CHARACTERIZATION, DISSOLUTION, AND ENHANCED SOLUBILIZATION OF
MULTICOMPONENT NONAQUEOUS PHASE LIQUID IN POROUS MEDIA

by

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DEDICATION

This manuscript is dedicated to my beautiful wife Julie who has loved, encouraged, and supported me through the process of completing my degree.
TABLE OF CONTENTS

LIST OF ILLUSTRATIONS......................................................... 8

ABSTRACT.................................................................................. 9

CHAPTER 1. INTRODUCTION. ......................................................... 11
  1.1. Research Statement.......................................................... 11
  1.2. Objectives........................................................................... 13
  1.3. Literature Review.............................................................. 14
    1.3.1. NAPL Compositional Dependence on Physical Properties, Phase
           Distribution, and Mobilization........................................... 14
      1.3.1.1. NAPL occurrence in porous media................................. 15
      1.3.1.2. NAPL Distribution and Constitutive Relationships.......... 17
      1.3.1.3. NAPL Mobility in the Subsurface................................. 23
      1.3.1.4. NAPL Physical Property Changes with
                Composition.................................................................. 28
  1.3.2. Multicomponent NAPL Dissolution Processes..................... 34
    1.3.2.1. Introduction to Remediation by NAPL Dissolution............ 34
TABLE OF CONTENTS - *Continued*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3.2.2</td>
<td>The Local Equilibrium Assumption</td>
<td>35</td>
</tr>
<tr>
<td>1.3.2.3</td>
<td>Rate-Limited NAPL Dissolution</td>
<td>37</td>
</tr>
<tr>
<td>1.3.2.4</td>
<td>Remediation of Multicomponent NAPL by Dissolution</td>
<td>43</td>
</tr>
<tr>
<td>1.3.2.5</td>
<td>Remediation of NAPL with Enhanced Solubilization</td>
<td>53</td>
</tr>
<tr>
<td>1.3.2.6</td>
<td>Multicomponent NAPL Solubility Enhancement</td>
<td>68</td>
</tr>
<tr>
<td>1.3.3</td>
<td>Additional Uncertainty and Needs for Future Research</td>
<td>76</td>
</tr>
<tr>
<td>1.4</td>
<td>Overview of Format</td>
<td>78</td>
</tr>
</tbody>
</table>

CHAPTER 2. PRESENT STUDY                                      81

REFERENCES.                                                88

APPENDIX A: Compositional Effects on the Physical Properties and Partitioning Behavior of a Diesel-PCE Nonaqueous Phase Liquid Mixture. 106

APPENDIX B: Multicomponent NAPL Dissolution 1: Steady State Cyclodextrin Enhanced Solubilization and Raoult's Law Behavior. 144

APPENDIX C: Multicomponent NAPL Dissolution 2: Transient Mass Transfer Limitation and Cyclodextrin Enhanced Solubilization 187
LIST OF ILLUSTRATIONS

Figure 1. Cyclodextrin structure and apolar cavity diagram. .......................... 64
ABSTRACT

Multicomponent nonaqueous phase liquids (NAPL) contaminating the subsurface can significantly inhibit remediation. One method of enhancing the rate of remediation of NAPL constituents, compared to pump-and-treat, involves source zone treatment with enhanced solubilization agents (ESAs) including cyclodextrins. Equilibrium cyclodextrin enhanced solubilization of simple 1, 2, and 3 component NAPL mixtures was examined to evaluate the applicability of Raoult’s Law. The results suggest that Raoult’s Law may be used to estimate equilibrium and early-time dynamic concentrations in contact with ideal NAPL mixtures, and Raoult’s Law may be used to estimate cyclodextrin enhanced groundwater concentrations for ideal NAPL mixtures. Solubility enhancement of NAPL compounds was dependent on the cyclodextrin concentration and independent of NAPL composition. Column experiments and numerical modeling were used to evaluate the dissolution behavior of the NAPL mixtures in water and a cyclodextrin solution to estimate mass transfer rates. The aqueous multicomponent dissolution followed Raoult’s Law, and the model-estimated lumped rate coefficients were independent of the NAPL composition. Addition of the cyclodextrin enhanced the dissolution and removal of compounds from residual NAPL due to an increase in the driving force (i.e. concentration gradient) and the mass transfer coefficient. The model results suggest that Raoult’s Law is applicable for ideal NAPL mixture dissolution in water, but potential nonideality was observed and caused the model simulation to deviate from the dissolution behavior for NAPL mixture cyclodextrin experiments. The cyclodextrin dissolution experiments were less rate-limited than aqueous
dissolution, and the mass transfer coefficients were quantified with the model. The results of the model suggest that NAPL mixture nonideality and intra-NAPL diffusion may also impact enhanced dissolution behavior. Additionally, the importance of NAPL mixture characterization was illustrated by evaluation of a mixture of PCE (tetrachloroethene) and diesel fuel collected from a site in Tucson, Arizona. A sample from the site was used to create mixtures with increasing PCE in the NAPL. Chemical evaluation of the complex NAPL was conducted, and physical property and phase partitioning testing was performed, which demonstrated the effect of NAPL composition on its distribution, interphase mass transfer, and potential mobilization.
CHAPTER 1. INTRODUCTION

