  

(1.1)

\( S_n \) is the NAPL saturation, \( V_n \) is the volume occupied by the NAPL in a control volume of the porous medium, and \( V_p \) is the volume of the pore spaces in the control volume. Thus \( S_n \) is a dimensionless measure that ranges from 0 (no NAPL present) to 1 (pores completely filled with NAPL). Residual saturation usually ranges from less than 0.1 to 0.5 (Mercer and Cohen 1990). The value of residual saturation depends on a number of factors descriptive of both the subsurface media and the chemical properties of the NAPL: 1) pore size distribution, 2) wettability of the NAPL, 3) viscosity of NAPL, 4) interfacial tension, 5) density of the NAPL, and 6) groundwater flow gradients. A NAPL contaminant (e.g., from a spill or leaky tank) will percolate through the subsurface leaving behind residual volumes in the pore spaces. The contaminant will flow preferentially through higher conductivity areas in a heterogeneous medium, resulting in heterogeneous distribution of NAPL saturation.
NAPL constituents are distributed throughout the subsurface not only via movement of the NAPL itself, but also through mass exchange among different phases. A NAPL source in the unsaturated zone potentially exchanges mass among four phases: the aqueous or dissolved phase, the vapor phase, the solid phase, and the NAPL phase. The physical processes affecting NAPL distribution in the unsaturated zone are further complicated by the movement of the water table. In the saturated zone, the problem is simplified because the vapor phase may be neglected, as in this research. NAPL constituents found in the saturated zone may include free-flowing and residual DNAPLs as well as LNAPLs held at residual. From a modeling perspective, characterization of a NAPL source in the saturated zone is generally an easier problem to address.

Characterization of NAPL in the field is difficult and expensive under the best circumstances and nearly impossible under the worst. Even measuring the presence of NAPL in a sample is not simple, requiring careful sample preservation and analytic methods (Feenstra et al. 1991). One of the complications is differentiating between contaminant that is sorbed to soil and contaminant that exists in the NAPL phase. In some cases direct observation of NAPL may be possible in monitoring wells; for example, coal tar may be easily identifiable as black gooey blobs in a sample of contaminated water or soil. However, sinking a monitoring well directly over a NAPL blob requires quite a bit of luck, and many NAPL constituents (e.g., solvents) are not visually noticeable in any case. Most characterization of NAPL contamination must rely on other types of measurements, for example dissolved concentrations or concentrations on soils (Feenstra et al. 1991). Even in this case, it is not clear what dissolved concentration levels are required to indicate the presence of NAPLs. Often very low aqueous concentrations of constituents are detected at known DNAPL sites. A general rule of thumb is to suspect NAPL contamination when constituents are present at one percent of aqueous solubility (U.S. Environmental Protection Agency 1992).

Compounding the difficulties of source characterization, field measurements of dissolved concentrations and head are sparse in practice—perhaps on the order of 50 to 100 measurements for a given site. Extensive sampling campaigns, such as the USGS Cape Cod tracer test (100,000 concentration measurements and 1,400 head measurements), are rare, primarily because they are costly and time consuming (LeBlanc 1991, Hess 1992). Taken alone, field measurements provide an incomplete picture of dissolved contamination and an ambiguous characterization of potential NAPL sources.

The above factors all motivate this research toward characterization of spatially distributed residual
NAPL saturation. Since dissolved contaminant concentrations are sensitive to the NAPL source properties, it seems reasonable to expect that measurements of dissolved concentrations could be used to infer something about source properties (e.g., strength, location). In a model of a NAPL source problem, one might imagine that the inputs are the initial conditions (i.e., the NAPL saturations, a given source geometry, porous media parameters) and the outputs are the resulting dissolved concentrations and NAPL source saturations at later times. In this research we address the reversal of this procedure: using the outputs to determine what the inputs might have been. This process is a type of inverse estimation and is found in various forms in nearly every scientific field. The choice of inverse method is extremely problem specific and furthermore, it is not clear without further investigation that a particular problem is solvable at all by inverse methods. Some on the many difficulties of inverse estimation are generally categorized as 1) a solution must exist, 2) the solution must be unique, and 3) the outputs must be sensitive to the inputs (but not too sensitive). If these conditions are not met the problem will be ill-posed and inversion will not be possible. As the processes considered become increasingly nonlinear, the danger that these conditions are not met also increases.

This goal of this research was to investigate to what extent inversion can be used to characterize a NAPL source. Our approach is to use physical models of subsurface processes to interpret relevant field measurements, potentially including measurements of dissolved and sorbed contaminant concentrations, hydraulic conductivity, and piezometric head.

Figure 1.1 presents the general idea behind the distributed NAPL source characterization problem. The two darker blobs on the left-hand side of the picture are NAPL phase sources (at residual saturation or less) composed of three contaminants (i.e., red, blue, and green). Both the total amount and chemical composition of residual NAPL vary spatially. The variability in NAPL composition affects the contaminant dissolution rate. In general, the contaminant present as the largest fraction of NAPL mass will dissolve at the fastest rate, relative to its pure phase solubility. The clouds emanating from the NAPL sources in Figure 1.1 are dissolved phase plumes. At a given measurement location (the well in the figure), the dissolved concentration of each constituent will change over time as the source composition changes. Thus the time history of concentration measurements from the well contains information about the contaminant mass present in the source. These measurements are related to the NAPL source by the physical processes transport and transformations in the subsurface.
The remainder of this thesis describes the development of a model and estimation method to address the distribution of residual NAPL sources. Chapter 2 provides a background to our creation of a NAPL system model, while Chapter 3 provides the basis of our estimation approach. Chapter 4 describes the formulation of a one-dimensional NAPL point source model and estimator. This problem was designed to assess the feasibility of characterizing a NAPL source from solute measurements before attempting a more complicated multi-dimensional problem. It also provides some useful insights on the design of NAPL monitoring systems. Chapter 5 presents the results of the one-dimensional analysis and evaluates the success of the estimation algorithm. We briefly present the conceptual design of the multi-dimensional model in Chapter 6, and Chapter 7 develops the model equations in detail. Finally, Chapter 8 presents some interesting results from the model and discusses a number of important issues involving the NAPL estimation problem.
Chapter 2

Modeling the Residual NAPL Problem

Up until the last decade, most investigation of immiscible fluids in the subsurface was conducted from the perspective of petroleum exploration and extraction. In fact, the term NAPL was coined in 1981 (Pankow and Cherry 1996). The first experimental research on non-dissolved phase liquids as contamination in the subsurface is usually attributed to Schwille (1988) who conducted laboratory experiments to observe how DNAPLs flow into porous media beginning in 1975. Much of the current hydrologic study of NAPLs concerns the small-scale behavior of immiscible fluids in water or models of multiphase flow (Abriola and Pinder 1985, Pinder and Abriola 1986, Faust et al. 1989, El-Kadi 1992). In this section, we focus on NAPL research concerning the distribution and fate of residual NAPL in the saturated zone. Special attention is paid to modeling residual NAPL dissolution (Sleep and Sykes 1993, Powers et al. 1994, Mayer and Miller 1996). Little if any of the current literature addresses the problem of systematically characterizing NAPL sources from measurements of dissolved concentrations. The goal of this section is to provide the framework for the development of our NAPL models, presented in Chapters 4 and 6.
2.1 Physical Processes of Residual NAPLs

Residual NAPL mass may undergo three phase exchanges in the subsurface: dissolution (NAPL phase to dissolved phase), sorption (NAPL phase to solid/soil phase), and volatilization (NAPL phase to air phase) plus potentially the reverse of each process. Figure 2.1 is a conceptual representation of these processes at a pore scale. This research will only address dissolution and sorption, those processes likely to occur in the saturated zone.

Many researchers have explored sorption mechanisms and rates for organic chemical sorption onto subsurface media (soils). When the organic content of the soil is high enough, sorption onto the organic matter present on soil particles is usually the dominant sorption mechanism (Schwarzenback et al. 1993). Thus sorption is often assumed directly related to the organic content of the soil (fo m).
Most researchers present sorption as either an equilibrium or a first order kinetic process. If the time scales of sorption are much smaller than the time scales of transport, an equilibrium sorption model is reasonable. A simple linear relationship between the dissolved contaminant concentration and the sorbed concentration is:

\[ c_{s,j} = K_{d,j} c_{a,j} \]  \hspace{2cm} (2.1)

Where \( c_{a,j} \) is the concentration of the chemical \( j \) in water, \( c_{s,j} \) is the sorbed concentration of \( j \), and \( K_{d,j} \) is the partitioning coefficient (see Appendix A for definitions of mathematical symbols). The partitioning coefficient varies based on the hydrophobicity of a given chemical. In groundwater transport of contaminants, sorption is usually incorporated into the transport equation as a retardation factor on contaminant movement.

Dissolution may also be represented as an equilibrium process, in this case between the aqueous and NAPL phases. In the case of a single component NAPL, the dissolved phase concentration is given by the pure phase saturated solubility of the chemical. Solubilities may be determined experimentally or estimated based on the structure of the chemical (Schwarzenback et al. 1993). For most chemicals of interest, solubility values may be found in the literature. DNAPL constituents generally vary in solubility from \( 10^4 \) to \( 10^{-2} \) mg of chemical/liter of water (Cohen and Mercer 1993), although some constituents may exhibit solubilities as low as \( 10^{-5} \) mg/L. Solubility may be affected by temperature, salinity, and the presence of cosolvents. In a NAPL mixture (i.e., more than one chemical present), the equilibrium dissolved concentration is called the effective solubility. NAPLs from a mixture dissolve competitively based on their pure phase aqueous solubilities, their activity coefficient in the NAPL mixture, and their mole fraction in the NAPL mixture. This relationship is generally based on Raoult's Law:
\[ c_j^{\text{eff}} = \left\{ \frac{m_j}{\sum_{j=1}^{N_j} m_j} \right\} \gamma_j c_j^{\text{sat}} \]  

where \( m_{o,j} \) is the moles of chemical \( j \) in the NAPL mixture, \( c_j^{\text{sat}} \) is the pure phase solubility of chemical \( j \) in water, \( c_j^{\text{eff}} \) is the effective solubility, and \( \gamma_j \) is the activity coefficient of \( j \) in the mixture. If the chemical components of a NAPL mixture are structurally similar, the activity coefficient is near unity (Banerjee 1984). Since the effective solubility of NAPL mixture components is related to their mole fraction in the mixture, the effective solubility of a chemical will change over time as mass is dissolved and the mole fraction in the NAPL mixture changes. Generally, the mixture left behind becomes increasingly less soluble (Mercer and Cohen 1990).

### 2.2 Dissolution

Early models of NAPL exchange with the aqueous phase tended to assume equilibrium dissolution. In lab column experiments, NAPL is seen at aqueous solubility for flow velocities of 10-100 cm/day (Anderson et al. 1992). However, concentrations equal to effective solubilities are rarely found in the field, even when NAPLs are known to be present (Pankow and Cherry 1996). Mackay and Cherry (1985) suggests that field concentrations are generally found at less than 10 percent of effective solubility. This discrepancy may be caused by heterogeneity in the NAPL distribution (leading to dilution), heterogeneity in the porous medium, mixing of stratified water in sampling wells, and/or mass transfer limitations that make dissolution appear to be a non-equilibrium process (Feenstra and Cherry 1988, Powers et al. 1991). Brusseau (1991) concluded that the equilibrium assumption is appropriate for subsurface pore velocities of less than 0.2 cm/hour, but that a non-equilibrium model is more appropriate for velocities greater than 1 cm/hour. The results of Burr et al. (1994) indicated that on a field scale, the selection of an equilibrium (versus non-equilibrium) sorption model is not significant in the face of aquifer heterogeneity. Some research suggests rate limited or non-equilibrium dissolution is an appropriate model when NAPL is present in large pools, at low saturation values, and at high groundwater flow velocities (Powers et al. 1992). Research by Imhoff
et al. (1993) concludes that the narrow width of dissolusion fronts observed in the laboratory suggests that the equilibrium relationship is achieved over small spatial scales (although this is affected by heterogeneity of the medium).

Non-equilibrium models of NAPL dissolution feature macro (i.e., larger than pore scale/nanometer scale) mass transfer rate coefficients that may be developed in various ways. A number of studies of residual NAPL dissolution indicate that dissolution rates may be estimated as a function of interfacial area and the Darcy flux of the groundwater (Miller et al. 1990, Parker 1991, Powers et al. 1992). In other studies, the transfer rate coefficients are functions of the NAPL saturation itself (Miller et al. 1998). Thus as the amount of NAPL decreases, dissolution slows. This tailing process is often seen in the field and is partially responsible for longevity of NAPL sources. In all cases, the rate coefficients are fit to empirical (usually column) data. Thus they apply over small scales of homogeneous media.

2.3 Identification of Residual NAPL

Residual DNAPL is difficult to measure and characterize in the subsurface. The presence of NAPL at a field site may be assessed by inspection if the volume content in the medium is sufficiently high (e.g., streaking is visible or free product is found in wells). However, residual NAPL in soil is usually well below this level. If a soil sample is taken within a NAPL zone, the NAPL saturation may be estimated in the laboratory (Feenstra et al. 1991). The total amount of contaminant is measured (i.e., sorbed and NAPL phase). Then the amount of NAPL phase present is back-calculated by estimating the maximum amount expected to be sorbed onto soil and comparing this value with the measured value. While this method may provide an assessment of the presence of residual NAPL, 1) it depends upon accurate estimation of sorption coefficients, and 2) it depends on having a soil sample from a NAPL zone. Since DNAPLs are generally deep in the subsurface, it is difficult (and uncommon) to have such samples.

It is also difficult to predict NAPL saturation based on porous media characteristics. Wilson et al. (1990) found that residual saturation cannot be predicted from soil texture because heterogeneity within the media and minor difference in texture (e.g., lenses) make a large difference in saturation. Further, residual saturation values in heterogeneous media tend to be larger than in homogeneous
media. Powers et al. (1992) found that graded sand held more NAPL in residual than uniform sand with the same mean grain size.

A limited number of experimental releases of NAPL have provided some insight into the distribution of residual NAPL in the subsurface. Kueper et al. (1993) studied the spatial distribution of residual NAPL after a release of PCE in the Border aquifer. They found residual NAPL saturation ranging from one to thirty-eight percent of available pore space. Spatial variability was very dependent upon soil grain size and the maximum nonwetting saturation along the drainage path (i.e., where continuous mobile NAPL was present). Their results also show that the ultimate distribution of residual NAPL is dependent on the rate of release of NAPL at the surface. Even for a homogeneous medium, $S_n$ should be expected to vary significantly. These results are similar to the range of reported values for NAPL retention of one to fifty percent (for widely varying media) by Mercer and Cohen (1990). Therefore, even a general knowledge of the initial NAPL source is insufficient to characterize the resulting residual distribution. This very difficulty is the motivation behind the research presented in this thesis.
Chapter 3

Estimation Methodology

The task of using models to characterize sources from field measurements may be viewed as a state estimation problem (McLaughlin 1995). Similar problems are examined in many fields, including medicine, astronomy, geophysics, economics, oceanography (Bennett 1992), and meteorology (Daley 1991). There is an extensive literature found in such journals as Inverse Problems. The relevance of any given estimation technique to a particular problem depends greatly on 1) the physical/chemical processes at work, 2) the nature of the sources, 3) the type and quantity of measurements available, and 4) the sensitivity of the measurements to the source. For present purposes, we focus on state estimation techniques developed for subsurface flow and transport applications. The use of inverse/state estimation methods for subsurface characterization has been reviewed by a number of authors (Yeh 1986, Kueper 1986, Carrera 1987, Ginn and Cushman 1990, Sun 1994, McLaughlin and Townley 1996). In particular, Zimmerman et al. (1998) recently compared the effectiveness of seven different inverse methods at solving the same test problems. It is not within the scope of this section to describe all inverse/state estimation methods. Instead it provides a context for our current research. Neuman (1973) describes two general categories of inverse methods: direct methods and indirect methods. The indirect methods systematically fit the output values of a model to observed values. The goal is to minimize the residual between the observed values and model predictions by adjusting parameters in the forward model. Direct methods, by contrast, assume that states (the results of the forward model) are known at all locations on the model grid. Then the solution of parameters may be posed as a linear problem. In groundwater problems,
however, states are only known at a few locations, if at all. Thus most researchers focus on indirect methods. Indirect methods are inherently non-linear and suffer problems of instability and non-uniqueness. Generally, regularization terms are added to the minimization to direct the estimation method toward the general vicinity of the solution.

In their review paper on inverse methods, McLaughlin and Townley (1996) characterize inverse methods by four criteria: 1) the way spatial variability is described, 2) the forward equation used to relate measurements to parameters, 3) the performance criterion chosen, and 4) the solution technique used. They show how a number of inverse algorithms can be described in a maximum a posteriori framework. These include linear methods (Hoeksema and Kitanidis 1984, Dagan 1985, Sun and Yeh 1992) and non-linear methods (e.g., maximum a posteriori methods, non-linear least squares, maximum likelihood methods, pilot point methods, and extended Kalman filtering).

Following the form of McLaughlin (1995), the state estimation problem consists of a set of model state equations, measurement equations, and a performance index to be minimized. The environmental variables used to characterize dissolution, groundwater flow, and contaminant transport in the vicinity of a NAPL source are called state variables. The temporal and spatial evolution of these variables is described by a set of partial differential equations called state equations. These equations are typically based on conservation laws and associated constitutive relationships that describe the physical system of our problem. The spatially distributed state equations of interest here are differential equations of the general form:

\[
\begin{align*}
\frac{\partial y}{\partial t} &= A(y, \alpha, u) + g(y, \alpha, u, \nu) \\
y(x, t) &= I(\alpha) \\
B(y, \alpha) &= 0
\end{align*}
\] (3.1)

In this equation \(y(x, t)\) is a vector of states, \(\alpha(x)\) is a vector of time-invariant parameters, \(u(x, t)\) is a vector of forcing functions, and \(\nu(x, t)\) is a vector of unknown model errors. The model errors are assumed to be zero in deterministic modeling applications but may be treated as random functions in stochastic modeling applications. \(A\) is a (usually) non-linear spatial operator that describes the relationships among the variables. \(g\) is the model error operator which is dependent
on $\nu(x,t)$, an uncorrelated random function. The operators $I$ and $B$ are the initial and boundary conditions, respectively, for the state equation. In this investigation, the states $(y)$ are NAPL residual saturations and solute concentrations. The parameters $(\alpha)$ include groundwater flow velocities, mass transfer coefficients, and initial conditions for the states. The state equations are the set of equations for dissolved phase contaminant transport, competitive dissolution, and sorption as well as physical constraints on some variables. The initial and boundary condition operators are specified concentration conditions.

The state equations may also be expressed in terms of the direct solution for the states as:

$$y = \mathcal{F}(\alpha, \nu) \quad (3.2)$$

$\mathcal{F}$ is the forward model (usually without $\nu$) of classical inverse theory. For nonlinear state equations, there is usually no explicit solution. The state equations must generally be solved numerically, after discretizing all states and parameters over a computational grid covering the region of interest. The resulting spatially discretized solution is a vector $y(\alpha, t)$ of states defined at the $N_y$ nodes of the computational grid, where $\alpha$ is now interpreted as a spatially discretized parameter vector. For convenience we assume that the parameters and states are discretized over the same computational grid.

The measurement equation relates field measurements to the states, the parameters, and a measurement error term at discrete times and locations $(p)$:

$$z^p = \mathcal{M}^p(y, \alpha) + \omega^p \quad (3.3)$$

$$z^p = \mathcal{M}^p[\mathcal{F}(\alpha, \nu), \alpha] + \omega^p$$

$$p = 1, 2, \ldots N_z$$
where $\mathcal{M}\hat{y}$ is a measurement operator which describes how the measurement $z^p$ is related to the states and parameters and $\omega^p$ is an additive random measurement error. Equation (3.4) provides a relationship between measurements and the forward model sources of variability and uncertainty which are the quantities to be estimated in the inverse problem. The value $\mathcal{M}\hat{y}(y, \alpha)$ is the model's prediction of the measurement $z^p$ obtained at location $x^p$ and time $t^p$. The measurement operator may be as simple as a linear function of the states (additive error) or something much more complicated. In this investigation the measurement equation relates field measurements of dissolved concentrations to the true values.

In our approach to inverse estimation uncertain variables $\alpha$, $\nu$, and $\omega$ in equations 3.1 through 3.4 are presumed to be random fields with specified prior statistics (mean and covariance). The goal of the estimation procedure is to find the values of these variables that give the best fit to available measurements, while satisfying the dynamical constraints imposed by the state equations.