1.1. Research Statement

Groundwater has become an important source for drinking water supply, and the cleanup, or remediation, of contaminated groundwater is continuing to be a significant problem for society. The contamination of groundwater by hazardous organic chemicals and the associated risk to humans and the environment have become issues of great importance over the last few decades. Much of the research motivated by subsurface contamination has been focused on dissolved, or adsorbed, constituents in aqueous systems. It is now clear that organic immiscible liquid in the subsurface occurs in the environment at numerous contamination sites, and compounds contained in petroleum fuels are some of the most frequently discovered contaminants at U.S. Environmental Protection Agency Superfund sites (Boulding, 1995). In addition, a majority of fuel stations experience a loss of fuel from leaks related to a variety of processes including improper installation, corrosion of storage tank/pipe materials, or consolidation and compaction of soils after installation.

Over the time period that the leak occurs, some volume of immiscible liquid, or nonaqueous phase liquid (NAPL), introduced into the subsurface becomes trapped in the porous medium. The trapped, or immobile, NAPL may only be displaced from the porous medium with anomalously high pore-water velocities that do not generally occur in groundwater systems (Wilson and Conrad, 1984; Willhite, 1986; Hunt et al., 1988). Hence, the primary means of NAPL contamination removal from groundwater systems has been dissolution of the compounds making up the NAPL into water, which are then transported
from the porous medium to the ground surface (via groundwater pumping) for treatment of the contamination. Dissolution can be defined as the transfer of chemicals from their original phase (i.e. NAPL) to a dissolved state in the contacting solution, which is generally water in groundwater systems. The residual volume of immobile NAPL at groundwater contamination sites, therefore, serves as the long-term source of groundwater contamination due to the amount of time required to dissolve all of the contaminant mass contained in the immiscible liquid (NAPL) phase. The typically low water solubilities (although generally above regulatory standards) of NAPL compounds suggests that decades of pumping may be required to remove the contamination from the subsurface by dissolution into water (NRC, 1994). According to the National Research Council, the presence of NAPL is the single most important factor limiting site cleanup (NRC, 1994).

It is now widely accepted that accurate risk assessment and design of effective remediation systems cannot be made without a full understanding of the mechanisms controlling NAPL dissolution (Mercer and Cohen, 1990; Miller et al., 1990; Bedient, 1991; Powers et al., 1991; Khachikian and Harmon, 2000; Oostrom et al., 2006). The bulk of the literature on this topic concerns mass transfer from a single-component NAPL into water, which has contributed greatly to our understanding of NAPL-contaminated sites. However, many hazardous waste sites contain multiple-component NAPLs (Mercer and Cohen, 1990; Borden and Kao, 1992; Luthy et al., 1994; Lee et al., 1999). Thus, further advances in the behavior of multicomponent NAPLs are required in support of groundwater remediation investigations.
1.2. Objectives

The body of research described in this document includes the evaluation of groundwater contamination processes and remediation techniques related to multicomponent NAPL contamination in groundwater systems at the pore scale. The general purpose of this research is to increase our understanding of the sources of groundwater contamination and processes that may be used to improve the remediation of multicomponent NAPL contaminated sites. The overall goal of the research is to enhance our understanding of the dissolution of multiple-component NAPLs in subsurface systems. The specific objectives include:

1. Evaluating NAPL mixture compositional effects on NAPL physical properties, partitioning between phases, and contamination distribution;

2. Investigating the effects of NAPL composition-dependent factors on dynamic dissolution of multicomponent NAPLs in saturated porous media;

3. Investigating the effect of NAPL composition and mass-transfer limitations on the enhanced dissolution of multicomponent NAPL caused by an innovative source zone remediation enhanced solubilization agent (ESA).

The goal of this research was to investigate the effects of compositional factors on the physical properties, phase partitioning, and kinetic mass-transfer limitations of dissolution of organic NAPL mixtures into groundwater and an ESA. ESA injection into source zones of contamination is an innovative remediation technique that may be used in
combination with groundwater pumping and above ground treatment (or pump and treat) to increase the efficiency of remediation. ESA compounds increase the groundwater solubility of hydrophobic chemicals contained in NAPL source zones, which increases the rate at which NAPL containing chemicals can be extracted from groundwater systems. Very little has been done to develop our understanding of the processes controlling dissolution of NAPL mixtures in the presence of ESAs (Khachikian and Harmon, 2000). To adequately characterize the human-health risks associated with such contamination, and to design effective remediation projects, it is essential that we gain a better understanding of the dissolution of multi-component NAPLs.

1.3. Literature Review

1.3.1. NAPL Compositional Dependence on Physical Properties, Phase Distribution, and Mobilization

Much of our understanding of NAPL contamination, multiphase distribution, and groundwater remediation has been borrowed from the petroleum industry and associated fields of research (Lake, 1989). The production of oil from groundwater saturated geologic formations is directly analogous to the remedation of immiscible NAPL from contaminated groundwater systems. Lake (1989), Cohen and Mercer (1993), and Pankow and Cherry (1996) all provide general background on the theory of multiphase flow, NAPL distribution in porous media, and NAPL mobilization.
1.3.1.1. NAPL occurrence in porous media

Nonaqueous phase liquid (NAPL) is a broad term used for any organic liquid that is immiscible with water (Pankow and Cherry, 1996). The most common NAPL is petroleum and its distillates. However, the term is also used to describe industrial solvents (trichloroethene or TCE and tetrachlorothene or PCE), polychlorinated biphenols or PCBs, wood preservatives such as creosote, and coal tar (Cohen and Mercer, 1993). There has been significant interest in the behavior of NAPL in the subsurface, since the discovery that chemical spills of these liquids can cause contamination of groundwater used for drinking water, and that many of the chemicals that make up these NAPLs are believed to be carcinogenic (Pankow and Cherry, 1996). The presence of NAPL in porous media such as groundwater aquifers has been found to be a source for long-term contamination of drinking water supplies. Additionally, a principle objective of the remediation of groundwater contamination should be the identification, characterization, and cleanup of the sources of contamination.

In general, NAPL is considered to be immiscible with water, which means that NAPL and water do not mix together as a single phase. However, the chemicals that make up the NAPL may have some ability to transfer, or partition, into water (Schwarzenbach, Gschwend, Imboden, 1993; Cohen and Mercer, 1993; Pankow and Cherry, 1996). The maximum amount that they can dissolve into water, which is the aqueous solubility, may be quite low compared to inorganic compounds such as salts. However, most NAPL compounds have solubilities that are quite high compared to aqueous drinking water
regulatory standards. NAPLs commonly contain toxic compounds with regulatory standards far below aqueous solubilities (NRC, 1994).

NAPLs are generally distinguished based on their density relative to the density of water. There are dense (DNAPL) and light (LNAPL) nonaqueous phase liquids that are more or less dense than water, respectively (Pankow and Cherry, 1996). Chlorinated solvents, such as TCE and PCE, are examples of DNAPLs, and petroleum distillates are examples of LNAPLs. LNAPLs tend to be detected after a spill, because they can occur as a floating product in wells. Similarly, LNAPLs tend to float on the groundwater table forming a lense of immiscible liquid on top of the water table. The LNAPL lense may tend to move with the elevation of the water table, which tends to smear the vertical distribution of the LNAPL in the aquifer (Pankow and Cherry, 1996).

DNAPLs are more dense than water, and do not float on top of the water table, unless immobilized by capillary forces. If ample DNAPL is spilled, it will displace the groundwater table, and sink into an aquifer. DNAPLs will migrate through the subsurface unless it encounters a less permeable porous media (e.g. fine silt, clay, or bedrock) that it cannot invade. Therefore, DNAPL source zones may be difficult to locate and characterize in groundwater systems (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