The overall quality of a given set of estimates and states is measured by the following discrete generalized least-squares performance index:

$$
J(\hat{\alpha}, \hat{y}, \nu) = \frac{1}{2} [z - \mathcal{M}(\hat{\alpha}, \hat{y})]^T C^{-1}_\omega [z - \mathcal{M}(\hat{\alpha}, \hat{y})] + \frac{1}{2} \hat{\alpha}^T \hat{\alpha}_\alpha^{-1} [\hat{\alpha} - \bar{\alpha}] + \frac{1}{2} \nu^T C^{-1}_\nu \nu
$$

(3.5)

The first term of this performance index is a standard weighted least-squares measure of the difference between all $N_z$ measurements ($z$) and the vector $\mathcal{M}(\hat{\alpha}, \hat{y})$ composed of the corresponding $N_z$ discretized model predictions. The weighting factor is the measurement error covariance matrix ($C_\omega$). The second term forces the estimates to stay close to specified prior parameter values. This term is weighted by the prior parameter covariance ($C_\alpha$). The third term measures the magnitude of the model error ($\nu$), weighted by the model error covariance ($C_\nu$). The hats ($\hat{\cdot}$) over the states and parameters indicate that these are estimates of the true values. These are called least-squares estimates because they minimize the generalized performance index of Equation (3.5). The least-squares estimation approach described here is discussed in more detail in 28.)
It is important to note that the model error and prior terms of the performance index regularize the estimation problem by making it less sensitive to anomalous measurements. Least-squares optimization problems usually have more than one local solution, making minimization of the performance index numerically difficult. By restricting the domain of the minimization algorithm, regularization alleviates some of the ill-posedness inherent to non-linear least-squares estimation (Sun 1994). Regularization is frequently required to obtain stable, physically reasonable estimates from real field data (McLaughlin and Townley 1996).

Reid and McLaughlin (1994) use a generalized least-squares approach to estimate a spatially distributed log transmissivity function from measurements of piezometric head. They approximate the transmissivity function by a discrete expansion in a series of basis functions called representers. The representers are related to the cross covariances between measurements and log transmissivities. The representer approximation yields a spatially discretized performance index similar to the one presented here. The discrete performance index is minimized with a Gauss-Newton algorithm. This approach produced significant uncertainty reduction when applied to a simple synthetic problem.

Reid (1996) expanded on her previous work by estimating three-dimensional hydraulic conductivity as well as head, and concentration using measurements of all three variables. She again parameterized the hydraulic conductivity field with representer expansions. The algorithm was successfully applied to data from a field site to test the effectiveness of the approach. Half of the measurements from the site were used in the algorithm, and the other half were withheld to test the accuracy of the estimator’s prediction.

The work of Sun (1997) furthered the above research by developing an estimation algorithm that includes sorption of the chemical contaminant onto soil. His technique estimates hydraulic conductivity, dissolved concentration, piezometric head, and chemical/soil partitioning coefficient fields. The predictions are conditioned on measurements of head, hydraulic conductivity, dissolved concentration, and fraction of organic matter in soil. Sun’s method follows Reid’s in its basis function expansion within an iterative Gauss-Newton estimator. However, Sun advances the sophistication of the approach by using an adjoint state approach to calculated the sensitivity coefficients and cross-covariances. Like Reid, Sun applies his method to a field site by using half of the measurements to condition the algorithm and the other half to test the accuracy of the estimation.
Valstar (2000) takes a similar approach to Reid and Sun. He developed an algorithm to estimate piezometric head and dissolved concentration fields from measurements of both states. He uses a variational approach to state estimation, similar to the approach used here. However, his problem assumes a conservative contaminant source with a known initial condition and an unsteady flow field. Valstar also includes model error in his performance index to account for uncertain forcing in the groundwater flow equation. He solves his estimation equations using representers for all states and parameters and adjoint variables.

As far as we are aware, very few attempts have been made to characterize NAPL contamination using inverse/state estimation methods. Jin et al. (1995) used a non-linear least squares technique to estimate residual NAPL saturations in a partitioning tracer column experiment. They estimated the average residual saturation over the entire column by fitting predictions and observed measurements. Wilson and Mackay (1995) conducted a similar study, again with partitioning tracers in a column experiment.

James et al. (1997) developed a method to estimate residual NAPL distribution using partitioning tracer data. The method is based on a stochastic derivation of covariances and cross-covariances among tracer temporal moments, residual NAPL saturation, pore water velocity, and hydraulic conductivity fields. They perform both an unconditional and a conditional analysis. The conditional analysis incorporates measurements with a Bayesian estimator technique. This algorithm was tested on a three-dimensional synthetic data set (a 5 x 4 x 2 meter domain) modeled after the partitioning tracer test conducted at Hill Air Force Base (Annable 1998). Using temporal moments (zeroth and first moments) for 72 simulated breakthrough curves, they created both a spatial prediction of residual NAPL and an estimate of the uncertainty of the prediction. Overall, the method reduced uncertainty in the estimated NAPL distribution by 25 percent. This method is similar, at least in its overall objective, to the research described in this report. However, it requires data from a partitioning tracer test, which are not available at most field sites. Nonetheless, the results of James et al. (1997) are a useful comparison to the results of our approach.

Most recently, Sidauruk et al. (1998) applied an inverse technique to determine the initial location, as a point, and the initial time of a contamination source in a two-dimensional porous medium. This work produced interesting inversion results, and is the closest research to what we have done in this thesis, however the sources they employed do not describe NAPL dissolution. Rather
they are of two types, either an instantaneous or continuous source term. The characteristics of competitive dissolution, or even time varying dissolution from a single component source, as well as the distributed nature of a NAPL source, were not included.
Chapter 4

One-Dimensional Problem

Formulation

The first part of this research was concerned with the feasibility of estimating NAPL source locations and compositions from dissolved-phase measurements. The feasibility question is important since the processes involved are non-linear and the sensitivity of the estimation to the measurements is unknown. Estimation of residual saturation from dissolved concentration measurements can succeed only if $S_n$ is sufficiently sensitive to the measurements. Otherwise the estimation problem will be ill-posed (i.e., the solution may be non-unique or very sensitive to small measurement errors). The success of the estimation is also affected by the degree of non-linearity of the forward model.

Our estimation method is based on a series of local linearizations of the forward model in the neighborhood of the current parameter estimates. If the forward model is very non-linear, even a local linearization may produce a poor parameter estimate.

In order to examine the feasibility of our estimation objective we constructed a one-dimensional problem. This one-dimensional problem is also useful for exploring the relative effectiveness of varying sampling strategies. While a multi-dimensional or distributed source problem would be too computationally expensive to run for multiple scenarios, the one-dimensional problem is very amenable to exploratory analysis.

In our 1-D formulation, the residual NAPL mixture is considered to be a point source of dissolved
phase contamination at an uncertain location. We treat the source as a time-varying concentration boundary condition for a groundwater transport model. The source concentrations are calculated from the dissolution of a NAPL mass. The unknown parameters are the initial masses of each constituent, or chemical, in the NAPL mixture and the location of the source. Measurements of dissolved concentration are used to estimate these parameters. The remainder of this section describes the mathematical formulation of the state equations, the measurement equation, and the estimation algorithm as well as the simulated problem, which represents the 'true' set of states estimated in the next Chapter.

4.1 State Equations

The state equations for this one-dimensional problem describe the movement and transfer of contaminant mass among the dissolved, sorbed, and NAPL phases. These equations may be written in terms of the notation introduced in Chapter 3:

\[
\frac{\partial c_{a,j}(x,t)}{\partial t} = A_c(c_{a,j}, s_j, m_j, x_s)
\]

\[
\frac{\partial m_j(x,t)}{\partial t} = A_m(c_{a,j}, s_j, m_j, x_s)
\]

\[
\frac{\partial s_j(x,t)}{\partial t} = A_s(c_{a,j}, s_j, m_j, x_s)
\]

The three states are the dissolved concentration \(c_{a,j}\), the NAPL phase concentration in moles \(m_j\), and the sorbed phase chemical concentration \(s_j\). These states are related to each other through the operators \(A_c\), \(A_m\), and \(A_s\) which are dependent upon all of the states as well as the source location, \(x_s\). Note that the model error is assumed to be zero in this one-dimensional example.

The dissolved phase portion of the model is described by the standard one-dimensional advection/dispersion equation including linear sorption (Bear 1979):
\[
\frac{\partial c_{a,j}(x, t)}{\partial t} = -v_a \frac{\partial c_{a,j}(x, t)}{\partial x} + D_{a,j} \frac{\partial^2 c_{a,j}(x, t)}{\partial x^2} - \frac{1}{n_e S_a} \frac{\partial s_j}{\partial t} = A_c(c_{a,j}, s_j, m_j, x_s) \tag{4.2}
\]

subject to the conditions:

\[
\begin{align*}
&c_{a,j}(x_s, t) - f(m_j, t) = 0 \\
&c_{a,j}(0, t) = 0 \\
&c_{a,j}(L, t) = 0 \\
&c_{a,j}(x, 0) = 0 = I(m_j, x_a) \\
\end{align*}
\]

\(j = 1, 2, 3\)

on the domain bounded by \(x = 0\) and \(x = L\). Note that the concentration boundary conditions are imposed at the uncertain source location, \(x_s\), as well as at \(x = 0\) and \(x = L\). The groundwater flow velocity \((v_a)\), the dispersion coefficient \((D_{a,j})\), and the effective porosity \((n_e)\) appearing in this state equation are constant and known, as well as independent of space. As is usual in groundwater transport modeling, the dispersion coefficient is dependent upon the model scale, and in our case is constrained by the Peclet number. Since this is a one-dimensional problem, the velocity does not vary in space and the dispersion coefficient may be viewed as averaged over other dimensions. Our system is considered fully saturated, thus \(S_a\), the water saturation, equals one except at the source location. The subscript \(j\) on the dissolved concentrations \((c_{a,j})\), the NAPL masses \((m_j)\), and the sorbed concentrations \((s_j)\) refers to a particular chemical in the NAPL mixture (three different chemicals are included in this analysis). The given initial concentration is zero at all locations. Thus \(t = 0\) represents a time just prior to emplacement of the NAPL source. Exchange between the dissolved phase and the sorbed phase enters into the state equation directly, while the exchange between the dissolved and NAPL phases is accounted for in the first boundary condition, which is imposed at location \(x_s\). The other two boundary conditions are standard specified concentration conditions on both edges of the domain.
Figure 4.1 depicts the dissolved phase transport in this one-dimensional point source problem. The problem domain is from 0 to \( L \) in the \( x \)-dimension. From the location of the point source, \( x_s \), concentration profiles develop throughout the domain, becoming more dispersed over time.

If we assume local chemical equilibrium between the aqueous and NAPL phase concentrations of each constituent, the state equation for the NAPL phase takes on the form:

\[
\frac{\partial m_j(x_s, t)}{\partial t} = -c_j^{\text{eff}}(x_s, t)Q = A_m(c_j, s_j, m_j, x_s) \\
\]

\[ j = 1, 2, 3 \]

(4.3)

where \( c_j^{\text{eff}} \) (moles of chemical/liter of water) is the equilibrium aqueous concentration with the NAPL phase, also called the effective solubility. This is the dissolved concentration that enters into the boundary condition for equation (4.2). \( Q \) (volume/time) is the flux of water through the source. The effective solubility for each constituent is described by Raoult’s Law, which equates the fugacity, the extent of a molecule’s tendency to leave a system, of two phases at equilibrium:

\[
c_j^{\text{eff}}(x_s, t) = c_j^{\text{sat}}(l)X_j = c_j^{\text{sat}}(l) \left\{ \frac{m_j(x_s, t)}{N_j \sum_{j=1}^{N_j} m_j(x_s, t)} \gamma_j \right\} \\
\]

(4.4)

where \( c_j^{\text{sat}}(l) \) is the saturation concentration of constituent \( j \) at temperature \( l \).
The effective solubility of each constituent is related to the pure phase aqueous solubility, $c_{j}^{sat}(l)$, the mole fraction of the constituent in the NAPL mixture, $\chi_j$, and the activity coefficient of the constituent within the mixture, $\gamma_j$. Note that the mole fraction depends non-linearly on the relative mass (in moles) of each constituent in the NAPL mixture, $m_j$. This formulation assumes use of the pure phase aqueous solubility relative to the liquid form of the pure phase (as indicated by the $l$). This is necessary since we have used the liquid reference state in the definition of fugacity. Thus at temperatures under which the chemical would be a gas or solid, the super-heated or sub-cooled liquid aqueous solubility should be used.

When the equilibrium relationship between the NAPL and aqueous phase is used and the model error is zero, the NAPL mass at any time is known as long as the initial mass is known. In other words, the initial NAPL masses at the point source, $m_{o1}, m_{o2}$, and $m_{o3}$ completely describe the state $m$.

If we further assume that the aqueous and sorbed phases are in equilibrium, the sorbed phase state equation is described by the linear sorption model (4.5) which relates sorbed concentration to dissolved concentration. The sorbed concentration, in turn, is related to the state $s$ by:

$$s_j = c_{s,j} \rho_s (1 - n_e) \quad (4.5)$$

where $\rho_s$ is the density of the soil itself (in $gm/cm^3$) and $n_e$ is the effective porosity (dimensionless).

By differentiating equilibrium sorption with respect to time and using (4.5), we produce:

$$\frac{\partial s_j}{\partial t} = \rho_s (1 - n_e) K_{d,j} \frac{\partial c_{a,j}}{\partial t} \quad (4.6)$$

$K_{d,j}$ ([mg chemical/mg soil]/[mg chemical/liter water]) is the aqueous/sorbed phase partitioning coefficient. Equilibrium sorption is traditionally incorporated into equation (4.2) as a retardation factor ($R_j$) that modifies the velocity and dispersion terms of the equation, where $R_j$ is defined as:
\[ R_j = 1 + \frac{1 - n_e}{n_e S_a} \rho_S K_{d,j} \]  \hspace{1cm} (4.7)

The state equation for the sorbed phase may be re-written as:

\[ \frac{\partial s_j}{\partial t} = (R_j - 1)n_e S_a \frac{\partial c_{a,j}}{\partial t} = \mathcal{A}_e(c_j, s_j, m_j, x) \]  \hspace{1cm} (4.8)

When equation (4.8) is substituted into equation (4.2), the result is the standard form of the one-dimensional advection-dispersion equation with linear sorption.

\[ \frac{\partial c_{a,j}(x,t)}{\partial t} = - \frac{v_a}{R_j} \frac{\partial c_{a,j}(x,t)}{\partial x} + \frac{D_{a,j}}{R_j} \frac{\partial^2 c_{a,j}(x,t)}{\partial x^2} \]  \hspace{1cm} (4.9)

The variation in the sorption rates for the different constituents depends entirely on their hydrophobicity as represented by the partitioning coefficient. \( K_{d,j} \) is related to the pure phase aqueous solubility of each chemical. We determine the \( K_{d,j} \) based on the partitioning of chemical \( j \) to the organic matter in the soil:

\[ K_{d,j} = K_{om,j} f_{om} \]  \hspace{1cm} (4.10)

\( K_{om,j} \) is the organic matter partitioning coefficient (mg chemical/mg organic matter) and \( f_{om} \) is the fraction of organic matter present in the soil. We calculate the \( K_{om,j} \) using the linear free energy relationship between the aqueous solubility and the \( K_{om,j} \) (Schwarzenbäck et al. 1993):
\[
\log K_{om,j} = -0.75 \log c_j^{sat}(l) + 0.44
\]  

(4.11)

The variables in the calculation of the partitioning coefficient are all assumed to be known and constant.

Equations (4.2) through (4.11) comprise the set of state equations used in our 1-dimensional example. Due to the phase equilibrium assumptions, the only unknown states in the model are the dissolved concentrations and the only unknown parameters are the three initial NAPL masses and the source location. The total number of scalar equations to be solved depends on the spatial and temporal discretization of the problem. For example, the transport equation (4.2) must be solved for each node point of the spatial grid and for each time step and each constituent. The ordinary differential equation (ODE) describing mass transfer from the NAPL source (4.3) must be solved for each time step and each constituent. If there are \( N_x \) spatial steps, \( N_t \) time steps, and \( N_j \) constituents, the total number of scalar equations is \( N_t N_j (N_x + 1) = N_e \). These \( N_e \) equations are solved simultaneously at the discretized times and locations. Solutions are calculated at equally spaced time steps but varying spatial steps in order to increase the resolution near the source location. The advection/dispersion equation is solved using a temporally fully-implicit Galerkin finite element solution. The mass balance ODE for the NAPL phase is solved with a fourth-order Runge Kutta technique. This solution insures that the total mass released from the point source does not exceed the initial source mass for any constituent. As mentioned above, the state equation solution generates a set of concentration profiles, in space and time, for each constituent in the NAPL mixture. The amount of mass present in the NAPL at any given time can also be tracked, but this information is not necessary for the estimation, since only the initial NAPL mass is considered a parameter in the estimation algorithm.

**4.2 Measurement Model**

Equipment limitations, variability in sampling techniques, small-scale spatial variability, and human error all contribute to the deviation of a measurement from the true value predicted by the
state equation solution of the preceding section. Therefore we assume that the vector of field measurements used for estimation \( (z) \) are corrupted by measurement noise:

\[
z_j^p = c_{a,j}^P + \frac{c_{a,j}^P(x^p, t^p)}{c_{a,j}^P(x^p, t^p) + z_s} \omega_j^p = M^P(c_j, m_j, x_s, \omega^P) \\
p = 1, 2, \ldots N_z \\
j = 1, 2, 3
\]

where \( \omega_j^p \) is normally distributed with a mean of zero and a variance \( C_\omega \). The subscript \( p \) is the measurement index, and \( N_z \) is the total number of measurement instances (times and locations). In this formulation, the measurement error will be multiplicative as \( c_{a,j}^P \) becomes small relative to \( z_s \) (the half saturation constant), and it will be additive as \( c_{a,j}^P \) becomes large relative to \( z_s \). This insures that measurements do not take on negative values, since concentration is a positive value in reality. For the one-dimensional problem, we simplify this equation by assuming \( z_s \) is equal to zero. Thus the measurement model reduces to an additive error term on the forward model:

\[
z_j^p = c_{a,j}^P(x^p, t^p) + \omega_j^p
\]

4.3 Estimation Equations

The goal of the estimation algorithm is to determine the values of the initial NAPL saturations and (in the one-dimensional case) the location of the NAPL point source. The best estimate of the spatially discretized states is the one that minimizes the discrete version of the generalized least squares criterion given earlier:
The first part of this performance index is a standard weighted least-squares term that measures the difference between measurements \( z_P \) and predictions of dissolved concentration \( M^p(\hat{c}) \). The second and third terms force the estimates to stay close to the prior estimates of the initial masses \( m_0 \) and the source location \( x_s \). The hats \( \hat{\cdot} \) on the masses, source location, and dissolved concentrations indicate that they are estimates. Note that in our case the measurement operator is linear and the explicit solution to the state equations may be substituted for the measurement operator. This formulation assumes that all constituents are measured at the same times and locations and neglects model error.

Equation (4.14) may be minimized by setting the variation (or total differentiation) of \( J \) equal to zero and solving explicitly for the unknown variation in \( \alpha \). This requires that the explicit concentration solution be linearized about the best available estimate \( \hat{\alpha}_k \) (obtained on iteration \( k \)):

\[
\hat{c}_{a,j} = \hat{c}_{a,j}(\alpha) \approx \hat{c}_{a,j}(\hat{\alpha}) + \left. \frac{\partial c_{a,j}}{\partial \alpha} \right|_{\hat{\alpha}} (\alpha - \hat{\alpha}) \quad (4.15)
\]

where \( \hat{\alpha} \) is the vector of estimates:

\[
\hat{\alpha}_k = \begin{bmatrix} \hat{m}_{10} \\ \hat{m}_{20} \\ \hat{m}_{30} \\ \hat{x}_s \end{bmatrix}_k \quad (4.16)
\]
The new $\alpha$ value ($\hat{\alpha}_{k+1}$) which minimizes (4.14) is obtained from the iterative Gauss-Newton algorithm (Tarantola 1987):

$$
\hat{\alpha}_{k+1} = \left[ \hat{\alpha} + \frac{\partial c_j}{\partial \alpha} \bigg|_{\hat{\alpha}_k} \right]^{-1} \frac{\partial c_j}{\partial \alpha} \bigg|_{\hat{\alpha}_k} \left[ C^{-1} \left( \frac{\partial c_j}{\partial \alpha} \bigg|_{\hat{\alpha}_k} \right) \right]^{-1} \left[ \partial c_j \bigg|_{\hat{\alpha}_k} \right] (\hat{\alpha}_k - \bar{\alpha})
$$

(4.17)

This method uses the first derivative of the measurement predictions with respect to estimated parameters, as well as an approximation of the second derivative. When no model error is included in the problem and an explicit expression for the state equation is substituted into the measurement operator, this method is identical to a variational method. Applications of Gauss-Newton solutions to subsurface problems may be seen in Reid (1996) and Sun (1997).

With each iteration $k$ of the algorithm, new values of the states and the sensitivity derivatives are calculated. The derivatives required in the linearization are calculated numerically with a finite difference approach:

$$
\frac{\partial c_{a,j}}{\partial \alpha_j} = \frac{c_{a,j}(\alpha + \delta \alpha) - c_{a,j}(\alpha)}{\epsilon}
$$

(4.18)

where $\delta \alpha_j = \epsilon \delta_{ij} (\delta_{ij} = 1$ if $i = j$ and 0 otherwise) $j = 1, 2, ..., N_\alpha$, and $\epsilon$ is some very small value (relative to $\alpha$). The sensitivity derivatives expressed in (4.17) are matrices of dimension $N_z$ by $N_\alpha$ (i.e., number of measurements by number of parameters). Since the derivatives are calculated from differences, each set of derivatives requires that the state equations be solved once for each parameter. Thus each iteration of the estimation requires $N_\alpha + 1$ solutions. Equation 4.17 is solved iteratively until the values of the parameters converge (i.e., the parameter estimates stop changing significantly). In this problem we use a convergence tolerance of 0.01 normalized log moles on the initial mass parameters and one grid node for the location of the source.