NAPL may enter the subsurface through a variety of processes. It can be spilled at the ground surface and then infiltrate through the soil to eventually meet with groundwater. It can be placed in storage tanks or pits, which have a potential to leak. It can be pumped directly into the subsurface through wells. NAPL is generally believed to enter the ground
from the surface by infiltration. Generally, NAPL migrates vertically through the unsaturated zone, where present, above the water table and comes in contact with the groundwater, assuming enough NAPL is spilled to allow migration to the water table. A minor fraction of NAPL spilled is generally retained along its flow path, called residual saturation (Cohen and Mercer, 1993; Pankow and Cherry, 1996). Additionally, compounds from the NAPL may become distributed through partitioning into the gas and water phases, and many compounds contained in NAPLs have been observed to adsorb to the solid surfaces of most porous media. Although NAPL, soil gas, and groundwater are considered immiscible phases, mass transfer of compounds may occur between any or all phases, which increases the distribution and extent of the contamination (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

1.3.1.2. NAPL Distribution and Constitutive Relationships

Once in the subsurface, NAPL forms a spatial distribution in the network of pore spaces in between the grains of the soil or aquifer system (Cohen and Mercer, 1993). If water and air are also present, they share a section of the pore spaces. The NAPL, water, and air all distribute themselves within the pores. This multiphase fluid system may be static or dynamic, but the movement of each phase may depend on all other fluids in the system (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

NAPLs present in the subsurface at contaminated sites provide long-term sources of groundwater contamination and may significantly limit the effectiveness of groundwater
remediation (NRC, 1994). Gasoline and diesel fuel are examples of light non-aqueous phase liquids (LNAPLs) (Kechavarzi, et al., 2005). They are also multicomponent NAPLs, because they are composed of many different compounds with very different chemical and physical properties. NAPL introduced into the subsurface becomes trapped at residual saturations (the percent of pore space occupied by LNAPL) due to capillary forces, and may not be capable of being displaced even with increased velocities due to pumping (Wilson and Conrad, 1984; Lake, 1989; Pennell et al., 1996).

Numerical models may be used to simulate multiphase flow to predict NAPL distributions in the vadose zone, which may improve our ability to characterize the contamination distribution and test remediation alternatives (Kechavarzi, et al., 2005). Modeling multiphase flow requires the coupling of fluid flow equations for each fluid contained in the porous medium, because the flow of each fluid depends on the other fluids. Parameterization and development of constitutive relationships for pressure (P) and saturation (S) is generally a source of uncertainty in 2 (air and water) or 3 (air, water, and NAPL) phase systems. Multiphase flow models require not only the input data for the material properties, but they also require the constitutive relationships that describe how the fluids distribute themselves in the porous media (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

Generally, the fluid contents are defined in terms of the fraction of the total void volume (Vv is the void volume for a bulk porous medium) occupied by each fluid, which ranges from 0 to 1 where 1 is the total porosity. The fluid saturations are:
\[ S_w = \frac{V_w}{V_v} \]  
\[ S_{nw} = \frac{V_{nw}}{V_v} \]  
\[ S_w + S_{nw} = 1 \]

where \( V_w \) and \( V_{nw} \) are the volumes of wetting and nonwetting fluids, respectively, and \( S_w \) and \( S_{nw} \) are the relative volumes of wetting and nonwetting fluids (Cohen and Mercer, 1993).

Wettability describes the relative ability for a fluid to coat the porous media in a multiphase immiscible fluid system. It is the preferential spreading ability of a fluid on a specific solid surface, which may be the grain surfaces of a groundwater aquifer (Mercer and Cohen, 1990). Generally, we consider water to be the wetting phase in water and air systems and water and NAPL systems. NAPL is considered an intermediate in wettability between water and air. There may be some aquifers that have relatively nonpolar aquifer material surfaces, possibly containing high organic matter, that would be preferentially wet by NAPL instead of water (Mercer and Cohen, 1990).

The contact angle, a measure of fluid wettability, is the angle a liquid makes with the solid phase when immersed in another immiscible fluid. It is a property of both the fluid and the solid phase, and it is dependent on the interfacial tension between the fluids. The contact angle is a measurement of the wettability of the solid (i.e. porous media) by the liquid. Generally, a system is water wet if the contact angle is less than approximately 70 degrees, and the system is considered NAPL wet if the contact angle is greater than approximately 110 degrees. Porous media has been found to be water wet with some exceptions such as Dolomite, Limestone, or high organic matter aquifer materials that do not carry a significant
surface charge (Craig, 1971; Anderson, 1986a; Mercer and Cohen). Capillary pressure is defined as the pressure difference across the fluid interface. Capillary pressure causes porous media to wick in the wetting fluid and displace the nonwetting fluid (Bear, 1988; Cohen and Mercer, 1993). The capillary pressure ($P_c$) is defined as the difference between nonwetting ($P_{nw}$) and the wetting ($P_w$) pressures:

$$P_c = P_{nw} - P_w = \frac{(2 \sigma \cos \theta)}{r}$$

where $\sigma$ is the interfacial tension, $\theta$ is the contact angle with the medium, $r$ is the radius of the pore. The capillary pressure must be overcome for a nonwetting NAPL to enter the largest pores of a water saturated porous media, which is also known as the threshold or displacement entry pressure (Cohen and Mercer, 1993).