State estimation theory also produces expressions for the updated, or posterior, covariances for the
parameters and states (Schweppe 1973). These equations evaluate the uncertainty associated with the final estimates and represent the Bayesian Cramer-Rao bound (or lower bound) on the estimate uncertainty when the prior probability density \( p_\alpha(\alpha) \) and posterior probability density \( p_{\alpha|\mathbf{z}}(\alpha|\mathbf{z}) \) are Gaussian (McLaughlin and Townley 1996):

\[
[C_\alpha^+]^{-1} \approx \left[ \frac{\partial c_{a,j}}{\partial \alpha} \bigg|_{\hat{\alpha}_k}^T C_{\alpha}^{-1} \frac{\partial c_{a,j}}{\partial \alpha} \bigg|_{\hat{\alpha}_k} + C_{\alpha}^{-1} \right]
\]

\[
C_y^+ \approx \frac{\partial c_{a,j}}{\partial \alpha} \bigg|_{\hat{\alpha}_k}^T C_{\alpha} \frac{\partial c_{a,j}}{\partial \alpha} \bigg|_{\hat{\alpha}_k}
\]

\[
\delta c_{a,j} \approx \frac{\partial c_{a,j}}{\partial \alpha} \delta \alpha
\]

The + on the left-hand-side covariances indicates that these are updated or posterior covariances. Note that these relationships do not depend on the values of the measurements themselves, only on the estimated sensitivity derivatives at measurement. The information (or inverse covariance) contained in the estimations (the posterior \( C_\alpha \)) is equal to the sum of the information in the measurements (the first term) and the prior information (the second term). As \( C_\alpha \) decreases, the confidence in the prior increases and the prior parameter information is weighted more heavily than the measurement information. The posterior covariance of the states depends only on the prior parameter covariance, the measurement error covariance, and the sensitivity derivatives \( \frac{\partial c_{a,j}}{\partial \alpha} \). As \( C_\alpha \) is more uncertain, the posterior \( C_y \) will also be more uncertain.

The estimation algorithm is graphically presented in figure 4.2. For each estimator iteration, the forward model is run \( N_\alpha + 1 \) times. The vast majority of the computational effort goes into calculating the Jacobian by differencing. A reasonably sized (in parameter space) problem would be quite expensive to evaluate using this method.

### 4.4 Simulated Problem

The estimation algorithm (4.17) could be applied to any set of measurements and prior statistics. In this analysis we have created a simulated set of measurements to evaluate the algorithm. Although
Figure 4.2: The Gauss-Newton based estimation algorithm. Each iteration brings the estimator closer to the true value of the parameters $\alpha$. At each iteration, the estimator requires the sensitivity of the states to each parameter.

1. **Initialize** $m_{10}, m_{20}, m_{30}, x_s$ to prior values.

2. **Forward Model Run**
   - Solve dissolution and transport equations.

3. **Calculate residuals**

4. **Calculate Jacobian**
   - For each of $i$ parameters.
   - Perturb $\alpha_i$ by $\Delta \alpha_i$.
   - **Run forward model**
   - Estimate derivative by difference at each measurement location.

5. **Gauss-Newton estimation**
   - Using Jacobian and residuals, update parameters.

6. **Assign updated values** to $m_{10}, m_{20}, m_{30}, x_s$.

7. **Converge?**
   - Update posterior covariances.
Prior mean | Prior variance | Simulated true value
---|---|---
**benzene initial mass**<br>\( \ln \left( \frac{m_{01}}{m_{ref}} \right) \)| 7.3 (120 kg) | 8.5 (400 kg²) | 8.3 (312 kg)
**toluene initial mass**<br>\( \ln \left( \frac{m_{02}}{m_{ref}} \right) \)| 6.8 (80 kg) | 8.4 (400 kg²) | 7.3 (132 kg)
**o-xylene initial mass**<br>\( \ln \left( \frac{m_{03}}{m_{ref}} \right) \)| 5.9 (40 kg) | 8.2 (400 kg²) | 5.3 (23 kg)
**Location of source**<br>(\(x_{0}\)) | 40 meters | 1,600 meters^2 | 69 meters

Table 4.1: Parameter values and prior statistics for simulated problem.

it is also possible to apply the algorithm to real field data, using synthetic data has a number of advantages: 1) with synthetic data the true values are known, thus it is possible to assess the accuracy of the algorithm; 2) we can generate many synthetic problems to test the algorithm under a variety of conditions; 3) with a synthetic data set we can test many different sampling strategies; and 4) getting access to real field data is difficult and time consuming. The disadvantage of using synthetic data is that the model generating the data exactly matches our model in the estimation algorithm. In reality, we would expect that the forward model does not capture all of the complex processes existing in nature. However, as a development tool, tests on synthetic data are still preferable to tests on real data; if the algorithm is not effective with the simulated data set, it is unlikely to work at a real field site.

First, a set of true parameter values was generated from assumed statistical properties for all random variables. Each variable was assumed to be normally distributed with given mean and variance. This particular problem has four parameters: the initial log mass of each of three NAPL constituents and the location of the source. The true parameter values and associated prior statistics are shown in Table 4.4. Note that the estimation algorithm works with the natural log of the total initial normalized (unitless) moles \( \ln \left( \frac{m_{0i}}{m_{ref}} \right) \) of each constituent at the source, and \( m_{ref} \) is taken to be unity. This insures that the algorithm will produce a positive value for the mass. Table 4.4 also presents each parameter in more commonly accepted mass units.
Table 4.2: Chemical constants used in the simulated problem.

<table>
<thead>
<tr>
<th></th>
<th>benzene</th>
<th>toluene</th>
<th>o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>78.1 (g/mol)</td>
<td>92.1 (g/mol)</td>
<td>106.2 (g/mol)</td>
</tr>
<tr>
<td>Density</td>
<td>0.88 (g/cm³)</td>
<td>0.87 (g/cm³)</td>
<td>0.88 (g/cm³)</td>
</tr>
<tr>
<td>Aqueous solubility (c_{l}^{sat}(l) at 25 C)</td>
<td>0.023 (mol/L water)</td>
<td>0.0056 (mol/L water)</td>
<td>0.0017 (mol/L water)</td>
</tr>
<tr>
<td>K_{om} (calculated)</td>
<td>46 (mol/mol org)</td>
<td>130 (mol/mol org)</td>
<td>320 (mol/mol org)</td>
</tr>
<tr>
<td>Retardation (calculated)</td>
<td>5.1 (unitless)</td>
<td>13 (unitless)</td>
<td>30 (unitless)</td>
</tr>
</tbody>
</table>

Table 4.3: Physical constants used in the simulated problem.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwater velocity (v_a)</td>
<td>0.1 m/day</td>
</tr>
<tr>
<td>Porosity (n_e)</td>
<td>0.3</td>
</tr>
<tr>
<td>Dispersion coefficient (D_{a,j})</td>
<td>1 m²/day</td>
</tr>
<tr>
<td>Bulk density of soil (p_{bd})</td>
<td>2.65 gm/cm³</td>
</tr>
<tr>
<td>Fraction organic matter in soil (f_{om})</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The prior mean and variance were chosen to produce a problem with significantly different amounts of each NAPL constituent at the source. Note that the prior variance is fairly high (i.e., two standard deviations is 40 kg). The constituents of the NAPL mixture are assumed to be known. We used a set of chemical properties consistent with benzene (C₆H₆), toluene (C₆H₅CH₃), and o-xylene (1,2-(CH₃)₂C₆H₄). These constituents are LNAPLs that are commonly studied and often present in mixture with each other. They are also useful for this problem because their pure phase aqueous solubilities vary by almost an order of magnitude. For the purposes of our problem, the NAPL source could be envisioned as residual LNAPL in a region of a moving water table (i.e., the NAPL is trapped in the unsaturated zone near the water table and then the water table moves above it). The chemical properties necessary to the estimation are presented in Table 4.4.

The forward model also requires some physical constants in order to calculate the states (dissolved concentrations). Again, these values are assumed to be known and constant and were chosen based on common aquifer properties. They are presented in Table 4.3.

The problem discretization is designed to produce a Courant number \((v_a * dt/dx)\) of 1 and a Peclet number \((v_a * dx/D_{a,j})\) of 1 near the source. This yields a spatial discretization \((\Delta x)\) of 10 meters (near the source) and a temporal discretization of 100 days. The model was run over a domain of
220 spatial steps \((N_x)\) and 100 time steps \((N_t)\). The simulated true results are presented in Figure 4.3. This figure shows the concentration of each chemical at the source (normalized by its aqueous solubility) as well as the concentration profile over the entire domain for three different times. The effects of the different solubilities are readily seen in this figure. The source concentration shows the results of competitive dissolution, and the domination of the most soluble constituents. In the concentration profiles, the peak of each constituent separates over time due to different retardation coefficients; the more soluble (less hydrophobic) constituents are retarded less than the more hydrophobic (less soluble) constituents. Thus the varying solubilities of the constituents have a chromatographic effect, separating the concentration profiles of the constituents from each other.

Given the parameters of this simulated problem, the total initial NAPL mass at the source is 458 kg. The total volume of this mass, calculated from the relative proportions of each constituent, is 0.54 cubic meters. With the given discretization and porosity, the total volume of voids in a grid cell near the source is 6 cubic meters. If the NAPL were distributed evenly throughout the cell, the saturation would be 0.09, on the low end for residual NAPL in the saturated zone. Clearly the saturation value is dependent entirely on the assumed NAPL distribution (e.g., if the source were distributed over a bulk volume of two cubic meters the saturation would be 0.9). These calculations are merely intended to provide a perspective on the magnitude of the sample problem. The next Chapter discusses the application of the estimation algorithm to this sample problem.
Figure 4.3: True model outputs for simulated NAPL problem. The dissolved concentration (normalized by the pure phase aqueous solubility) is shown over all time. Dissolved concentration profiles over the model domain are shown at three different times.

Solute Concentration Profile at 5 Years

Solute Concentration Profile at 15 Years

Solute Concentration Profile at 25 Years
Chapter 5

Estimation Results

Tests of the estimation algorithm developed in Chapter 4 confirm that it accurately (usually with ten percent) predicts the location and mass of the NAPL point source. We used the algorithm both to explore the feasibility of a larger NAPL estimation problem and to examine the efficacy of different measurement strategies. Although the one-dimensional problem does not represent the real complexities of a multi-dimensional problem, it may be viewed as a rough solution to source estimation along a streamline. Based on the success of this algorithm, we have formulated a multi-dimensional distributed source problem (presented in Chapter 7.)

5.1 Measurement Strategies

The results of the estimation algorithm are entirely dependent upon the chosen measurement strategy, (i.e., where and when samples are taken.) At a field site there is likely to be only one measurement design; with a simulated problem, we can test the algorithm for different strategies. The advantage of the one-dimensional problem is that it is small enough to enable repeated runs of the estimation algorithm, providing a way to determine the accuracy and cost of estimates obtained with different sampling configurations. To explore this capability, we have created 16 different measurement strategies. There are four strategies each for sets of 5 (Strategies 5a-d), 10 (Strategies 10a-d), 30 (Strategies 30a-d), and 60 (Strategies 60a-d) measurements. Each measurement con-
sists of a dissolved concentration sample for each of the three contaminants (i.e., benzene, toluene, o-xylene). The sampling strategies were not chosen in a rigorous optimal fashion, but rather to illustrate the tradeoff between accuracy and cost for a range of different sampling alternatives. The strategies were varied to explore the importance of the total number of samples, the sampling locations and the sampling times. The sixteen strategies in this analysis are shown in Figure 5.1.

For each strategy, measurements were derived from the measurement equation presented in Chapter 4. The additive random measurement error ($\omega$) was assumed to be normally distributed with a mean of 0.0 and a variance ($\sigma^2_\omega$) of 0.05 in units of normalized concentration (0 to 1). Note two standard deviations is approximately 40 percent of the maximum concentration value. In cases where the measurement error was negative and greater than the true value at that location, the measurement was given a value of zero, thus preventing physically impossible negative concentrations. The measurement units are normalized (non-dimensionalized) aqueous concentrations. The concentrations are normalized by the pure phase aqueous solubility of each chemical. Since the solubilities of benzene, toluene, and o-xylene differ almost an order of magnitude, non-normalized concentrations could not be displayed on the same plot.

The estimates obtained for each measurement strategy are derived from a particular set (or realization) of the random problem inputs (initial masses, source location, and measurement errors). The observed performance of the estimator (as measured by differences between true and estimated values) depends, in part, on the particular realization selected. An extended Monte Carlo (multi-replicate) analysis would be necessary to rigorously test the effects of different measurement strategies. Nevertheless, the single replicate results given here provide a feeling for the effect of sampling configuration on estimation accuracy.

### 5.2 Parameter and Model Fit

Figures 5.2 through 5.5 show the error between the true and estimated parameter values (normalized by the true values) for each measurement strategy. So a perfectly exact fit would have an absolute normalized error of zero and an estimate that was off the true value by 100 percent would have an absolute normalized error of one. In general, all the strategies do a good job of estimating the initial NAPL mass and source location. The worst estimates have an error of half the true value, and the
Figure 5.1: Map of measurement strategies for the estimation algorithm. Each star indicates a concentration measurement taken for each chemical constituent. The strategy number indicates the number of measurements, varying from 5 to 60.
best are nearly perfect fits. Of the four parameters being estimated, the location of the source is usually the least accurate. The mass of the benzene (the most soluble chemical) is usually estimated better than any other parameters. In these results, it is clear that the number of measurements is not the most important factor in the success of a sampling strategy. For example, in this particular realization of measurements, Strategy 5a (with only 5 measurements) outperforms many of the other strategies. In contrast, Strategy 10a has twice as many measurements, but performs more poorly than 5a. This effect is the result of measurement spacing, (i.e., the 5a measurements are spaced at 50-meter increments while the 10a measurements are spaced at 10-meter increments.) Thus 5a covers a distance of 250 meters while 10a covers 100 meters. The larger spacing better characterizes the concentration profile from the simulated NAPL source. In both strategies, measurements are taken at a single time (19 years). Similar comparisons may be made among all sixteen strategies from the results in shown in Figures 5.2 through 5.5.

Figures 5.6 and 5.7 present the fits of the model predictions to the measurements for Strategy 60a, and Figures 5.8 and 5.9 present the same information for Strategy 60b. Each of these strategies samples two wells at many times, and many locations at two times, for a total of 60 measurements. The figures present four concentration profiles, two each over distance and time, for each strategy. The predicted model is displayed with a solid line (for each chemical), while the true model is represented by a dotted line. Measurement locations and times are marked with stars. The predicted model matches the true model more closely for Strategy 60a than for Strategy 60b. The difference in the results of the two strategies is primarily due to the location of the wells; the samples in Strategy 60a do a better job of capturing the contaminant profile than do those of 60b. The wells in Strategy 60b do not sample the concentration profiles for toluene and o-xylene at all, and never intercept the peak for the benzene. In contrast, the wells in Strategy 60a sample across the peak concentration of all three constituents. This assessment is seen clearly in Figure 5.10, which superimposes the measurement strategies (white stars) on the true concentration profiles for each chemical. Part of the reason that the estimator is able to fit the peaks of two chemicals for which it has no measurement information is that the solution is loosely constrained by the prior. In this case the prior information told the estimator to expect the existance of toluene and xylene in the range of the amounts shown above as prior statistics. The combination of this constraint, along with the information from the benzene measurements, enabled the estimator to fit the toluene and xylene profiles. Of course the profiles of these two chemicals are better fit when measurements of
Figure 5.2: Fit of estimated parameters to true values for strategies 5a-5d. The absolute value of the difference between the estimate and the true value for each is normalized by the true value of the parameters.
of the parameters.

Figure 5.3: Plots of estimated parameters. The absolute value of the difference between the estimate and the true value for each is normalized by the true value.
Figure 5.4: Fit of estimated parameters to true values for strategies 30a-30d. The absolute value of the difference between the estimate and the true value for each is normalized by the true value of the parameters.
Figure 6.6: Plot of estimated parameters to the values for strategies 60a-60d. The absolute value of the difference between the estimate and the true value for each is normalized by the true value.

Parameter Estimates for Strategy 60a

Parameter Estimates for Strategy 60b

Parameter Estimates for Strategy 60c

Parameter Estimates for Strategy 60d
these chemicals are present. The better placement of sampling wells in strategy 60a is also reflected in the convergence of the estimation algorithm. Under strategy 60a the estimator converged within five iterations while strategy 60b had not converged within tolerance after 15 iterations (see Figure 5.16).

5.3 Evaluation of Uncertainty

Figures 5.11-5.14 present the prediction error (model prediction minus true value) for the Strategy 60a and 60b profiles. The error is normalized by the posterior concentration standard deviation \( \sigma_p \), as calculated by Equation (4.19). If these prediction errors were normally distributed, we would expect approximately 95 percent of them to fall between +2 and -2 (two standard deviations of a unit normal distribution). For the most part, this is what we observe. Moreover, the prediction errors obtained for our problem are very persistent over both time and space. This pattern reflects the effect of the three initial NAPL masses on dissolved concentration at all subsequent times and locations. Note that where little contamination is present (either in the predicted or true models) the prediction residuals do exhibit a more scattered pattern. This is most apparent in Figure 5.12 at early times.

As a quantification of the persistence, we can evaluate the approximate lag one concentration correlation coefficients \( \rho_1 \) for the four distance and time profiles shown in Table 5.3. The measure of how correlated a residual is with its nearest or lag one (in space or time) neighbor is generally calculated as the ratio of the square of the covariance, \( \text{cov}(c_1,c_2) \), to the product of the variances of sample (Jenkins and Watts 1968). In Table 5.3 these coefficients are given by:

\[
\rho_{1,j} = \frac{1}{N_t - 1} \sum_{t=1}^{N_t-1} \frac{\partial c_{a,i}}{\partial \alpha} \left| \frac{C_\alpha \partial c_{a,i}^T}{p_t p_{t+1}} \right|_{t+1}
\]

\[
j = 1, 2, 3
\]

Note that we have used the derived posterior covariance from equation 4.19 in the numerator of this
Figure 5.6: Measurement residuals for strategy 60a versus distance. The dotted line shows the 'true' model value while the solid lines are the predicted model based on the estimates.
Figure 5.7: Measurement residuals for strategy 60a versus time. The dotted line shows the 'true' model values while the solid lines are the predicted model based on the estimates.
Figure 5.8: Measurement residuals for strategy 60b versus distance. The dotted lines show the 'true' model values while the solid lines are the predicted model based on the estimates.
Predicted Model and Measurements at 350 Meters

Figure 5.9: Measurement residuals for strategy 60b versus time. The dotted lines show the 'true' model values while the solid lines are the predicted model based on the estimates.
Figure 5.10: Concentration profiles for each chemical with superimposed measurement strategies. The white stars show the measurement locations and times for strategies 60a and 60b.
Figure 5.11: Prediction error normalized by the posterior covariance ($\sigma_y^+$) versus distance for strategy 60a.
Normalized Prediction Errors at 200 Meters

Normalized Prediction Errors at 250 Meters

Figure 5.12: Prediction error normalized by the posterior covariance ($\sigma_y^+$) versus distance for strategy 60a.
Figure 5.13: Prediction error normalized by the posterior covariance ($\sigma_y^+$) versus distance for strategy 60b.
Figure 5.14: Prediction error normalized by the posterior covariance ($\sigma^+$) versus distance for strategy 60b.
Table 5.1: Lag one correlation coefficients for normalized prediction errors.

<table>
<thead>
<tr>
<th></th>
<th>11 years</th>
<th>19 years</th>
<th>200 (350) meters</th>
<th>250 (400) meters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Strategy 60a</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.88</td>
<td>0.89</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>toluene</td>
<td>-0.51</td>
<td>-0.26</td>
<td>0.98</td>
<td>0.88</td>
</tr>
<tr>
<td>o-xylene</td>
<td>-0.64</td>
<td>-0.50</td>
<td>0.98</td>
<td>0.90</td>
</tr>
<tr>
<td><strong>Strategy 60b</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>benzene</td>
<td>0.88</td>
<td>0.90</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>toluene</td>
<td>-0.51</td>
<td>-0.26</td>
<td>0.70</td>
<td>0.60</td>
</tr>
<tr>
<td>o-xylene</td>
<td>-0.64</td>
<td>-0.50</td>
<td>0.76</td>
<td>0.70</td>
</tr>
</tbody>
</table>

The derived correlation coefficients confirm what is apparent in the figures: There is a high positive correlation among the normalized residuals in the distance profiles, and the correlation is slightly stronger in the Strategy 60a residuals than in the Strategy 60b residuals.

In large part the success of the estimation algorithm depends on how well the linearization of the forward model approximates the true model. For this particular problem, the forward model is not only non-linear, but it is also not monotonic. While this characteristic will not necessarily hamper the effectiveness of the algorithm in estimating states and parameters, it does affect the accuracy of the calculated posterior covariances. Sensitivity analyses of the forward model to the estimated parameters suggest that the local linearization may not necessarily be valid over the range of parameter values covered by the posterior covariance. Since the posterior covariances are based on this linearization, the calculated covariances may not be a good representation of the uncertainty in the estimates.

### 5.4 Evaluation of Measurement Strategies

In Figure 5.15 we compare the tradeoff between estimation accuracy and sampling cost for different measurement strategies. The accuracy performance measure used in this figure is the average normalized posterior standard deviation of the parameters:

\[
J_A = \frac{(\sigma_{m1}^+ / \sigma_{m1}) + (\sigma_{m2}^+ / \sigma_{m2}) + (\sigma_{m3}^+ / \sigma_{m3}) + (\sigma_{z}^+ / \sigma_{z})}{4}
\] (5.2)
Strategy Marginal cost of uncertainty reduction / percent reduction
5d
10d $6,490
30a $22,190
60a $49,530

Table 5.2: Marginal cost of uncertainty reduction (relative to Strategy 5d) for Pareto optimal sampling strategies.

A value of one indicates almost no improvement over the prior, and a value of 0.5 represents an average of 50 percent improvement on the prior. Note that $J_A$ is independent of the measurements themselves, since it depends only on the sensitivity derivatives at measurement locations and times.

The total cost of each sampling strategy depends on the number of sampling locations ($N_{xz}$) and the number of times a sample is taken ($N_{zt}$):

$$J_C = a_w N_{xz} + a_s N_{zt}$$

where $a_s = $100 per sample chemical-suite analysis and $a_w = $10,000 per each new well installation required.

Assessing the sampling strategies with these two measures allows identification of Pareto optimal strategies. For our purposes, the Pareto optimal strategies are those which cannot be improved upon without sacrificing either accuracy/uncertainty or cost. The Pareto optimal strategies are 5d, 10d, 30a, and 60a. All other strategies are inferior to these—either incurring higher cost without any associated reduction in uncertainty or more uncertainty without any associated reduction in cost. The worst strategy in terms of performance is 10b, with no improvement on the prior. Table 5.2 shows the marginal cost of reduction in uncertainty, relative to Strategy 5d, for the four optimal strategies.

As mentioned earlier, the 16 sampling strategies were chosen to illustrate a range of different sampling options. What all four optimal strategies have in common is that they sample at multiple times—from 5d which samples one well five times over the course of 2 years, to 60a which samples
two wells 10 times each. Results obtained for the set of strategies displayed in Figure 5.4 reveal several insights about sampling design:

- **Location.** Perhaps the most obvious, and important, factor in determining success in estimation is whether the sampling is conducted near the contamination (i.e., whether the measurements contain any information about the source). This was seen to be the primary difference between Strategies 60a and 60b, but may also be seen in the dominance of 5d over 5c, 10a over 10b, and 30a over 30b. These pairs of strategies only differ in fortuitous well placement. The wells of 60b, 10b, and 5c miss most of the contaminant concentration profiles.

- **Characteristic Scale.** Another important factor is whether the sampling configuration captures enough of the concentration profile to characterize the source. Since the estimation algorithm can use information about how the NAPL chemicals interact with each other, measurements that show a significant difference in the relative concentration of each chemical produce better estimates. Therefore the spatial coverage of the strategy is very important. A good example of this is the dominance of Strategy 5a over 10a. Strategy 5a, with half as many measurements, covers roughly twice as much distance as Strategy 10a and produces a much higher reduction in uncertainty. This factor is also seen in the dominance of 5a over 5b and 5b over 30a.

- **Multiple Times.** Another way of getting information about the changes in relative chemical concentration is sampling over multiple times. In general, it is less expensive to sample an existing well than to install a new one, so sampling at multiple times (rather than multiple locations) will always be preferable in terms of cost. To be useful, the sampling times must be far enough apart to capture the interaction among the different NAPL constituents. This characteristic time scale is completely problem dependent (e.g., size of the source, properties of the groundwater flow system) so a specific time scale for all problems is not identifiable. However, for field scale problems, sampling on the order of at least years is probably necessary. All of the Pareto optimal strategies sample at multiple times. Another example is Strategy 10d, which improves over Strategy 5a by adding a second sampling time—even though the spatial coverage of sampling is smaller.

It should be noted once more that these results are based on a single realization of the NAPL source problem. A different source (i.e., with different initial masses in a different location) could yield
different relative performance results for the sampling configurations examined in this section. To thoroughly explore the characteristics of these sampling strategies, the estimation algorithm should be evaluated for a number of different realizations.

5.5 Computational Effort

As a final note on the performance of the one-dimensional estimator, the amount of computation effort depends primarily on the difficulty of the estimation. In this sample problem with four parameters, each iteration of the estimator requires five forward model runs. As can be seen in Figure 5.16, the estimator required a number of iterations before reaching convergence. Even the
case of strategy 60a which was designed to be an easy fit required five iterations. Strategy 60b actually ended with the maximum 15 iterations. So the marginal additional difficulty in fitting the data of strategy 60b resulted in a tripling of the computer run time. Also interesting is that the parameters related to the NAPL mass converge relatively quickly; it is the source location parameter \((x_s)\) that drives the number of iterations required. Even in strategy 60a, where the source location estimation takes a direct path to the true solution, it requires four steps to get there. Based on the work done with this one-dimensional estimator and later experience with a distributed estimation problem, the source location (as opposed to strength) is characteristically the more difficult part of the problem.

Figure 5.16: Estimator convergence (all four parameters) for sampling strategies 60a and 60b.
The distributed source problem takes a decidedly different form than the one-dimensional point source problem of Chapter 4. In that case we coupled the NAPL point source to the transport equation through a specified concentration (type I) boundary condition. This is impractical in multiple dimensions for numerous reasons. First, the model should be flexible enough to handle many potential source geometries (beyond a point source). Second, there is no advective concentration flux through a specified concentration model node. If a NAPL source is present in a zone or multiple zones, the model could not adequately represent the movement of downgradient dissolved contaminant through the source. Finally, the approach taken in Chapter 4 offers no control over the maximum amount of mass allowable in a source (i.e., there could be more mass than will fit in the pore space). In one dimension this was not as much a concern. Thus for the multidimensional model, we work in terms of fractional saturations rather than masses. Dissolution of the NAPL is tracked into the aqueous phase with a gradient driven source term in the transport equation. This chapter describes our conceptual model in more detail.

Instead of a fictional non-dimensional point source, we are concerned with source masses that exist in a specified volume. Furthermore, sources may potentially exist at all locations in the problem domain (i.e., a distributed source). This invites expression of the source as a continuous property. Figure 6.1 illustrates the development of this idea. At the pore scale (Figure 6.1a), residual NAPL
mixtures of mass \((M_{n,n})\) occupy a given fraction of the total volume \((\theta_n)\) or a fraction of the total void space \((S_n)\).

\[
\theta_n = \frac{M_{n,n} \rho_n}{V_T}
\]

\[
S_n = \frac{M_{n,n} \rho_n}{n}
\]

At a larger scale (i.e., multiple pores, Figure 6.1b) we can repeat this calculation of \(\theta_n\) or \(S_n\) with a new residual NAPL mass and new total volume. It is clear that the volumes Figure 6.1a and b have very different residual NAPL saturations. If we average the NAPL content over too large a volume, we lose descriptive detail (e.g., overestimate NAPL content in areas where NAPL is not present and underestimate it where NAPL is present). Therefore, to go from the microscopic or pore scale to the continuum or macroscopic scale (e.g., on the order of centimeters), we utilize the concept of a representative elementary volume (REV) (Bear 1979). We then say that the volume fraction of NAPL \((S_n)\) is a continuous property, with values at any mathematical point in the problem domain (Figure 6.1c).

The difference between NAPL saturation and other continuous properties in the subsurface (e.g., hydraulic conductivity) is that at many (or most) locations the value of the NAPL saturation is zero. From a modeling perspective, this is not necessarily a problem, but it does create some difficulties when addressing prior statistics for the NAPL state.

The other major conceptual change in the distributed source model is how we represent the exchange of mass between the NAPL and aqueous phases. Whether or not we assume a chemical equilibrium between these two phases, it is unlikely that dissolved chemical concentrations would reach chemical equilibrium over a large (i.e., measurement) scale. The low concentrations relative to equilibrium are attributed to irregular distribution (see Figure 6 below), heterogeneous flow patterns, dilution, and/or non-equilibrium mass transfer. Recently, a number of studies have supported the idea that most of the seemingly non-equilibrium dissolution of the NAPL phase may be explained by heterogeneity of the NAPL distribution and in the porous media (Sorens et al. 1998, Unger et al. 1998). To capture this effect, we consider the dissolution process at two scales: the local scale (e.g., centimeters) and the model scale (e.g., tens of meters).
Figure 6.1: Definition of NAPL saturation as a macroscale property. At the pore scale, NAPL saturation is defined by the volume fraction of the pore containing NAPL (a). At a larger scale, heterogeneity in NAPL distribution is lost by calculating an average NAPL saturation (b). Therefore we treat NAPL saturation as a continuous property, defined everywhere in space (c).

Figure 6 illustrates our conceptualization of dissolved phase concentrations at the numerical model grid scale. In a given model grid cell, areas nearest to NAPL sources will be at chemical equilibrium (effective solubility), however areas with no NAPL present will have dissolved concentrations less than equilibrium values. The overall concentration in the cell will not necessarily reach equilibrium. As will be discussed later in this thesis, we must solve the state equations numerically on a discrete grid. Furthermore, in order to model processes at a field scale (hundreds of meters to kilometers), the model discretization must be large compared to scales of chemical equilibrium. If variability in NAPL distribution like that shown in Figure 6 is averaged over a model cell, the model will underestimate the NAPL saturation or even predict no NAPL present at all. Our model formulation addresses this variability by representing mass transfer at the model scale as a kinetic process.

A number of processes other than chemical kinetics may contribute to the non-equilibrium concentrations seen at field sites:
The time scales needed for dispersion through an entire grid cell are large. The size of the model grid cells alone means that it takes much longer to come to chemical equilibrium throughout an entire cell. For a typical organic chemical, the aqueous molecular dispersion coefficient is $10^{-5}$ cm$^2$/s. The coefficient roughly provides a time scale for chemical equilibrium since the spread ($\sigma_x$) associated with diffusion is $\sigma_x = (2Dt)^{1/2}$. At this rate, molecules travel approximately 1 cm in each direction from the source in a day. An area the size of a model grid cell (e.g., 1 meter) would take 6 days to reach equilibrium in the absence of advective transport.

- Heterogeneity in the porous medium and subsequent heterogeneity in the velocity field lead to mixing and dilution of saturated contaminant concentrations.

- In some areas of the porous medium, mass transfer from the NAPL phase may be diffusion limited (e.g., in dead-end pores or other areas where advection is not the contaminant transport mechanism) rather than advective transport limited.

- Heterogeneity in the distribution of NAPL phase throughout a model cell will also affect the extent of dilution. In addition, the rate of dissolution of the NAPL is related to the interfacial (or contact) area between the NAPL and aqueous phases as well as the velocity with is lower in areas of high NAPL saturation. For a given volume of NAPL in a given area, an evenly distributed source would be expected to dissolve more quickly than a heterogeneously distributed source.
Most researchers (Mayer and Miller 1996, Miller et al. 1998, Frind et al. 1999) currently use a first-order equation to model aqueous-NAPL phase mass transfer. The question, then, is how to develop a mass transfer rate coefficient (Miller et al. 1998). To date, most experimental work towards this end involves small-scale (a few centimeters) column experiments of a single NAPL component in a homogeneous medium. A good review of empirical models for mass transfer rates may be found in Miller et al. (1998). The mass transfer rates are developed as functions of Reynolds number (velocity, viscosity), Sherwood number (diffusion), Schmidt number (diffusion, viscosity), varying grain size measurements, NAPL saturation, uniformity indexes, contact area between NAPL and water, and various assumptions about the shape of NAPL blobs. These relationships are far too complicated for our purposes in this analysis. At a field scale, the literature contains little examination of \( \mu \) as either an empirical or analytically derived parameter. The only use of such a parameter at something near a field scale is found in Frind et al. (1999). The line of reasoning is that higher NAPL saturations result in faster dissolution rates. The parameters \( a \) and \( b \) are related to properties of the NAPL and porous media, not to mention scale. How to evaluate these parameters is currently highly uncertain and likely site-specific. We adopt a similar model, recognizing that the choice is not ideal. However, based on the uncertainty in current approaches to modeling NAPL dissolution, especially as applied to large scales, a more complex model is hard to justify:

\[
\mu = a[S_n(t)]^b
\]

(6.2)

where \( \mu \) is the field scale mass transfer coefficient (FSMTC) (1/time), \( a \) is a parameter (1/time), \( b \) is a dimensionless parameter, and \( S_n \) is the total NAPL saturation, also dimensionless (both \( a \) and \( b > 0 \)).

The topic of how the FSMTC should be determined is vast and still in the early stages of research. We will return to this discussion later in this thesis, but for the most part determination of this parameter is not a focus of the current work. The next chapter presents the development of the model state equations for the distributed NAPL source problem based on the conceptual model described here.
Chapter 7

A Distributed NAPL Model

This chapter describes the development of the distributed (multi-dimensional) source residual NAPL model. Based on the conceptual model discussed in the previous section, we derive a set of model state equations from first principles. The key features of the model are: 1) the distributed nature of the source (i.e., any node in the model domain may have residual NAPL), 2) representation of the NAPL phase as fractional saturations as opposed to masses, 3) coupling of groundwater flow, residual NAPL dissolution, and contaminant transport processes, and 4) accommodation of a chemical mixture within the NAPL source. Whereas in the one-dimensional problem the states were a point mass of each chemical, in the multi-dimensional model the states are the NAPL fractional saturation at every point in the model domain. Given a set of initial and boundary conditions, the model computes the dissolved/aqueous phase concentration of each constituent as well as tracking the change, or lack thereof, in the NAPL source. The standard groundwater modeling parameters (transmissivity, dispersivity, porosity, chemical properties) as well as the field scale mass transfer coefficient are also required inputs. The resulting model may be used to explore the effects of different NAPL source configurations and varying model parameters. Some examples of different NAPL sources are presented at the end of this chapter.
7.1 Model State Equations

The general description of multiphase fluid behavior may be derived from a statement of mass balance among phases and species. We consider a control volume (Figure 7.1) in which there are four potential phases (\(\kappa = \text{vapor} \, [v], \text{solid} \, [s], \text{aqueous} \, [a], \text{and NAPL} \, [n]\)) and some number of species within those phases (\(i = \text{air} \, [v], \text{water} \, [a], \text{soil} \, [s], \text{and N-chemical constituents} \, [j]\)). For each species (\(i\)) in each phase (\(\kappa\)), the total mass (\(M_{\kappa,i}\)) present in the control volume (\(V_T\)) at any given time is related to the fluxes into and out of the control volume as well as the exchange of mass among phases within the control volume. We consider an advective flux (\(F_{\kappa,i}\)) and a dispersive flux (\(\vartheta_{\kappa,i}\)) in each direction, for each species in each phase. Each species may be present in any of the phases. The exchange of mass from one phase to another is represented by \(I_{\beta,\kappa,i}\) (i.e., exchange of mass from phase \(\beta\) to phase \(\kappa\)).

The mass balance for this control volume is expressed mathematically (adapted from Abriola and Pinder (1985)):
where:

\[ \rho_\kappa = \text{volume averaged density of phase } \kappa \text{ in the control volume}, \]
\[ \theta_\kappa = \text{volume fraction of phase } \kappa \text{ in the control volume}, \]
\[ \eta_{\kappa,i} = \text{mass fraction of species } i \text{ in phase } \kappa \text{ in the control volume}, \]
\[ v_\kappa = \text{velocity (vector) of phase } \kappa, \]
\[ D_{\kappa,i} = \text{dispersion coefficient (vector) of species } i \text{ in phase } \kappa, \]
\[ I_{\kappa,i} = \text{total inter-phase exchange of species } i \text{ to phase } \kappa \text{ in the control volume}, \]
\[ I_{\beta,\kappa,i} = \text{inter-phase exchange of species } i \text{ from phase } \beta \text{ to phase } \kappa \text{ in the control volume}. \]

This statement assumes no external sources or sinks of mass (e.g., no pumping, no chemical decay).

Equation (7.1) is completed with the following constraints:

\[
\sum_{i=1}^{N_i} \eta_{\kappa,i} = 1 \tag{7.2}
\]
\[
\sum_{\kappa=1}^{N_\kappa} \theta_\kappa = 1
\]
\[
\sum_{i=1}^{N_i} I_{\kappa,i} = I_\kappa
\]
\[
\sum_{\kappa=1}^{N_\kappa} I_{\kappa,i} = 0
\]

These constraints insure that mass is conserved over species and phases. The first requires that in a given phase, the mass fractions of each species present sum to the total mass of the phase. The second equation constrains the volume fractions such that the sum of the volume of all phases is not greater than the total volume. The third and fourth constraints apply to the inter-phase exchange rates. The total change of mass of a given phase must be equal to the contributions (i.e., change in mass) of each species to that phase (third constraint). Finally, for a given species, mass
is conserved over all phases or the total change in mass is zero (fourth constraint).

When equation (7.1) is summed over each phase and each species and the constraints (7.2) are applied, the result is a set of coupled partial differential equations describing all of the mass fractions and volume fractions in the system. In the current formulation there are 4*(3 + Nj) mass fractions (e.g., with 3 chemical constituents there would be 24 mass fractions). However, our conceptual description of the problem allows some simplifications. Since we are considering a NAPL source in the saturated zone only, we neglect the vapor phase and air species (ηv,i = ηκ,v = 0). We make the further simplifications that the soil (i = s) and water (i = a) species do not change phases (Iκ,a = Iκ,s = 0), and only exist in the solid and aqueous phases, respectively (ηa,s = ηn,s = ηs,a = ηn,a = 0). Practically, this means we are neglecting water in the sorbed phase and water in the NAPL phase. We are now left with only 2 + (3*Nj) mass fractions and 3 volume fractions:

**mass fractions**

- $\eta_{s,s}$  soil in the solid phase
- $\eta_{a,a}$  water in the aqueous phase
- $\eta_{s,j}$  chemical $j$ in the solid phase
- $\eta_{a,j}$  chemical $j$ in the aqueous phase
- $\eta_{n,j}$  chemical $j$ in the NAPL phase

for $j = 1,2,...,N_j$ chemicals

**volume fractions**

- $\theta_a$  aqueous phase
- $\theta_s$  solid phase
- $\theta_n$  NAPL phase

### 7.1.1 Species balances

Conservation of mass in the control volume leads to a continuity equation for each of the $(2 + j)$ species. Each of the species balances takes advantage of the last constraint in (7.2): the inter-phase exchange of a species over all phases is equal to zero. As stated earlier, we assume that soil is only
present in the solid phase. We also assume an immobile medium, i.e., there is no movement of the solid phase and \( \mathbf{v}_s = 0 \), \( \mathbf{D}_{s,i} = 0 \). Thus the mass of soil in the control volume doesn’t change over time. The soil species balance becomes:

\[
\frac{\partial}{\partial t} (\rho_s \theta_s \eta_{s,s}) = 0 \tag{7.3}
\]

The water species is also assumed to be present only in a single phase. The species balance is:

\[
\frac{\partial}{\partial t} (\rho_a \theta_a \eta_{a,a}) + \nabla \cdot (\rho_a \theta_a \eta_{a,a}) - \nabla \cdot (\rho_a \theta_a \mathbf{D}_{a,a} \nabla (\eta_{a,a})) = 0 \tag{7.4}
\]

The chemical species, on the other hand, are present in all three phases. Since our problem statement describes a residual or immobile NAPL the only movement of chemicals occurs in the aqueous phase, \( \mathbf{v}_n = 0 \), \( \mathbf{D}_{n,i} = 0 \). For each chemical species \( j \) the species balance is:

\[
\frac{\partial}{\partial t} (\rho_a \theta_a \eta_{a,j} + \rho_n \theta_n \eta_{n,j} + \rho_s \theta_s \eta_{s,j}) + \nabla \cdot (\rho_a \theta_a \mathbf{v}_{a,j} \eta_{a,j}) + \nabla \cdot (\rho_a \theta_a \mathbf{D}_{a,j} \nabla (\eta_{a,j})) = 0 \tag{7.5}
\]

7.1.2 Phase balances

Whereas the species balances assure that all of the mass of a particular species is conserved, the phase balances assure that the total mass of all species in a phase is equal to the mass lost or gained from that phase. Each of these balances takes advantage of the fact that the sum of all dispersive fluxes in a phase must equal zero. In addition, each phase balance invokes the first constraint that the sum of all the species mass fractions within a phase is equal to one. In the solid phase, soil and chemical species are present:
\[
\frac{\partial}{\partial t} (\rho_a \theta_a) + \sum_{j=1}^{N_j} I_{s,a,j} = 0
\] (7.6)

Again, an immobile medium is assumed. In the aqueous phase, water and chemical constituents are present:

\[
\frac{\partial}{\partial t} (\rho_a \theta_a) + \nabla \cdot (\rho_a \theta_a \mathbf{v}_a) - \sum_{j=1}^{N_j} I_{s,a,j} - \sum_{j=1}^{N_j} I_{n,a,j} = 0
\] (7.7)

In the NAPL phase, only the chemical constituents are present. Note that this phase is immobile:

\[
\frac{\partial}{\partial t} (\rho_n \theta_n) - \sum_{j=1}^{N_j} I_{n,a,j} = 0
\] (7.8)

Equations 7.3 through 7.8 require additional information to be solved. This information is how chemical mass moves among the three phases, since water and soil mass do not change phase. While expressing the species and phase balances, we use the aqueous phase as a reference state and assume that all mass transfer occurs through this phase. Therefore there is no direct mass transfer between the solid and NAPL phases \((I_{s,n,j} = I_{n,s,j} = 0)\). We are left with only chemical mass transfers between the aqueous-solid \((I_{a,s,j} \text{ and } I_{s,a,j})\) phases and the aqueous-NAPL \((I_{n,a,j} \text{ and } I_{a,n,j})\) phases.