Traditional conceptualization of multiphase flow conceptualizes porous media as a bundle of capillary tubes that develop a bulk saturation in response to a bulk capillary pressure (wetting phase pressure subtracted from non-wetting phase pressure), which is a function of the pore size distribution and the interfacial tension. NAPL forms a spatial distribution of saturations in the network of pore spaces in between the soil or aquifer grains. If water and air are also present, they share a section of the pore spaces. The NAPL, water, air all distribute themselves within the pores, and contribute to the overall fluid saturation. The distribution of phases is dependent on the capillary pressure difference between the phases, which suggests that it is dependent on the physical properties of the fluids and the medium. A significant body of research has been produced in the hydrology and soil physics fields evaluating, measuring, and predicting the pressure versus saturation relationships in
Several mathematical functions have been developed to describe the multiphase constitutive relationships that have been observed to occur. van Genuchten (1980) developed a closed form relationship for the prediction of the constitutive relationship for the water-air system in agricultural soils. Then, Parker and others (1987) extended the general form of the van Genuchten model for any 2 phases:

$$\bar{S} = \frac{(S - S_m)}{(1 - S)} = \left[1 - (\alpha h)^{\frac{1}{n}}\right]^{-m} \tag{5}$$

where $S_m$ is the residual saturation, $h$ is the capillary pressure for each two phase system, and $\alpha$ and $n$ are fitting parameters ($m = 1 - (1/n)$). Parker et al. (1987) used the constitutive model to predict pressure versus saturation relationships for NAPL, water, and air two phase systems. The fitting parameters were estimated for each set of phases.

Researchers have also extended the van Genuchten form of the constitutive relationships to the three phase immiscible system. The three phase model for the pressure versus saturation relationship generally assumes that NAPL is an intermediate in wettability between water and air (Kechavarzi et al., 2005). For most NAPLs, surface and interfacial tensions make them intermediate between water and air for wettability. Therefore, NAPL is non-wetting compared to water and wetting compared to air. We might expect the water to wet the medium, NAPL to wet the water (i.e. NAPL not in contact with the medium), and air to wet the NAPL (i.e. air not in contact with water). Recent investigations have been able to collect images of NAPL in 2 and 3 phase systems (Schnaar and Brusseau 2005; 2006;
Brusseau et al., 2006).

Extension of two phase relationships to three phase systems (air, water, and NAPL) assumes interfacial tensions at the interface between the continuous gas and liquid phases are independent of the number and the proportions of liquids (Kechavarzi et al., 2005). Total liquid saturation depends on capillary pressure between air and NAPL, and water saturation depends on capillary pressure between NAPL and water. Three phase saturations are:

\[
S_{w}^{aow} = S_{w}^{aow}(h_{ow}) \tag{6}
\]

\[
S_{t}^{aow} = S_{w}^{aow} + S_{o}^{aow} = S_{o}^{aow}(h_{ao}) \tag{7}
\]

where the notation \(aow\) is for the 3-phase system containing air, oil (NAPL), and water.

\[
\overline{S}_{t}^{aow} = \left[1 - (\alpha_{ao} h_{ao})^{n}\right]^{-\frac{1}{n}} \tag{8}
\]

and

\[
\overline{S}_{w}^{aow} = \left[1 - (\alpha_{ow} h_{ow})^{n}\right]^{-\frac{1}{n}} \tag{9}
\]

The average saturation is calculated for water and total liquid (the difference is the NAPL saturation) using the two phase pressures \((h_{ow} \text{ and } h_{ao})\) and fitting parameters \((\alpha \text{ and } n)\).

The phenomena in which a process depends on the previous history of the process is called hysteresis. It is known to occur in multiphase immiscible systems in intermediate saturation ranges, which complicates the prediction of constitutive relationships (Kechavarzi et al., 2005). The effect of changes in pressure on saturation can be very different if the changes are occurring as an imbibition or drainage process. Hysteresis is created by a
combination of pore processes including saturation of variable pore sizes, pathway (imbibition or drainage) dependent residual saturations, and non-wetting fluid entrapment (Lenhard et al., 2004).