### 7.1.3 Inter-phase exchange

As in the one-dimensional formulation, sorption is considered to be a linear equilibrium process. We believe this is a reasonable assumption since 1) both soil and water exist everywhere throughout the model domain, and 2) the time scales of sorption (on the order of hours (Holmen and Gschwend
are fast relative to both advective transport time scales and the time steps of the numerical model (on the order of tens of days). The equilibrium solid/water partitioning relationship is expressed in terms of the aqueous concentration of chemical \( j \) (\( c_{a,j} \)). Assuming a dilute aqueous solution (i.e., the contaminant contributes a negligible amount to the density of the aqueous phase), \( c_{a,j} \) may be expressed as a function of the mass fraction:

\[
\eta_{a,j} = \frac{c_{a,j}}{\rho_a} \quad (7.9)
\]

where \( \rho_a \) is the density of water.

The transfer of chemical mass (\( j \)) from the aqueous to the solid phase is then described as:

\[
\frac{\partial s_j}{\partial t} = I_{a,s,j} = K_{d,j} \rho_s (1 - \epsilon_s) \frac{\partial c_{a,j}}{\partial t} = -I_{s,a,j} \quad (7.10)
\]

The partitioning coefficient \( (K_{d,j}) \) is in units of (mass of \( j \) on soil per mass of soil) / (mass of \( j \) in water per volume of water). This mathematical statement assumes that the contribution of the chemical to the mass and volume of the solid phase is very small compared to the contribution of the soil (i.e., \( \rho_s \approx \rho_{s,s} \) and \( \theta_s \approx \theta_{s,s} \)).

The exchange of chemical mass between the NAPL and aqueous phases (dissolution and repartitioning to NAPL phase) was discussed in Chapter 6. In sum, our formulation applies different models of dissolution at two scales. At the local scale, we assume chemical equilibrium as modeled by Raoult’s Law:

\[
c^{eff}_j = c^{sat}_j \left\{ \frac{m_j}{\sum_{j=1}^{N_j} m_j} \right\} \gamma_j \quad (7.11)
\]
This equation is in the same form as presented in Chapter 4. This form of competitive dissolution directly relates NAPL saturation ($S_j$) or NAPL mass to the dissolved concentrations. The equilibrium assumption holds as long as the time scales of phase exchange are long enough to cover distances of interest. At typical groundwater velocities chemical equilibrium between the dissolved and NAPL phases would be expected to persist at approximately the centimeter scale via dispersion mechanisms. For our purposes, the equilibrium relationship is used solely to translate the effective solubility to a fractional saturation value.

NAPL-water interphase exchange itself is expressed as:

$$I_{a,n,j} = -p(c_{e}^j - c_{a,j})\theta_a = -I_{n,a,j} \quad (7.12)$$

Where $p$ is the field scale mass transfer coefficient (in units of 1/time) discussed in Chapter 6. We assume that $p$ is a relatively simple function of NAPL saturation:

$$\mu(x, t) = a[S_n(x, t)]^b \quad (7.13)$$

Where $a$ and $b$ are parameters describing the power law dependence of $\mu$ on $S_n$. This mass transfer coefficient only explicitly varies with the NAPL saturation, and allows the model to quantify the effects of dilution and heterogeneity on equilibrium dissolution. Guiguer and Frind (1994) use a similar form of the mass transfer coefficient as a generic correlation to NAPL saturation. A recent study by Unger et al. (1998) found that the $S_n$ based dissolution model of Guiguer and Frind yielded comparable results to a more complicated model that included a Reynolds number and grain size correlation (Mayer and Miller 1996). Given these results and the lack of established dissolution models in the literature, we believe that the simple $S_n$-based model is the best choice for this research.

These mass balances and constitutive relationships complete the set of state equations. Now we proceed to make a number of additional assumptions that further simplify our mathematical de-
scription of NAPL phase exchange and transport.

7.1.4 Simplification of equations

The first species balance Equation (7.3) tracks soil mass, which is not particularly the focus of this analysis. Since we are assuming that the soil does not move or exist in phases other than the solid phase, this equation becomes trivial; any change in mass of the solid phase is due to the change in chemical mass sorbed. Rearranging the equation yields:

\[
\frac{\partial M_s}{\partial t} = \frac{\partial M_{s,n}}{\partial t} = I_{a,s}
\]

(7.14)

Note that the problem formulation assumes all sorbed chemical mass has come from the aqueous phase. The rate of change of sorbed mass is equal to the inter-phase exchange expression, \( I_{a,s} \).

Equation (7.4) may be simplified by applying the dilute solution assumption: the mass of chemical \( j \) in the water is very small compared to the mass of water itself. The fraction of water in the aqueous phase is approximately equal to one. When this term is constant, the diffusive flux term of the equation drops out. By further assuming an incompressible fluid, the density of the aqueous phase is approximately constant. Then the water species equation becomes a sum of fluxes (water mass balance) over the control volume, recognizable as the groundwater flow equation:

\[
\frac{\partial}{\partial t}(\theta_a) = -\nabla \cdot (\theta_a \mathbf{v}_a) = \frac{\partial M_a}{\partial t}
\]

(7.15)

In the discussion below, Equation (7.7), the aqueous phase balance, will reduce to the same expression.

Rearranging the chemical species balance (7.5) for each chemical constituent leads to the transport equation for each chemical constituent in the aqueous phase. Again we assume a dilute solution,
which allows the mass balance to be expressed in terms of concentrations:

\[
\frac{\partial M_{a,j}}{\partial t} + \frac{\partial M_{s,j}}{\partial t} + \frac{\partial (c_{a,j} \theta_a)}{\partial t} + \nabla \cdot (\theta_a v_a c_{a,j}) - \nabla \cdot (\theta_a D_{a,j} \nabla c_{a,j}) = 0
\]  

(7.16)

The inter-phase exchange relations above by definition describe the change in mass in the sorbed phase and the NAPL phase. Substituting in these expressions and applying the standard definition of a retardation factor (given in Chapter 4):

\[
\frac{\partial (c_{a,j} \theta_a)}{\partial t} + \nabla \cdot (\theta_a v_a c_{a,j}) - \nabla \cdot (\theta_a D_{a,j} \nabla c_{a,j}) = \mu (c_{j}^{\text{eff}} - c_{a,j}) \theta_a - n_e S_a (R_j - 1) \frac{\partial c_{a,j}}{\partial t}
\]

(7.17)

The final form of our transport equation comes from applying the chain rule to the first and second terms of the above equation, using the relation from Equation (7.15), and rewriting in terms of water saturations rather than volume fractions:

\[
\frac{\partial (c_{a,j})}{\partial t} = -\frac{v_a}{R_j} \nabla (c_{a,j}) + \frac{1}{R_j S_a n_e} \nabla \cdot (S_a n_e D_{a,j} \nabla c_{a,j}) + \frac{\mu (c_{j}^{\text{eff}} - c_{a,j})}{R_j}
\]

(7.18)

This equation is subject to the homogeneous boundary and initial conditions:

\[
c_{a,j}(\Omega, t) = 0 \text{ on the domain boundary } \Omega
\]

\[
c_{a,j}(x, 0) = 0
\]

(7.19)

Note that the effective solubility of chemical \( j \) in the transport equation is a function of the residual NAPL saturation. Other parameters in Equation (7.18) are also a function of states: velocity \( (v_a) \), retardation \( (R_j) \), and dispersion \( (D_{a,j}) \), are all functions of the water saturation \( (S_a) \), and the
field scale mass transfer coefficient \( (\mu) \) is a function of the NAPL saturation \( (S_n) \). The solid phase balance (7.6) reduces to a trivial expression of the inter-phase exchange of chemical into the sorbed phase (the same expression that the soil species balance produced):

\[
\frac{\partial M_s}{\partial t} = \sum_{j=1}^{N_j} K_{d,j} \mu_s (1 - n_e) \frac{\partial C_{a,j}}{\partial t} = I_{a,s}
\]  

(7.20)

The next phase balance (7.7) produces the standard groundwater flow equation after applying the assumptions: a) the chemical constituent in the aqueous phase is a dilute solution, b) water is incompressible, and c) the inter-phase exchange terms are much smaller than the other terms in the expression and may be neglected. The first two assumptions are the same as those used in Equation (7.15), and allow \( \rho_a \) to be treated as a constant. After applying the third assumption:

\[
\sum_{j=1}^{N_j} I_{s,a,j} + \sum_{j=1}^{N_j} I_{n,a,j} << \rho_a \frac{\partial}{\partial t} (\theta_a) + \rho_a \nabla \cdot (\theta_a v_a)
\]  

(7.21)

The water phase balance becomes identical to equation (7.15), the groundwater flow equation. In terms of saturations, the flow equation is:

\[
\frac{\partial (S_n n_e)}{\partial t} = -\nabla \cdot (S_n n_e v_a)
\]  

(7.22)

The flow equation is completed by substituting in the generalized form of Darcy's Law. This yields the non-linear Richards equation:

\[
\frac{\partial (S_n n_e)}{\partial t} = \nabla \cdot [K_{rw} (S_n) \nabla h]
\]  

(7.23)
where \( h \) is hydraulic head, \( K \) is the saturated hydraulic conductivity, and \( k_{rw} \) is the relative permeability. In a system of constant boundary conditions, no (or little) recharge, and a nearly incompressible medium, the groundwater flow field will only change as the water saturation changes. As NAPL dissolves, the total volume occupied by NAPL will decrease and the volume occupied by the water will subsequently increase. However, the change in \( S_a \) over time is like to be small since 1) the residual NAPL volumes are small compared to \( S_a \), and 2) NAPL dissolution occurs slowly—on the order of tens to hundreds of years for a typical source (Pankow and Cherry 1996). Thus over a model time step (e.g., tens of days), \( S_a \) will be approximately constant. For this reason, we use a steady-state groundwater flow equation in our model. Meanwhile, small changes in \( S_a \) can result in large changes in the relative permeability. The empirical relationship between water saturation and permeability is usually represented as a power law model (e.g., Brooks-Corey (Brooks and Corey 1966)):

\[
k_{rw}(S_a) \approx f(n_c S_a)^d
\]

(7.24)

where \( f \) and \( d \) are fitting parameters. Then the steady-state groundwater flow equation with a variable hydraulic conductivity that depends on the NAPL dissolution model through the dependence on \( S_a \) is:

\[
\nabla (K k_{rw}(S_a) \nabla h) = 0 \quad (7.25)
\]

The boundary conditions applied to (7.25) are:

\[
\begin{align*}
h(\Omega_1, t) &= h_c \\
\bar{n} \cdot \bar{q}(\Omega_2, t) &= 0
\end{align*}
\]

(7.26)
In other words, these are simple no-flow ($\Omega_2$) or constant head ($\Omega_1$) boundaries. More complicated boundary conditions could be applied to the model at a marginal computational cost. Although there are technically no initial conditions necessary to solve (7.25), it does require a value for $S_a$ to initialize the relative permeability.

The final phase balance (7.8) describes the NAPL dissolution process. Writing the equation in terms of saturations and applying the dissolution inter-phase exchange model, we produce:

$$\frac{\partial}{\partial t}(\rho_n S_n) + \sum_{j=1}^{N_j} \mu(c_j^{\text{eff}} - c_{a,j}) S_a = 0$$

(7.27)

From this point, we further simplify the equation by combining it with Raoult's law and covert moles of NAPL into fractional saturations using the identity:

$$\left\{ \begin{array}{c}
m_j \\
\sum_{j=1}^{N_j} m_j
\end{array} \right\} = \left\{ \frac{S_j \rho_j}{\rho_{\text{mw}} m w_j} \right\}$$

(7.28)

After some simplification, the NAPL dissolution equation becomes:

$$\frac{\partial}{\partial t}(\rho_n S_n) + \mu S_a \left[ \frac{1}{\rho_{\text{mw}}} \sum_{j=1}^{N_j} \left( \frac{S_j \rho_j \gamma_j}{m w_j} \right)^{\text{sat}} - \sum_{j=1}^{N_j} c_{a,j} \right] = 0$$

(7.29)

This equation requires an initial condition of the fractional NAPL saturation:

$$S_j(x, t = 0) = S_{j0}(x)$$

(7.30)
and is completed with the volume averaged quantities:

\[
\rho_n = \left\{ \frac{\sum_{j=1}^{N_j} S_j \rho_j}{S_n} \right\}
\]

(7.31)

\[
\rho_{mw} = \sum_{j=1}^{N_j} \frac{S_j \rho_j}{mw_j}
\]

\[
S_n = \sum_{j=1}^{N_j} S_j
\]

where \(\rho_j\) is the density of pure phase chemical \(j\) and \(mw_j\) is its molecular weight.

Since we are interested in the dissolution of each individual component from the NAPL mixture, we can re-write (7.29) with the time derivative expressed in terms of \(S_j\) rather than \(S_n\):

\[
\frac{\partial S_j}{\partial t} + \mu S_a \left[ \frac{1}{\rho_{mw}} \frac{S_j \gamma_j c_{sat}}{mw_j} - \frac{c_{a,j}}{\rho_j} \right] = 0
\]

(7.32)

### 7.1.5 Numeric solution of state equations

Along with boundary and initial conditions, Equations (7.18), (7.25), and (7.32) are the final state equations for our three-dimensional distributed source NAPL problem. Together they produce a system of \((2j + 1)\) coupled partial differential equations summarized in Table 7.1. Note that the dissolution and transport equations both depend on the dissolved concentration and the residual NAPL saturation. Additionally, all of the state equations contain parameters that also depend on the states.

We solve the set of equations using a Galerkin finite element method (over linear triangular elements) combined with a fully-implicit finite difference temporal discretization. It would be easy to discuss at some length the relative merits of different numerical methods (and there are many
such books). For this analysis, suffice it to say that the finite element approach offers flexibility for coupled problems and minimizes problems of numerical dispersion. The Galerkin technique (as opposed to the co-location or subdomain methods) is the most commonly used in groundwater modeling (Celia and Gray 1992). This method uses the basis functions of the trial space (in our case linear triangular basis functions) as the weighting functions in the residual minimization and is equivalent to a variational principle, when one exists for the given problem. As applied to our state equations, each state \((S_j, S_a, c_{a,j})\) is discretized at grid nodes and is represented with the trial basis functions. Other parameters \((D_{a,j}, v_a, R_j, \mu)\) are considered constant over elements. The spatially discretized (but continuous in time) state equations are also presented in Table 7.1.

The finite element discretization produces a set of ordinary differential equations in the discretized states \(S_j(t), S_a(t), c_{a,j}(t)\) with the coefficient matrices \(A, B, F, G, H, K,\) and \(L\). All of the coefficient matrices are dependent on the discretization (i.e., the basis functions and finite element grid). In addition, all of the coefficient matrices except \(A\) and \(B\) are dependent on the states. Table 7.1 includes the discrete steady-state groundwater flow equation that solves for the flow field as a function of water saturation. Since we have not made the hydraulic head a state in our formulation, the groundwater flow equation does not produce a solution for a state, but is nonetheless necessary for calculating the velocity field for the other state equations. A detailed description of the finite element discretization of the model state equations is presented in Appendix B.

As mentioned above, we use a fully-implicit finite difference discretization in time for the state equations. We use the fully-implicit formulation to maximize stability of the solution. Due to the non-linearities in the equations (i.e., the parameters depend on the states), each equation must be solved iteratively. On each iteration, the set of discrete equations for each state is solved with a bi-conjugant gradient algorithm that uses a partial Cholesky decomposition pre-conditioner. Other, and probably more efficient, solvers could potentially be used for this problem, however we are limited to solvers that can address non-symmetric matrices. We chose the bi-conjugant gradient method primarily for ease of implementation. For the iterative part of the algorithm, we utilize a Picard method, both for ease of execution and efficiency. The Picard method, as opposed to gradient-based search algorithms (e.g., Newton-Raphson), does not require evaluation of derivatives. The derivatives for this problem would have to be calculated numerically and could be quite costly. The Picard method likely requires more iterations than a gradient based method,
Final State Equations

\[ \frac{\partial c_{a,j}}{\partial t} = -\frac{v_e}{R_j} \nabla (c_{a,j}) + \frac{1}{R_j S_{a_n e}} \nabla \cdot (S_{a_n e} D_{a,j} \nabla c_{a,j}) + \frac{\mu}{R_j} (c_{a,j}^{sat} - c_{a,j}) \]
\[
S_{a,j}(x,0) = S_{a,j}(0)
\]
for each \( j \)

\[ \frac{\partial S_j}{\partial t} = -\mu S_a \left( \frac{1}{\rho_{mw} m_{w_j}} c_{j}^{sat} - \frac{c_{a,j}}{\rho_j} \right) \]
\[ S_j(x,0) = S_{j,0}(x) \]
for each \( j \)

\[ \nabla (K k_{ru}(S_a) \nabla h) = 0 \]
\[ S_a(x,0) = S_{a,0}(x) \]

Spatially Discretized State Equations

\[ \frac{d c_{a,j}(t)}{dt} = B^{-1} [c_{a,j}(t) F + H] \]
for each \( j \)

\[ \frac{S_j(t)}{dt} = A^{-1} [G S_j(t) + K c_{a,j}(t)] \]
for each \( j \)

\[ Lh = 0 \]

with \( H(S_j, S_a, a, b), F(S_j, S_a, a, b), G(S_a, S_j), K(S_j, a, b), L(S_a) \)
\( A \) and \( B \) constants

Table 7.1: State equations for multi-dimensional NAPL source problem.
but for this problem could prove to be more stable.

In summary, the steps of the solution to the state equations are:

1. Initialize the model with a velocity field, initial $S_j$, initial $S_a$, and initial $c_{a,j} = 0$;
2. Calculate the effective solubility, $\rho_{mw}$, $\rho_n$, $S_n$, and $\mu$ for the current NAPL saturations;
3. Solve the dissolution model for NAPL saturations at new time $= t + 1$;
4. Solve the groundwater flow equation using the water saturations for time $= t + 1$ and update the velocity field for time $= t + 1$;
5. Return to step 2 and recalculate parameters dependent on NAPL saturation. Iterate until convergence of the NAPL saturations for time $= t + 1$;
6. Input NAPL saturations, water saturation, and effective solubility (for time $= t + 1$) from the dissolution model into the transport model;
7. Solve the transport equation for the new dissolved concentration (time $= t + 1$) of each chemical;
8. Return to step 2 using concentration value and saturations for time $= t + 1$. Iterate until NAPL saturations and dissolved concentrations for time $= t + 1$ converge;
9. Advance one time step. Saturations and concentrations from step 8 become values for time $= t$. Return to step 2.
10. Continue algorithm (steps 2-9) until final time step.

7.2 Model Results for Selected Sources

We utilize the model to demonstrate two different NAPL source geometries. The first is a point source intended to confirm the results we expect based on experience with the one-dimensional model. The second is a large (relative to the model domain) square source. Within the source, the distribution of NAPL is spatially uniform. Both sources contain a NAPL mixture similar to that
used in Chapters 4 and 5: the mixture of the LNAPLs benzene, toluene, and o-xylene. Both of the examples are calculated on a 51 by 51 node grid with 10 meter discretization, Peclet number of 1, and Courant number also of 1. The model is run for 100 time steps of 40 days each.

**Point Source**

The first source tested parallels the one-dimensional point source presented earlier. In the distributed model, residual saturation of three chemicals exists as a single node in the model domain. The initial fractional saturations at this node are as follows: benzene (0.2), toluene (0.1), and o-xylene (0.02). As would be expected, the model results are similar to those seen from the one-dimensional model. The NAPL source dissolved relatively quickly and evidence of competitive dissolution is apparent from the change in NAPL saturation at the source (see Figure 7.2). This Figure shows that over the time scale of the model the NAPL dissolves almost completely with the most soluble component disappearing first.

Figure 7.3 presents the dissolved plume from this model run at two different times, \( t = 10(400 \text{ days}) \) and \( t = 70(2800 \text{ days}) \). The concentrations are shown normalized by the pure phase solubility of the given constituent. At the initial time, almost none of the least soluble component, xylene as shown in the third row, is present in the dissolved phase while the benzene plume (top row) is well established. At the later time, the benzene source is almost completely gone (this may be verified by checking against Figure 7.2). At still later times, 4000 days, the center of mass of the benzene dissolved plume shifts from the NAPL source as a separate slug. At this time the toluene and xylene plumes still look as if they result from a continuous source.

**Square Source**

As mentioned above, the problem modeled here is a largish (100 by 100 meter) square source. At each source in this node, the fractional saturation of NAPL is: benzene(0.2), toluene (0.1), o-xylene (0.01). This source stands in marked contrast to the point source above. Here, the NAPL source changes almost imperceptibly in the modeling time of a decade. The dissolved phase plumes are quite what would be expected from a continuous contaminant source (Figure 7.2).

More interesting is the groundwater flow field about this source. Figure 7.2 shows the x- and y-components of flow (in m/day) for the model domain. Due to the boundary conditions we used,
Figure 7.2: Residual NAPL saturation in point source over time.
Figure 7.2: Spatial distribution (in meters) of dissolved concentration from point source. Each color

toluene and o-xylene at two different times, 400 days and 2,800 days.

This shows the normalized by the pure phase aqueous solubility concentration plumes of benzene.

\[ \begin{align*}
& t = 400 \text{ days} \\
& t = 2,800 \text{ days}
\end{align*} \]
Figure 7.4: Spatial distribution (in meters) of dissolved concentration from large uniform NAPL source. Each column shows the normalized (by the pure phase aqueous solubility) concentration plumes of benzene, toluene, and o-xylene at two different times, 400 days and 4,000 days.
Figure 7.5: Flow field (aqueous phase) in the vicinity of a large square NAPL source. The axis are spatial dimensions (in meters).

Flow is primarily in the x-direction, from left to right on the figure. Note that the magnitude of flow away from the source is over twice as large as that within the source. This is not surprising but it is rather gratifying that the model confirms intuition. The Figure also illustrates some details about the flow field; the flow is fastest (three times what it is in the NAPL source) on the top and bottom edges of the source. Since the dissolution model is gradient driven, these are the places where the NAPL dissolves the fastest (i.e., dissolved mass is removed from these areas quickly by higher advective flux.)

The dissolution characteristics within the NAPL source are illustrated in Figure 7.6. This figure shows the fractional saturation of the most soluble chemical, benzene, over time. The top plot is from a model node near the front edge of the source (where the flow velocity is slightly higher...
than within the source). Here the NAPL saturation is steadily declining, although from the plot's scale, it is doing so quite slowly. The bottom two plots show the NAPL fraction saturation for benzene at a node in the middle of the source and at the opposite edge of the source. At these nodes the fractional saturation does initially decline but then begins to increase. The model is allowing dissolved constituent to re-partition into NAPL phase. Again the change is quite small, but this is primarily due to the uniformity of the source. As clean (i.e., no contaminant is present) water passes through the source it becomes saturated with dissolved phase NAPL constituents. The re-partitioning effect is the result of dissolved phase constituents encountering a region where the NAPL effective solubility is less than what is already in the aqueous phase. This effect would likely be more pronounced in a source in which the NAPL fractional saturations varied in space. However, as can be seen from the result presented here, differential dissolution (in space) produces the same effect.
Figure 7.6: Residual saturation of benzene in a large square NAPL source. The top plot shows the dissolution of benzene from the NAPL phase at a node on the leading edge of the source. The second and third plots show the re-solution of benzene into NAPL phase at nodes in the middle and on the trailing edge of the source.
Chapter 8

Discussion of Two-Dimensional Model

The research presented in this thesis would not be complete without an examination of certain salient questions posed at the beginning. These questions certainly were not resolved by this research, but rather wrestled into some uneasy peace. The common theme of the unresolved issues is ‘what role does this factor play in the source characterization process?’ (i.e., how does it affect the sensitivity of measurements to source characteristics?) The factors we believe are both uncertain and central to the estimation process are the FSMTC (both the model and its parameters), competitive dissolution of a NAPL mixture, the prior statistics for the NAPL state, and the general geometry of the source. This chapter is meant to be a brief qualitative look at some of the larger sources of uncertainty we encountered in this research.

8.1 Field Scale Mass Transfer Coefficient

The FSMTC has been discussed throughout this thesis. This is a reflection of both the importance of this factor to the numerical modeling of NAPL processes and the uncertainty in the field about what such a factor should be. As was done in Chapter 6, one can make a qualitative list of the variables that probably affect the size of the FSMTC. Quantifying this effect, or even determining which variables (e.g., pore size distribution, viscosity) are important to include is quite difficult. The literature contains many different models of this coefficient; a few are presented here as examples.
Table 8.1: Mass transfer rate parameters fit to Borden data (from Guigier, 1993).

<table>
<thead>
<tr>
<th></th>
<th>(a_j)</th>
<th>(b_j)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCM</td>
<td>2.48</td>
<td>1.32</td>
</tr>
<tr>
<td>TCE</td>
<td>5.43</td>
<td>1.54</td>
</tr>
<tr>
<td>PCE</td>
<td>1.87</td>
<td>2.10</td>
</tr>
</tbody>
</table>

For a review of approaches see Miller et al. (1998).

The use of a gradient driven mass transfer to represent the dissolution of NAPL is based on a model of diffusion across a stagnant boundary layer (Sherwood et al. 1975). At a small scale the idea is that the rate constant multiplying the gradient is proportional to the diffusion rate through the layer and inversely proportional to some small boundary layer thickness. The units on this rate constant are per time. Of course the rate constant that most researchers use is applied at a much larger scale, on the order of centimeters.

Two studies (Guiguer 1993, Frind et al. 1999) calibrated the parameters of FSMTC to the Borden emplaced NAPL experiment. The source consisted of a NAPL mixture of chloroform, trichloroethylene, and perchloroethylene over a 1 meter by 0.5 meter by 1 meter volume (still relatively small by field scales). In Guiguer (1993) a simple relationship is used for the FSMTC, much like the one used in our research:

\[
\mu_j = a_j(S_n(t))^{b_j}
\]  

(8.1)

where \(b_j\) and \(a_j\) are the fitting parameters. The general explanation of this sort of relationship is that the time invariant part (\(a_j\) in units of per time) is representative of media properties and the exponent that modifies the time varying total NAPL saturation (\(b_j\)) is meant to account for the NAPL chemical characteristics, geometry, and interfacial area. In this study a different FSMTC is used for each chemical constituent \(j\). The results of his calibration are shown in Table 8.1.

In a later analysis, the group at Waterloo modified their model of the FSMTC to include more variables and slightly changed the fitting parameter (Frind et al. 1999):
where $Sh$ is the Sherwood number at the scale of REV (cm scale), $D_j$ is the aqueous diffusivity of constituent $j$ ($L^2/T$), $d_{50}$ is the median grain size diameter ($L$), $S_n^i$ is the total NAPL saturation at point $i$, $S_{no}$ is the initial value of the total NAPL saturation, and $f_j^i$ is the fractional volume of component $j$. The Sherwood number is an empirical relationship often based on the Reynolds number and/or other parameters (e.g., the Schmidt number). Unlike the previous analysis, there is only one $Sh$ value for all three NAPL constituents. Frind uses a Sherwood number based on a Powers et al. (1994) column experiment and alters the $Sh$ value to fit the Borden data. The diffusion coefficients for the three chemicals (used in the cited work) are on the order of $10^{-10} m^2/s$ and the median grain size diameter is 0.15 mm. They were able to calibrate the model to the Borden data with a range of parameter values ($Sh = 10^{-2} - 10^{-5}$); this large range is partially due to the fact that the hydraulic conductivity within the source was unknown and it was also adjusted. Values of $b$ used are 0, 0.5, 0.75, and 0.96. These values are all curiously smaller than those fit in the Guiguer work a few years earlier, although to be fair they do not compare directly. What is gained by including a measure of diffusivity, the mean grain size, and the fractional NAPL saturation (as opposed to the total NAPL saturation) when the range of possible fits for the parameters is so large?

There is a body of experimental work that calibrates mass transfer models to column data, almost all in homogeneous systems (Powers et al. 1992, Powers et al. 1994, Mayer and Miller 1992, Miller et al. 1990, Imhoff et al. 1993, Geller and Hunt 1993). These researchers use variants on the mass transfer rate model shown above from Frind et al. (1999), fitting from one to six parameters with a large range of values. Even so, much work still needs to be done to understand NAPL-aqueous phase mass transfer within small scale homogeneous situations (see Miller et al. (1998)). At the larger field scale, replete with heterogeneity, the results of column experiments are almost not applicable. Intuitively, as the scale increases, the FSMTC should decrease according to some characteristic length that involves the NAPL distribution and the relationship between the model scale and the local mass transfer scale (the scale at which an equilibrium relationship might be observed).
As an illustration of the effect of the FSMTC on modeling NAPL dissolution and transport, we created a small model example. Figure 8.1 illustrates how a small difference in the FSMTC makes a fairly larger difference in NAPL dissolution. This example uses a smooth (Gaussian in space) NAPL mixture source with a total saturation of 0.16. Here we use the FSMTC model developed in Chapter 7, so there is a single rate coefficient for all three chemicals. The parameters of our model are varied slightly (a from 0.5 to 0.8 (per day) and b from 1 to 1.8) where:

\[ \mu = a[S_n(t)]^b \] (8.3)

As expected, changes in b have a larger effect than changes in a. Note that in the top plot the lower value of b yields almost complete dissolution of the source while using the higher one yields less than a third of the source dissolved at the end of the model time. Regardless of how complicated one makes the computation of the FSMTC, the fact remains that models of NAPL dissolution are very sensitive to small changes in this parameter. In fact, Unger et al. (1998) performed a modeling analysis of NAPL dissolution models and concluded that the formulation and selection of parameters for the dissolution model was a larger source of uncertainty than uncertainty in the NAPL distribution or the characteristics of the aquifer. This is definitely a research area in which there is still much work to be done.

### 8.2 The Effect of Multiple Chemicals

An important question from the beginning of this research was how a mixture of chemicals behaved differently from a single constituent NAPL source. Most modeling and experimentation with NAPLs involve a single chemical. Our idea was that the competitive dissolution from a source mixture contains more information about the source than does dissolution from a single constituent source. To begin exploring this question, we created five model cases of a NAPL source. All five sources have the same geometry, a relatively small source with NAPL saturations smoothly distributed (Gaussian) in space. The problems were run on a 21 by 51 node model domain (10 meter discretization) for 100 times steps of 40 days each. The first source contains a chemical mixture
Figure 8.1: NAPL dissolution from source under a range of FSMTC parameters.
(again, with properties of benzene, toluene, and xylene). The total NAPL saturation in the center of the source (the maximum value) is 0.16. We then created a NAPL source that has an identical total NAPL saturation as the first source, but it is only comprised of a single constituent. The single constituent chosen was the most soluble one (benzene) which is also proportionately the most dominant one in the chemical mixture. The test was thus designed to be conservative.

The change in the total NAPL saturation over time (at a node in the middle of the source) for these two cases is shown in Figure 8.2. The model confirms the intuitive expectation that the single component NAPL dissolves more quickly than the mixture. An interesting note is that the mixture is primarily composed of benzene (60 percent by molar volume) but still dissolves significantly more slowly. In fact, the rate of dissolution of benzene alone (i.e., benzene in the mixture) is also slower than the rate of dissolution of benzene in the single constituent source (see Figure 8.5).

The other three cases involve a perturbation of the NAPL source saturation present in the first two. Figure 8.3 shows the total NAPL saturation at a single node for the chemical mixture cases. The first case (3chem) is the same case from the previous figure. The other two cases have the same source geometry as 3chem, but the initial total NAPL saturation is 20 percent higher, \( s_n = 0.19 \). In one case (p-3chem) the saturations of all three chemicals are increased proportionally. In the other (pv-3chem) only the saturation of the most soluble constituent (benzene) is increased, although the total NAPL saturation is the same as in case p-3chem. These results show distinctive behavior of the three different sources. First, it does not appear that the smaller source (3chem) will disappear before the larger sources (p-3chem and pv-3chem). Rather it appears that they are converging toward a similar model at some long time. Although these cases (3chem and p-3chem) contain the same proportions of each NAPL component the nonlinearities of the model result in different dissolution characteristics. Second, the proportion of each chemical within the mixture (p-3chem and pv-3chem) produce different dissolution behaviors at later times (at earlier times the total NAPL dissolution is almost the same). The proportion of each chemical in the mixture is also important to the persistence of the source. Cases 3chem and pv-3chem contain the same amount of toluene and xylene (the combined initial saturation of toluene and xylene is 0.06, more than the total saturation left at the source at the end of the model run).

Figure 8.4 presents the parallel results for the single chemical case. Case 1chem is the same as the single chemical source of Figure 8.2 and case p-1chem has a 20 percent larger initial saturation.
Figure 8.2: Total residual NAPL dissolution for equivalent saturation cases of a single constituent and a three constituent mixture.
Figure 8.3: Total residual NAPL dissolution for a chemical mixture: three cases.
The relationship of $1_{\text{chem}}$ to the larger source ($p-1_{\text{chem}}$) is similar to that seen for the chemical mixture cases. Finally, Figure 8.5 isolates the behavior of benzene for the five cases. From this figure it is easy to see that in the chemical mixtures the dissolution rate for benzene is not only less that the rate in the single chemical sources, but it also decreases less over time than in the single chemical sources. Interestingly, the dissolution rate for benzene (i.e., $\frac{dS_p}{dt}$) appears to be converging to the same value for all five cases at long times (see the bottom plot of Figure 8.5.)

Figures 8.6 and 8.7 show the dissolution of toluene and xylene, respectively, from the three cases of NAPL mixtures. The behavior of both of these constituents is similar. Aside from the obvious, the dissolution rate for toluene is much faster, the figures illustrate the effect of the FSMTC relationship as opposed to the effect of competitive dissolution on the rates that each chemical disappear. For
Saturation of first chemical (benzene) at node 200

Saturation of first chemical (benzene) at node 200

Rate of dissolution for Benzene

Figure 8.5: Fractional saturation of benzene in NAPL source for all five cases.
both chemicals, the dissolution rate (the bottom plot) is higher for case p3chem, the one in which there is a greater amount of all three NAPL constituents, than the baseline (3chem). This faster rate is a result both of a larger amount of each chemical in the source as well as the dependence of the FSMTC on the total NAPL saturation. However, in the pv-3chem case, the fractional saturation of toluene and xylene are held constant and only the fractional saturation of benzene increases. Thus the mole fraction (the fraction of toluene as part of the NAPL mixture) decreases yet the dissolution rate still increases. This can only be attributable to the effect of the higher total NAPL saturation on the FSMTC. The same result is seen for the xylene example. On the other hand, this effect is small and only changes the fractional saturation of each chemical (top plot) slightly. The bulk of the increase in the dissolution rate for case 3chem must be attributable to factors other than the FSMTC, since p-3chem and pv-3chem have the same FSMTC.
Figure 8.7: Fractional saturation of xylene in NAPL source for three cases.
8.3 Residual NAPL Source Configuration and Prior Statistics

The estimation approach used for the one-dimensional problem in this thesis required some formulation of prior statistics, mean and covariance, for the estimated states—the NAPL saturation. Likewise, prior statistics are necessary for in a Bayesian formulation of the two dimensional problem. However, actually determining what these statistics should be is quite difficult. For the one-dimensional problem, with its point source, we chose a mean value for each chemical that created what would be a reasonable saturation value. Presumably, one might have some knowledge of the general amount of contaminant spilled/emplaced and could use this to determine a prior mean value. The prior covariance for the same problem was in fact simply variances on each mean value; all cross-covariances were assumed to be zero. While this may have been a fair assumption for the one dimensional estimation problem, in two dimensions there is definitely some spatial structure/correlation in soil properties, and thus one would expect a related correlation structure in NAPL saturations.

The question here is what do NAPL sources look like? Up until this point we have not discussed multiphase flow and the movement of NAPL through the subsurface, and the discussion here is only to note that residual NAPL is present in the path non-residual NAPL has followed. The amount of NAPL that can be held at residual also depends significantly on porous media properties as well as fluid properties. The few field studies that examine the residual NAPL distribution from a spill/source show large heterogeneity in saturations. Heterogeneity in the porous media lead to the development of preferential flow paths for the NAPL (Rivett et al. 1992, Kueper et al. 1993, Broholm et al. 1999). Furthermore, the residual distribution is also affected by the rate of release and length of time of release. Hofstee et al. (1998) found that continuous spills are more likely to enter low conductivity lenses than are pulse spills. Poulsen and Kueper (1992) also found that a dripped release of NAPL resulted in a more extensive area of residual contamination than an instantaneous release of the same amount. Finally, small scale variability in permeability and capillarity also determine the value of residual that may be held by a porous media. In sum, it is very difficult to determine a general extent and distribution of NAPL saturation for use as prior statistics.

On the other hand, the prior statistics we use are a regularization term, a tuning knob of sorts
for the estimator. To that end they need not be completely accurate but rather reasonable and sufficient to restrict the estimator such that it won’t converge to a nonglobal minimum. In the case of NAPL residual saturation, development of a prior is problematic. All along we have been assuming that measurements of residual saturation itself are unavailable, which would imply that prior statistics derived from data for this state are also unavailable. Perhaps the simplest approach to developing the prior would be assuming a uniform mean value for NAPL saturation and using a smooth, easy to use, covariance relationship. The idea of the estimator, after all, is to improve on the prior using the forward model and measurements.

There are other more sophisticated approaches worth mentioning and perhaps including in this work at a future date. First, given time prior statistics could be developed using a Monte Carlo method. This would involve generating realizations of porous medium properties as well as some spill location and duration, perhaps within a zone. These inputs could be used with a multiphase flow model allowed to run until all NAPL is at residual saturation (Essaid and Hess 1993, Hess 1992). However, other researchers have found that use of geostatistical realizations result in more spreading of the NAPL than a realistically structured subsurface data (Whittaker et al. 1999). Second, a correlation model that relates residual saturation to porous media properties could be used to develop a set of prior statistics for residual saturation based on geostatistics of the media properties (e.g., permeability) (Chevalier and Fonte 2000). In the case of Chevalier and Fonte (2000), parameters for the model are fit to sandbox experiment data. Finally, a stochastic analysis could be used to derive the relationship between residual saturation and media properties, as an effective property and/or to derive the extent of NAPL spreading (Jacobs 1999). However, development of a prior mean still requires some judgement about where the source is. Even though the porous media everywhere throughout the model domain could retain a given amount of NAPL at residual, NAPL will only be present where a spill or some other sort of emplacement has occurred.

8.4 Summary

Here at the end of this research, many questions about characterizing NAPL sources remain unanswered. In this section we have only begun to explore some of the most prominent. From the above results, it is clear that the choice of mass transfer coefficient, at any scale, is critical to
model results. Even small changes in this parameter produce very different dissolution scenarios. On the one hand this is somewhat discouraging, since there is so much uncertainty surrounding this parameter. A more optimistic view of the FSMTC would be that this great sensitivity of the model to the parameter suggests its amenability to estimation. Certainly given a known NAPL source (location and strength), an estimator conditioned with dissolved concentrations would likely be able to predict the FSMTC. What is less certain is if the parameter may be predicted with any uncertainty reduction when the source location and strength are also unknown. The sensitivity of the model to the composition of a NAPL mixture, as demonstrated above, is also a promising result for future estimation work. Perhaps the best conclusion for this section is that we have shown dissolved concentrations, the model results, are in fact sensitive to the NAPL source (i.e., different sources and conditions produce notably different results). Clearly more work is needed in the area of NAPL estimation problems; the results of this research suggest such efforts would be fruitful.
Chapter 9

Conclusions

This research explored the possibility of using readily available measurements of dissolved contaminant concentrations to characterize a NAPL source. In a one-dimensional analysis, we approached this task as a state estimation problem, viewing both the dissolved concentrations and NAPL saturations as states that vary over time and space. As a modeling/state estimation method, the research took the following form:

- Our method was based on a stochastic description of subsurface variability. States and parameters were considered to be random variables characterized by means and covariances.
- NAPL dissolution and sorption were modeled as equilibrium processes.
- We used a generalized least-squares performance index to fit predicted state values to measurements while including regularization terms derived from prior statistics for uncertain model parameters.
- We minimized the performance index with an iterative Gauss-Newton algorithm that produces estimates of the states and parameters.
- The algorithm successfully predicted the source strength and location of a point source NAPL mixture.
- Using the estimator, we analyzed the effectiveness of 16 different sampling strategies for a sample source location problem. The Bayesian approach produced a quantitative analysis of
uncertainty reduction enabling direct comparison of the sampling strategies prior to inclusion of measurement data.

The one-dimensional analysis of Chapters 4 and 5 demonstrated that dissolved concentration measurements are sensitive to NAPL source composition and location—sensitive enough to form the basis of an estimation method. In the one-dimensional case, this formulation is computationally cheap enough to allow numerous estimation runs and thus exploration of varying data gathering strategies. At least for the sample problem, we showed that sampling strategies that rely on repeated measurements at the same location can perform as well or better than sampling strategies featuring multiple measurement locations.

We continued this work in two dimensions by developing a model that incorporated a distributed NAPL source. In this model, multicomponent residual NAPL may exist at any node of the model domain.

- We selected a set of state equations that model NAPL dissolution as a first order kinetic process. This produces a mass flux source term for the groundwater transport equation.

- We developed a coupled groundwater flow, NAPL competitive dissolution, dissolved phase transport model code. The basis of the model is fractional NAPL saturation as a continuous spatial property. In and of itself, this model is a useful tool for experimenting with the effects of NAPL source configurations.

- Initial analyses performed with the model illustrate how different NAPL sources produced significantly different dissolved phase results, with different characteristic time scales. We also used the model to show how changes in the NAPL source composition alter the overall dissolution rate and how small changes in the field scale mass transfer coefficient result in large changes in dissolution time.

Ideally, this research would have developed an estimator for the two dimensional system analogous to the one dimensional method. Although we were not able to produce such results in the scope of this thesis, we feel that our formulation is the basis of promising future work, especially in light of the success of similar methods (Reid 1996, Sun 1997, Valstar 2000).
Original Contributions

This research includes original contributions to the field of subsurface NAPL characterization in a few broad categories:

- The one-dimensional estimator accurately predicts NAPL source strength and the location of a point source. The sampling strategy comparison presented in Chapter 5 demonstrates how the estimator may be used to further understand the characteristics of NAPL sources; experiments involving different sources or sampling strategies could certainly be easily accomplished. Any source dissolution and transport situation that might be considered one dimensional (e.g., a column experiment) could also be modeled with the estimator. In a review paper this year discussing the current state of NAPL source knowledge and research needs, Khachikian and Harmon (2000) concludes:

  ‘Classical inverse modeling techniques (Yeh 1986) have not yet been applied to NAPL dissolution scenarios to identify parameters such as location and strength of NAPL sources.’

The work presented in this thesis is one of the first attempts to answer this need.

- Using the estimator, we were able to examine and compare characteristics of sampling design (i.e., location, sampling times, and characteristic scale) and determine the uncertainty reduction resulting from each configuration. Since the posterior covariance (post-measurement uncertainty) is based on the model sensitivity, we analyzed the strategies without actual measurement data. In other words, the estimator uses the prior information to determine the sensitivity of the problem to measurements at different locations and times (at the first iteration). At later estimator iterations, as the guess improves, the model sensitivity is based on the current guess. The sensitivities alone can direct profitable locations and times for further sampling.

- Because of the particular simplifications we used in developing our coupled flow / dissolution / transport model, it simulates field scale NAPL source problems in feasible run times. These characteristics (e.g., only residual NAPL, fully saturated system, simple dissolution rate coefficient) could also be viewed as model limitations. But we believe this model is uniquely formulated to allow analysis of residual NAPL mixtures as distributed sources, something
that would be too cumbersome in a larger more inclusive model. Furthermore, the formulation of the model in terms of fractional saturations rather than masses looks to a larger scale simulation than other models (Mayer and Miller 1996, Frind et al. 1999). Granted our model could benefit from further development, but as conceived it is a quite useful tool for describing NAPL source characteristics. Further sensitivity analyses utilizing this model are discussed below.

In general, inverse modeling of NAPL sources has thus far not relied on dissolved contaminant concentrations (as in this work) but on other measures that are less plentiful (e.g., radon (Semprini et al. 2000), partitioning tracers (Jin et al. 1995)).

**Limitations**

Our approach is based on a number of assumptions and limitations that have been discussed throughout this report. Many of these are simplifications were made to ease the computational burden of the model and estimator. Others were necessitated by a lack of precedent or time to develop new methodologies. Almost all of these limitations represent areas for further research. The primary limitations are:

- Simplification of physical processes: In many places we make assumptions that allow us to represent physical processes in more convenient terms. For example, we assume a steady-state description of groundwater flow that neglects recharge. Additionally, our model of NAPL dissolution is not specifically related to porous media properties, nor does it account for diffusion limited zones (e.g., dead-end pores) within the media. As is often the case with issues of model complexity, it is not clear how crucial these simplifications are to an accurate description of physical reality. Further analysis that compares our models to more sophisticated (and more computationally intensive) models would provide a great deal of insight into the nature of these assumptions.

- Omission of potentially significant processes: The models we have constructed do not address a number of physical processes. For example, chemical reactions and biodegradation are not included in the groundwater transport mode. Inclusion of these processes may or may not improve our representation of reality, but it would most certainly increase the computational
burden on the estimator.

- Form of prior information/covariance structure: The random variables in this analysis (states and parameters) are all described with assumed prior statistics. In some cases (e.g., NAPL saturation) we have no data on which to base the prior. Furthermore, our methodology assumes a Gaussian structure to the random variables. There is no particular reason to believe that this is a correct assumption. Additionally, the estimator as formulated does require prior information in the form of which chemical constituents are present.

- Application to synthetic data: Testing the one dimensional estimation algorithm on synthetic data has both advantages and disadvantages. In a synthetic problem, unlike a field problem, we know the answer that the estimator is trying to find. This allows us to assess the accuracy of the estimator. On the other hand, there is no guarantee that the synthetic data, which after all is generated by the same simplified models we use in the estimator, bear any relation to real field data. One way to address this concern is to generate synthetic data with a more complicated forward model than the one used in the estimator. Another method is to test the estimator with an appropriate set of real field data.

- Incorporation of model error: The current analysis did not incorporate model error in the performance index. This could be a way to account for known processes (e.g., recharge) that are not explicitly included in the model and/or estimation.

- Scope of the problem: We limited the NAPL source problem to a NAPL/water phase system in which NAPL is at residual saturation or less. Much NAPL contamination (especially LNAPL) contamination exists in the unsaturated zone and about the water table. A model/estimation method that represented a three phase system would be desirable. Further, a method that allowed the possibility of NAPL pools would more realistically represent the NAPL characterization problem.

Ideas for Future Work

The state estimation approach developed in this thesis appears to be a promising avenue for NAPL source characterization. In particular, the results presented in Chapters 5, 7, and 8 indicate that there is enough information in available field concentration measurements to use them as the basis for estimation of NAPL sources. The primary difficulties that we experienced had to do with
accurately calculating the necessary sensitivity derivatives in a computationally feasible manner. Exploring different methods of arriving at these derivatives, or even applying a non-gradient based estimation method to our conceptual problem would be a good direction for future research. A wish list of potential research in this area could be quite extensive; here we limit ourselves to what is an extension of the work in this thesis. First and foremost, we would continue the one- and two-dimensional research in this thesis with final development of a discretely formulated estimator based on a variational approach. This approach relies on calculating the adjoint of the forward model, thus a simple model is desirable. A working adjoint approach would provide a computationally cheap method of evaluating the sensitivity derivatives necessary for estimation of the NAPL source. The result would be an estimation algorithm that produces predictions of uncertainty reduction for different configurations of dissolved phase measurements (as in the one-dimensional case) as well as state (NAPL saturation) estimates. Based on initial work on the adjoint approach, we believe that it can be successfully applied to this problem. Another vast area for work is a more robust development of the prior information/prior statistics used in the estimator (this was discussed in Chapter 8). The estimation method could also include other sources of uncertainty (any of the model parameters could be treated as random variables), but most prominently the field scale mass transfer coefficient. This is perhaps the most uncertain of the modeling parameters for the NAPL source problem. However, as mentioned earlier, the more states and parameters estimated, the more computationally expensive and difficult the estimation becomes.

The two-dimensional model itself invites quite a few improvement suggestions. The model would be more useful if it could represent unsaturated systems as well as saturated ones, and certainly extension of the model to three-dimensions would provide a more realistic representation of physical processes (e.g., bypassing). Even in its current state, the coupled flow / dissolution / transport model may be used for sensitivity analyses of many sources of uncertainty in the NAPL problem. Within this work we examined the effect of source geometry, the field scale mass transfer coefficient, and how mixtures behave differently than single component sources. In future work, the model could be used to show the effects of heterogeneity (i.e., of the porous media parameters). As a tool, the model could be used to determine quasi-effective parameters (e.g., velocity) for a heterogeneous system where an analytic result is not available. On the other hand, the simple model developed here is more amenable to inclusion in an estimation method because of its simplicity. A more complex model relies on more measurement and parameter data, and the initial motivation for this
research was a lack of data in NAPL source problems.

As a final note, even a working estimator of the sort described here is unlikely to ever be a workhorse routinely used to assess field sites. In general, inverse methods are difficult to apply—even to 'quasi-linear' groundwater flow problems (Zimmerman et al. 1998). This is even more true for the NAPL problem. The real utility of these methods is as a tool for exploring the behavior of residual NAPL systems and quantifying the relative importance of different parameters and processes. Hopefully the work presented here serves as a foundation toward that eventual end.
### Appendix A

#### Table of Variables and Operators

<table>
<thead>
<tr>
<th>Variables</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>fitting parameter for FSMTC</td>
</tr>
<tr>
<td>$a_s$</td>
<td>cost per chemical sample analysis</td>
</tr>
<tr>
<td>$a_w$</td>
<td>cost per well installation</td>
</tr>
<tr>
<td>$b$</td>
<td>fitting parameter for FSMTC</td>
</tr>
<tr>
<td>$c_{\kappa,i}$</td>
<td>concentration of $i$ in phase $\kappa$</td>
</tr>
<tr>
<td>$c_j^{eff}$</td>
<td>effective solubility for $j$ in water</td>
</tr>
<tr>
<td>$c_j^{sat}$</td>
<td>pure phase saturated solubility for $j$ in water</td>
</tr>
<tr>
<td>$C_y$</td>
<td>state covariance function matrix</td>
</tr>
<tr>
<td>$C_\omega$</td>
<td>measurement error covariance matrix</td>
</tr>
<tr>
<td>$C_\nu$</td>
<td>model error covariance function matrix</td>
</tr>
<tr>
<td>$C_\alpha$</td>
<td>prior parameters covariance matrix</td>
</tr>
<tr>
<td>$D_{\kappa,i}$</td>
<td>dispersion coefficient of $i$ in phase $\alpha$</td>
</tr>
<tr>
<td>$f_{om}$</td>
<td>fraction organic matter</td>
</tr>
<tr>
<td>$F_{\kappa,i}$</td>
<td>advective flux</td>
</tr>
</tbody>
</table>

**UNITS NOTATION:** $D = $ dollars, $M = $ mass, $L = $ length, $T = $ time, $mol = $ moles.

The units notation "varies" indicates a general variable that may represent specific variables of differing units.
### Variables

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h$</td>
<td>hydraulic head</td>
<td>[L]</td>
</tr>
<tr>
<td>$h_c$</td>
<td>specified head</td>
<td>[L]</td>
</tr>
<tr>
<td>$i$</td>
<td>index for species ($n=$chemical, $a=$water, $v=$air, $s=$soil)</td>
<td>-none-</td>
</tr>
<tr>
<td>$I_{\beta,\kappa,i}$</td>
<td>interphase exchange of $i$ from phase $\beta$ to phase $\kappa$</td>
<td>[M/T/L$^3$]</td>
</tr>
<tr>
<td>$I_{\kappa,i}$</td>
<td>total interphase exchange of $i$ into phase $\kappa$</td>
<td>[M/T/L$^3$]</td>
</tr>
<tr>
<td>$I_{\kappa}$</td>
<td>total interphase exchange into phase $\kappa$</td>
<td>[M/T/L$^3$]</td>
</tr>
<tr>
<td>$j$</td>
<td>index for NAPL chemical ($n$)</td>
<td>-none-</td>
</tr>
<tr>
<td>$J$</td>
<td>performance index</td>
<td>-none-</td>
</tr>
<tr>
<td>$J_A$</td>
<td>performance measure for accuracy</td>
<td>-none-</td>
</tr>
<tr>
<td>$J_C$</td>
<td>performance measure for cost</td>
<td>[D]</td>
</tr>
<tr>
<td>$k$</td>
<td>estimation iteration index</td>
<td>-none-</td>
</tr>
<tr>
<td>$k_{rw}$</td>
<td>relative permeability</td>
<td>-none-</td>
</tr>
<tr>
<td>$K$</td>
<td>hydraulic conductivity</td>
<td>[L/T]</td>
</tr>
<tr>
<td>$K_{d,j}$</td>
<td>sorption coefficient for chemical $j$</td>
<td>[$M/L^3$]</td>
</tr>
<tr>
<td>$K_{om}$</td>
<td>organic matter partitioning coefficient</td>
<td>[$M/M^3$]</td>
</tr>
<tr>
<td>$L$</td>
<td>end-point of 1-D problem domain</td>
<td>[L]</td>
</tr>
<tr>
<td>$m_j$</td>
<td>moles of $j$ in NAPL phase</td>
<td>[moles]</td>
</tr>
<tr>
<td>$M_{\kappa,j}$</td>
<td>mass in $V_T$ of $j$ in phase $\kappa$</td>
<td>[M]</td>
</tr>
<tr>
<td>$mw$</td>
<td>molecular weight</td>
<td>[M/mol]</td>
</tr>
<tr>
<td>$n_e$</td>
<td>effective porosity</td>
<td>[L$^3$/L$^3$]</td>
</tr>
<tr>
<td>$N_\alpha$</td>
<td>number of parameters</td>
<td>-none-</td>
</tr>
<tr>
<td>$N_\beta$</td>
<td>number of phases</td>
<td>-none-</td>
</tr>
<tr>
<td>$N_\kappa$</td>
<td>number of phases</td>
<td>-none-</td>
</tr>
<tr>
<td>$N_j$</td>
<td>number of chemicals constituents</td>
<td>-none-</td>
</tr>
<tr>
<td>$N_i$</td>
<td>number of species (air, water, soil, chemicals)</td>
<td>-none-</td>
</tr>
<tr>
<td>$N_e$</td>
<td>number of equations</td>
<td>-none-</td>
</tr>
</tbody>
</table>

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<table>
<thead>
<tr>
<th>Variables</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_t )</td>
<td>number of time steps</td>
</tr>
<tr>
<td>( N_x )</td>
<td>number of spatial steps</td>
</tr>
<tr>
<td>( N_y )</td>
<td>number of discrete states</td>
</tr>
<tr>
<td>( N_z )</td>
<td>number of measurements ((N_z = N_{zz} + N_{zt}))</td>
</tr>
<tr>
<td>( N_{zz} )</td>
<td>number of measurement locations</td>
</tr>
<tr>
<td>( N_{zt} )</td>
<td>number of measurement times</td>
</tr>
<tr>
<td>( p )</td>
<td>measurement index</td>
</tr>
<tr>
<td>( Q )</td>
<td>flux of water through the 1-D source ([L^3/T])</td>
</tr>
<tr>
<td>( q )</td>
<td>groundwater flow ([L/T])</td>
</tr>
<tr>
<td>( R_j )</td>
<td>retardation factor of chemical ( j )</td>
</tr>
<tr>
<td>( s_j )</td>
<td>sorbed concentration ((\text{mg chemical/mg organic matter})) ([M/M])</td>
</tr>
<tr>
<td>( S_a )</td>
<td>water saturation ([L^3/L^3])</td>
</tr>
<tr>
<td>( S_j )</td>
<td>NAPL fractional saturation of chemical ( j ) ([L^3/L^3])</td>
</tr>
<tr>
<td>( S_n )</td>
<td>total NAPL saturation ([L^3/L^3])</td>
</tr>
<tr>
<td>( S_r )</td>
<td>residual NAPL saturation ([L^3/L^3])</td>
</tr>
<tr>
<td>( t )</td>
<td>time dimension ((\text{days})) ([T])</td>
</tr>
<tr>
<td>( u )</td>
<td>model forcing function vector</td>
</tr>
<tr>
<td>( v_\kappa )</td>
<td>velocity of phase ( \kappa ) ([L/T])</td>
</tr>
<tr>
<td>( V_n )</td>
<td>volume of NAPL in control volume ([L^3/L^3])</td>
</tr>
<tr>
<td>( V_p )</td>
<td>volume of pore spaces in control volume ([L^3/L^3])</td>
</tr>
<tr>
<td>( V_v )</td>
<td>volume of voids in control volume ([L^3/L^3])</td>
</tr>
<tr>
<td>( V_T )</td>
<td>total volume ([L^3])</td>
</tr>
<tr>
<td>( x )</td>
<td>spatial dimension ([L])</td>
</tr>
<tr>
<td>( x_s )</td>
<td>location of point source in 1-D problem ([L])</td>
</tr>
<tr>
<td>( y )</td>
<td>model state vector</td>
</tr>
<tr>
<td>( z )</td>
<td>measurement vector</td>
</tr>
</tbody>
</table>

*UNITS NOTATION:* \( D = \text{dollars}, M = \text{mass}, L = \text{length}, T = \text{time}, \text{mol} = \text{moles}.*

*The units notation "varies" indicates a general variable that may represent specific variables of differing units.*

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### Variables

<table>
<thead>
<tr>
<th>Variable</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>$z_s$</td>
<td>measurement half saturation constant -varies-</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>model parameter vector -varies-</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>phase index (NAPL=n, vapor=v, aqueous=a, solid=s) -none-</td>
</tr>
<tr>
<td>$\chi_j$</td>
<td>mole fraction of constituent $j$ in NAPL mixture [mol/mol]</td>
</tr>
<tr>
<td>$\gamma_j$</td>
<td>activity coefficient of constituent $j$ in NAPL mixture [mol/mol]</td>
</tr>
<tr>
<td>$\vartheta$</td>
<td>dispersive flux [M/T/L$^3$]</td>
</tr>
<tr>
<td>$\beta$</td>
<td>phase index (NAPL=n, vapor=v, aqueous=a, solid=s) -none-</td>
</tr>
<tr>
<td>$\eta_{\kappa,i}$</td>
<td>mass fraction of $i$ in phase $\kappa$ [M/M]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>field scale mass transfer rate coefficient [1/T]</td>
</tr>
<tr>
<td>$\theta_{\kappa}$</td>
<td>volume fraction of phase $\kappa$ [L$^3$/L$^3$]</td>
</tr>
<tr>
<td>$\rho_{\kappa}$</td>
<td>volume averaged density of phase $\kappa$ [M/L$^3$]</td>
</tr>
<tr>
<td>$\rho_{\text{mw}}$</td>
<td>weighted averaged molar density [mol/L$^3$]</td>
</tr>
<tr>
<td>$\rho_1$</td>
<td>lag one correlation coefficient -varies-</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>standard deviation -varies-</td>
</tr>
<tr>
<td>$\nu$</td>
<td>process/model error vector -varies-</td>
</tr>
<tr>
<td>$\omega$</td>
<td>measurement error vector -varies-</td>
</tr>
</tbody>
</table>

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### Operators

- **A**: state equation operator
- **A_c**: state equation for chemical mass in the dissolved phase
- **A_s**: state equation for chemical mass in the sorbed phase
- **A_m**: state equation for chemical mass in the NAPL phase
- **B**: boundary conditions for state equation
- **F**: forward operator
- **G**: model error operator
- **I**: initial conditions for state equation
- **M**: measurement operator

**UNITS NOTATION:** $D = \text{dollars}$, $M = \text{mass}$, $L = \text{length}$, $T = \text{time}$, $\text{mol} = \text{moles}$.

The units notation "varies" indicates a general variable that may represent specific variables of differing units.
Appendix B

Forward Model Solution

This Appendix provides the details of the numerical solution to the distributed NAPL model state equations formulated in Chapter 7. In the rest of this Appendix, we call this solution the forward model, although technically the forward model also includes the measurement equations presented in Chapter 7. The forward model consists of discrete forms of the state equations along with a solution algorithm. Since the state equations are all non-linear, the state solution must either solve the state equations iteratively, linearize the state equations, or both. In all cases this forward model solution approaches the non-linearities with an iterative approach. This Appendix first derives the coupled discrete state equations based on a fully-implicit in time finite element discretized in space formulation and then describes the solution method.

B.1 Approach to Discretization

Both the forward model and estimation algorithms are solved on a regular triangular grid that alternates direction by row and column. The discretization in the x- and y-directions is not required to be equal, but is equal for many of the simulations. Each grid element is made up of three nodes identified in counter-clockwise order by a node number and global spatial coordinates. The elements are numbered sequentially by column in order to keep computational bandwidth to a minimum. The model grid is fully described by two matrices: 1) a coordinate matrix that contains the list of
global node numbers and coordinates, and 2) an incidence matrix that contains the list of elements
and nodes that make up the elements. In describing the discretized state equations, we refer to the
local node numbers for each element as 1, 2, 3, with corresponding coordinates \((x_1, y_1)\), \((x_2, y_2)\),
and \((x_3, y_3)\) (see Figure B.1).

The finite element formulation minimizes the residual of an equation (e.g., the groundwater flow
equation) multiplied by some weighting function. The equation is approximated (or discretized) by
a series of trial functions/basis functions. In the Galerkin method, the weighting function chosen
is the same as the basis function used for discretization. The minimization of the residual at each
node \(i\) over the domain \(D\) for the continuous operator \(\mathcal{F}\) is:

\[
R_i = \int_D \phi_i \mathcal{F}[f(x,t)] \, dA
\]

(B.1)

where \(\phi_i\) is the weighting function at node \(i = 1, 2, \ldots N_n\). In the discrete form of the state equa-
tion, the distributed parameters and/or states are represented as a sum of basis functions and
corresponding parameters. For the distributed state \(f(x,t)\):

Figure B.1: Triangular element with local area coordinates.
\[ f(x, t) \approx \hat{f}(x, t) = \sum_{j=1}^{N_n} \phi_j(x) \hat{f}^j(t) \]  

(B.2)

where \( \hat{f}(x, t) \) is the basis function approximation to the state \( f(x, t) \), and \( \hat{f}^j(t) \) is a spatially discrete value at node \( j = 1, 2, \ldots N_n \). When the basis function expansion is substituted into the residual equation the equation becomes:

\[ R_i(t) = \int_D \phi_i(x) \sum_{j=1}^{N_n} \phi_j(x) \hat{f}^j(t) dA \]  

(B.3)

The domain can alternatively be split into elements, and the basis functions integrated over each element:

\[ R_i(t) = \sum_{N_e} \int_E \phi_i(x) \sum_{j=1}^{N_n} \phi_j(x) \hat{f}^j(t) dA \]  

(B.4)

The forward model solution uses linear basis functions, shown in Figure B.1. Over the triangular element, the linear basis function \( \phi_j \) is a plane that equals one at node \( j \) and equals 0 at all other nodes. Thus the basis function \( \phi_j \) only has a non-zero value within elements comprised partly of node \( j \), and the integral of the basis functions over each element is only dependant on the three local nodes that comprise the element, \( i, j = 1, 2, 3 \). So for a given element, the integral evaluation produces 9 potential cases of node values for \( i \) and \( j \), or a local element patch of the coefficient matrix:

\[
\begin{bmatrix}
\int_E \phi_1 \phi_2 \hat{f} dA \\
\int_E \phi_1 \phi_3 \hat{f} dA \\
\int_E \phi_2 \phi_3 \hat{f} dA
\end{bmatrix}
\]  

(B.5)
Figure B.2: Linear triangular basis functions.

The linear triangular basis functions expressed mathematically are:

\[
\begin{align*}
\phi_1 &= \frac{1}{2} A_n [(x_2 y_3 - x_3 y_2) + (y_2 - y_3) x + (x_3 - x_2) y] \\
\phi_2 &= \frac{1}{2} A_n [(x_3 y_1 - x_1 y_3) + (y_3 - y_1) x + (x_1 - x_3) y] \\
\phi_3 &= \frac{1}{2} A_n [(x_1 y_2 - x_2 y_1) + (y_1 - y_2) x + (x_2 - x_1) y]
\end{align*}
\]  

(B.6)

over the element described by local nodes 1, 2, 3. \(A_n\) is the area of the triangular element calculated as:

\[
A_n = \frac{1}{2} \det \begin{bmatrix} 1 & 1 & 1 \\ x_1 & x_2 & x_3 \\ y_1 & y_2 & y_3 \end{bmatrix}
\]  

(B.7)

The basis function have the property \(\phi_1 + \phi_2 + \phi_3 = 1\) and \(dA = 2A_n d\phi_1 d\phi_2\). By substituting out \(\phi_3\), the \(x - y\) integral is replaced with a basis function integral which may easily be evaluated.
\[ \int_{E} f(\phi_1, \phi_2, \phi_3) \, dA = 2A_n \int_{\phi_1=0}^{1} \int_{\phi_2=0}^{1-\phi_1} f(\phi_1, \phi_2) \, d\phi_1 \, d\phi_2 \quad (B.8) \]

The evaluation of such integrals for piecewise linear basis functions is presented in a very accessible way by (Celia and Grey, 1992):

\[ \int_{E} \phi_1^a \phi_2^b \phi_3^c \, dA = 2A_n \frac{a! \, b! \, c!}{(a + b + c + 2)!} \quad (B.9) \]

for \( a, b, c > 0 \).

Since these basis functions are linear space (i.e., in \( x \) and \( y \)) the gradient of the basis function is a constant dependant only upon the element coordinates:

\[
\begin{align*}
\nabla \phi_1 &= \frac{1}{2} A_n [(x_3 - x_2) + (y_2 - y_3)] \\
\nabla \phi_2 &= \frac{1}{2} A_n [(x_1 - x_3) + (y_3 - y_1)] \\
\nabla \phi_3 &= \frac{1}{2} A_n [(x_2 - x_1) + (y_1 - y_2)]
\end{align*}
\quad (B.10)
\]

Equations (B.8) and (B.10) are the identities that will be used in the remainder of this Appendix to develop the discretized state equations for the distributed NAPL model.

Now that we have achieved spatial discretization, we turn to solving the state equations in time. To this end we use backwards finite difference/fully implicit scheme. This form is more difficult to solve than the fully explicit discretization, but is stable over a larger range. The general form of the fully implicit discretization in time is:
\[ \frac{df}{dt} = A(f)f + B(f) \]
\[ f^{t+1} - f^t = \Delta t(A^{t+1}f^{t+1} + B^{t+1}) \]  
(B.11)
\[ f^{t+1} = \{I - \Delta tA^{t+1}\}^{-1}\{f^t + \Delta tB^{t+1}\} \]

Note that in this example (as in the forward model) the coefficient matrices are dependent on the states. Thus the fully implicit discretized state equations are nonlinear in the states and must be solved iteratively. We use a simple Picard iteration:

\[ f^{n+1} = [I - \Delta tA^n]^{-1}[f^{t-1} + \Delta tB^n] \]
\[ f^n = f^{n+1} \]  
(B.12)

At each iteration \((n)\) solve for \(f^{n+1}\) using coefficient values based on \(f^n\). Reset \(f^n\) to \(f^{n+1}\) and continue until some convergence criterion is met \((f^n - f^{n+1}) < tol\). The Picard iteration is a somewhat naive solution method and has the potential to converge badly. In the case of the distributed NAPL forward model, it appears to be a sufficient solution method. Alternatives are gradient based methods (e.g., Newton-Raphson) and/or linearization techniques (e.g., Runge Kutta).

### B.2 The Flow Model

The flow model solves steady-state homogeneous groundwater flow equation as given in Chapter 7:

\[ \nabla \{K(S_a, x)\nabla h(x)\} = 0 \]  
(B.13)

Both the hydraulic head \(h\) and hydraulic conductivity \(K\), are nodal values in this formulation,
and potentially vary in space. The hydraulic head is the unknown value, thus we discretize it over the problem domain. Hydraulic conductivity is known, insofar as we make it a function of a nominal water saturation value. It would be computationally easier to treat the hydraulic conductivity as an elemental value, but since it is a function of $S_a$ which is itself a nodal value, we use a nodal $K$. Thus we have basis function expansions for both distributed variables in the finite element discretization:

$$h(x) \approx \hat{h}(x) = \sum_j \phi_j(x) \hat{h}^j$$

$$K(x) \approx \hat{K}(x) = \sum_l \phi_l(x) \hat{K}^l$$

(B.14)

where $\hat{h}^j$ and $\hat{K}^l$ are discrete values of head and conductivity, respectively, at locations $j$ and $l = 1, 2, ..., N_n$. Substitution of these approximations into the residual equation yields:

$$R_i = \int_D \phi_i \sum_l \sum_j \left\{ \nabla \hat{K}^l \phi_l (\nabla \hat{h}^j \phi_j) \right\} dA$$

(B.15)

for each node $i = 1, 2, ..., N_n$ over the 2-dimensional problem domain $D$. After applying Green's theorem to the second order derivative, the expression becomes:

$$R_i = \sum_l \sum_j \int_D \phi_i \nabla(\phi_j \hat{h}^j) \nabla(\phi_l \hat{K}^l) dA$$

$$+ \sum_l \sum_j \int_{\Omega} \left\{ \phi_i \hat{K}^l \phi_l \nabla(\hat{h}^j \phi_j) \right\} \cdot \hat{n} ds$$

$$- \sum_l \sum_j \int_D \nabla(\phi_i \hat{K}^l \phi_l) \nabla(\hat{h}^j \phi_j) dA$$

(B.16)

where $\Omega$ is the domain boundary. The boundary integral term (i.e., the second integral) is equal to the water flux across the boundary, $q_b$. This term could be included on the right hand side
of the matrix equation and used for specified flux boundary conditions. In this model, however, we assume either a no-flow \( q_b = 0 \) or a specified head condition on the boundaries, so the term becomes zero and drops out completely.

The integration of this equation over the model domain is equal to the sum of the integrations over each element, \( E \). Thus the equation may be re-stated in terms of local element nodes. After applying the chain rule and collecting and canceling terms, the residual expression becomes:

\[
R_i = \sum_{N_e} \left\{ \sum_i \sum_j - \nabla(\phi_i) \nabla(\phi_j) \hat{h}^2 \hat{K}^{ij} \left( \int_E \phi_i \, dA \right) \right\} = 0 \tag{B.17}
\]

Within each element, \( N_e \), the nodes \( i, l, \) and \( j = 1, 2, 3 \) generate nine potential cases for this equation. However, the element integral is only a function of \( \phi_l \), so in all cases \( \int_E \phi_l \, dA = \frac{A_e}{3} \). The matrix equation for each element (in local node numbers) is then:

\[
\begin{bmatrix}
(\nabla \phi_1)^2 & \nabla \phi_1 \nabla \phi_2 & \nabla \phi_1 \nabla \phi_3 \\
\nabla \phi_2 \nabla \phi_1 & (\nabla \phi_2)^2 & \nabla \phi_2 \nabla \phi_3 \\
\nabla \phi_3 \nabla \phi_1 & \nabla \phi_3 \nabla \phi_2 & (\nabla \phi_3)^2
\end{bmatrix}
\begin{bmatrix}
\hat{h}_j^i = 1 \\
\hat{h}_j^i = 2 \\
\hat{h}_j^i = 3
\end{bmatrix} = 0
\tag{B.18}
\]

expressed succinctly as:

\[
Lh = 0 \tag{B.19}
\]

Along with the set of boundary conditions this is the discretized state equation presented in Chapter 7. This equation is solved for hydraulic head at each model time step (as the saturation field changes). Based on the results, flow and velocity fields are calculated (linearly interpolated) and used in the dissolution and transport models. Solution of the model as a whole is discussed late in this Appendix.
B.3 The Dissolution Model

While the flow and transport modules use the finite element method to discretize spatial derivatives, the dissolution model contains no spatial derivatives. In this case the model equation is solved at each grid location \( i \). The state equation developed in Chapter 7:

\[
\frac{\partial S_j}{\partial t} + \mu S_a \left[ \frac{c_{j_{sat}} \gamma_j}{\rho_{mw} w_j} S_j - \frac{c_j}{\rho_j} \right] = 0
\]

(B.20)

\[ c = 1, 2, \ldots N_c \]

becomes:

\[
\frac{dS_j^i}{dt} + \mu^i S_a \left[ \frac{c_{j_{sat}} \gamma_j}{\rho_{nw} w_j^i} S_j^i - \frac{c_{a,j}}{\rho_j^i} \right] = 0
\]

(B.21)

All variables are nodal values as is consistent with the rest of the model. We solve this non-linear ordinary differential equation in time as a fully-implicit finite difference/backwards Euler discretization:

\[
\left[ I + G(S_j^{i+}) dt \right] S_j^{i+} = S_j^i + K(S_j^{i+}, c_{i+}^{i+}) dt
\]

\[
G(S_j^{i+}) = \mu^i S_a \frac{c_{j_{sat}} \gamma_j}{\rho_{nw} w_j^i}
\]

\[
K(S_j^{i+}) = \mu^i S_a \frac{1}{\rho_j^i}
\]

(B.22)

The superscript \( i \) represents the grid node location, the + indicates the value is at the new time, and absense of the + indicates the value at the old time. So \( S_j^{i+} \) is the value of the NAPL saturation at time = \( t + 1 \), while \( S_j^i \) is the value at the old time = \( t \), both at node \( i \). \( I \) is the identity matrix. Note that both coefficient matrices \( G \) and \( K \) are dependant upon the new state \( S_j^{i+} \), since their components \( S_a, \rho_j, \) and \( \rho_{nw} \) are all dependant on the NAPL saturation. This is the discretized
dissolution equation as presented in Chapter 7. This nonlinear equation is solved at each time step using a Picard iteration method.

### B.4 The Transport Model

We use a standard approach to contaminant transport modeling, from the advection dispersion equation derived in Chapter 7:

\[
R_j S_a n_e \frac{\partial c_j}{\partial t} - \nabla \cdot (S_a n_e D_j \nabla c_j) + (S_a n_e v) \nabla c_j - (S_a n_e \mu) (c_j^{\text{eff}} - c_j) = 0 \quad (B.23)
\]

as above:

\[
c_j^{\text{eff}} = c_j^{\text{nat}}, \gamma_j \frac{\rho_j S_n j}{n w j \rho_{m w}} \quad (B.24)
\]

The velocity and dispersion fields are given from the flow model, and the value for the effective solubility can be calculated from the saturation values output from the dissolution model. The unknowns in this equation are the dissolved concentrations, \(c_j\). The states, \(c_j\), \(c_j^{\text{eff}}\), and \(S_a\) as well as the parameter \(\mu\) are nodal values, while the velocity \((v)\), the dispersion \((D)\), the retardation factor \((R_j)\), and the porosity \((n_e)\), are all elemental values. In this case the Galerkin technique utilizes the basis function substitutions:

\[
\hat{c}_j(x) = \sum_k \phi_k(x) \hat{c}_j \quad (B.25)
\]

\[
\hat{S}_a(x) = \sum_l \phi_l(x) \hat{S}_{al}
\]

\[
\hat{c}_j^{\text{eff}}(x) = \sum_m \phi_m(x) c_j^{\text{eff}} m
\]
At node $i$, the residual equation over the problem domain becomes:

$$R_i = \int_D \phi_i(x) [(\partial \frac{\partial c_j}{\partial t}) - \nabla (S_{a ne} D_j \nabla c_j)]$$

$$+ (S_{a ne} \nu \nabla c_j) - S_{a ne} \mu_{c_j}^{eff} + S_{a ne} \mu_{c_j}^{eff}] dA$$

(B.26)

The residual at each node is set equal to zero and the basis function relationships are substituted into the residual error equation. As we did earlier in this appendix, the integrals are split into a sum of integrals over each element. The notation $i, k, l, m, \ldots = 1, 2, 3$ refers to the three nodes that comprise the element:

$$R_i = \sum_{N_e} \sum_{k} \sum_{l} \phi_i \phi_j \phi_k \phi_l \frac{dc_j}{dt} dE$$

$$- \sum_{N_e} \sum_{k} \sum_{l} \phi_i \nabla (S_{a ne} \phi_j D_j \nabla (\phi_j c_j^k)) dE$$

$$+ \sum_{N_e} \sum_{k} \sum_{l} \phi_i \phi_j \phi_k \phi_l \mu_{c_j}^{eff} \phi_m dE$$

$$- \sum_{N_e} \sum_{k} \sum_{l} \phi_i \phi_j \phi_k \phi_l \mu_{c_j}^{eff} \phi_m dE$$

(B.27)

After evaluating the integrals and simplifying, the first term becomes:
\[
\sum_{N_e} \frac{R_{j}^{E} n_{e}^{E} A_{n}^{E}}{60} \begin{bmatrix}
6 & 2 & 2 \\
2 & 2 & 1 \\
2 & 1 & 2 \\
\end{bmatrix}
\begin{bmatrix}
S_{a}^{l=1} \\
S_{a}^{l=2} \\
S_{a}^{l=3} \\
\end{bmatrix}
\begin{bmatrix}
2 & 2 & 1 \\
2 & 6 & 2 \\
1 & 2 & 2 \\
\end{bmatrix}
\begin{bmatrix}
S_{a}^{l=1} \\
S_{a}^{l=2} \\
S_{a}^{l=3} \\
\end{bmatrix}
\begin{bmatrix}
2 & 1 & 2 \\
1 & 2 & 2 \\
2 & 2 & 6 \\
\end{bmatrix}
\begin{bmatrix}
S_{a}^{l=1} \\
S_{a}^{l=2} \\
S_{a}^{l=3} \\
\end{bmatrix}
\frac{dc_{j}^{k}}{dt}
\]

or

\[
B \frac{dc_{j}}{dt}
\]

(B.28)

The same general method is applied to the second term. This term includes a second derivative, so to simplify we also apply Green’s theorem. The boundary terms drop out for our given boundary conditions (see Chapter 7). After simplification, the second term becomes:

\[
\sum_{N_e} n_{e}^{E} D_{a,j}^{E} A_{n} \sum_{l} S_{a}^{l} \begin{bmatrix}
\nabla \phi_{1} \\
\nabla \phi_{2} \\
\nabla \phi_{3} \\
\end{bmatrix}
\begin{bmatrix}
\nabla \phi_{1} & \nabla \phi_{2} & \nabla \phi_{3} c_{j}^{k} \\
\end{bmatrix} = F^{1} c_{j}
\]

(B.29)

Again following the same procedure, the third term becomes:

\[
\sum_{N_e} \frac{n_{e}^{E} v_{E} A_{n}}{12} \begin{bmatrix}
2 & 1 & 1 \\
1 & 2 & 1 \\
1 & 1 & 2 \\
\end{bmatrix}
\begin{bmatrix}
S_{a}^{l=1} \\
S_{a}^{l=2} \\
S_{a}^{l=3} \\
\end{bmatrix}
\begin{bmatrix}
\nabla \phi_{1} \\
\nabla \phi_{2} \\
\nabla \phi_{3} \\
\end{bmatrix} c_{j}^{k} = F^{2} c_{j}
\]

(B.30)

The fourth term becomes:
Finally, the fifth term is similar to the first term:

\[
\frac{nE_{\mu E}A}{30} \begin{bmatrix}
6 & 2 & 2 \\
2 & 2 & 1 \\
2 & 1 & 2
\end{bmatrix} \begin{bmatrix}
S^{l=1}_{a} \\
S^{l=2}_{a} \\
S^{l=3}_{a}
\end{bmatrix}
\begin{bmatrix}
2 & 2 & 1 \\
2 & 6 & 2 \\
1 & 2 & 2
\end{bmatrix} \begin{bmatrix}
S^{l=1}_{a} \\
S^{l=2}_{a} \\
S^{l=3}_{a}
\end{bmatrix}
\begin{bmatrix}
2 & 1 & 2 \\
1 & 2 & 2 \\
2 & 2 & 6
\end{bmatrix} \begin{bmatrix}
S^{l=1}_{a} \\
S^{l=2}_{a} \\
S^{l=3}_{a}
\end{bmatrix}
\cdot c_{j}^{3} = F^{3}c_{j} \quad (B.32)
\]

With like terms combined \((F^{1} + F^{2} + F^{3} = F)\), the final discretized transport equation is as presented in Chapter 7:

\[
B \frac{dc_{j}(t)}{dt} = [c_{j}(t)F + H]
\quad (B.33)
\]

Finally, we again discretize in time with a fully implicit finite difference method:
\[ B - F(S_j, S_a, \mu)\Delta t|c_j^+ = Bc_j + H(S_j, S_a, \mu)\Delta t \] (B.34)

Note that the dissolution and transport equations are nonlinearly coupled. Again we use a Picard type approach to iteratively solve the two sets of equations pseudo-simultaneously.

B.5 Numerical Solution

The general algorithmic procedure for the forward model was discussed in Chapter 7. In sum, for each time step the model runs in a loop (until convergence) of the flow module, the dissolution module, and the transport module. Additionally, the dissolution module itself is run iteratively to convergence. We developed the model in the MATLAB environment, later compiling to C code.

The model requires a number of inputs. First a finite element grid is necessary. Two input files, one of node coordinates and one comprised of the grid incidence matrix (i.e., which nodes are in which elements) are required. The flow model takes a matrix of nodal transmissivity values and elemental porosity values as inputs. The flow module is completed with input boundary conditions. Both the dissolution and transport modules rely on an input file of chemical properties: molecular weight, density, organic matter partitioning coefficient, and pure phase aqueous solubility. Additional soil properties (i.e., fraction of organic carbon, bulk density, dispersivity (as a matrix)) are also required for the transport module. The transport module requires boundary condition inputs for specified concentration boundaries (the upgradient perpendicular to flow boundary in this model configuration).

Finally, the entire model must be initialized with the initial condition of each state, \( c_j \) and \( S_j \) at each node.

Outputs of the forward model include, of course, the states \( c_j \) and \( S_j \) at each node and time step. Additional outputs are the groundwater flow field at each time step, the effective solubility at each node and time step, and the total normalized model convergence error at each time step.


Reid, L., 1996: A functional inverse approach for three-dimensional characterization of subsurface contamination, PhD thesis, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA.


Sun, C., 1997: A stochastic approach for characterizing soil and groundwater contamination at heterogeneous field sites, PhD thesis, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA.