The extension of the constitutive model to account for hysteresis involved the definition of apparent saturation to account for non-wetting fluid entrapment, which is defined as the sum of the effective saturation of a continuous phase and the effective saturation of any other entrapped fluid (Kechavarzi et al., 2005). The NAPL infiltration hysteresis is dependent on the history of saturation, the effective saturation of the entrapped fluid, the effective saturation of the wetting fluid, and the saturation path reversal (Lenhard, 1992). The constitutive relationships for hysteretic systems vary for imbibition and drainage, and fitting parameters ($\alpha$ and $n$) are required for each set of phases for both the imbibition and drainage curves.

1.3.1.3. NAPL Mobility in the Subsurface

The previous sections described the dependence of the pressure versus saturation constitutive relationships on the fluid properties such as the interfacial tension between each immiscible fluid. The capillary pressure impacts the distribution of phases and, therefore, the relative volume of NAPL retained in the porous media. However, the NAPL distribution at the pore scale is also related to the morphology of the NAPL phase. Several excellent review papers and books provide background on NAPL contamination in groundwater systems and previous research describing the remediation of NAPL source zones (Mercer
Residual saturation is the term used to describe the immobile NAPL content in porous media when the saturation remains constant after drainage or displacement (Mercer and Cohen, 1990). Residual saturation tends to form as NAPL moves along the flow path, which tends to reduce the volume of mobile NAPL as the residual is spread out along the zone through which the NAPL moved. Residual saturations occur when NAPL becomes trapped in porous media due to capillary forces, and it tends to vary between 0.1 and 0.2 (Mercer and Cohen, 1990). The amount of NAPL retained at residual saturation depends on the properties of the NAPL, the porous media, heterogeneity, and the flow system (Miller et al., 1998). Mercer and Cohen (1990) suggest that the occurrence and amount of residual NAPL saturation depends on the pore size distribution, fluid wettability, fluid viscosity to density ratio, interfacial tension, gravity and buoyancy forces, and the hydraulic gradient. NAPL distributions at higher saturations are generally mobile, but they may become immobile depending on the hydraulic system. Some examples of high saturation zones are
a LNAPL free product lenses trapped above a water table and a DNAPL spill that collects at the contact of a aquifer above a lower permeability aquitard. These high saturation NAPL distributions are called pools (Pankow and Cherry, 1996).

Entrapment of NAPL at residual saturation is believed to occur within two conceptual frameworks termed snap-off and flow bypassing (Chatzis et al., 1983). Snap-off entrapment of NAPL occurs in high aspect ratio pores. The water is believed to flow along the sides of pores (water wet systems). Instead of moving behind the NAPL and displacing the NAPL as a piston, the water flows around the NAPL body and enters the next pore throat before the NAPL is displaced, which forms a preferential path of water around the NAPL. The bypassing entrapment is believed to occur in a pore structure represented by a pore doublet model (Chatzis et al., 1983), and should not occur when pores have similar throats on both sides. When one arm of the doublet pore is smaller than the other, the displacing water will bypass the NAPL in the larger doublet pore.

Previous studies have shown that NAPL mobilization in the subsurface is governed by the balance of the viscous, gravitational, and capillary forces (Larson et al., 1981; Dawson, 1997). Feenstra and Cherry (1988) have suggested that NAPL migration and entrapment is affected by the NAPL source volume, the area of infiltration, the time of release, the properties of the NAPL, the properties of the porous media, and the groundwater flow regime. Once entrapped, NAPL can only be mobilized if the gravitational force or viscous force of flowing water is large enough to surpass the capillary force that immobilizes the NAPL body. Mobilization potential depends on the geometry of the pore network, the
interfacial tension between the NAPL and water, the fluid density difference, the wettability of the porous medium, and the applied hydraulic gradient. Entrapped residual NAPL will remain immobile as long as capillary forces dominate. These forces are generally evaluated in terms of capillary and bond numbers (Larson et al., 1981). NAPL mobilization potential can be evaluated in terms of the capillary and bond numbers. The capillary number is the ratio of the viscous force to the capillary force (Ng et al., 1978; Morrow and Songran, 1981; Wilson and Conrad, 1984). The capillary number \( N_{ca} \) can be calculated from:

\[
N_{ca} = \frac{k \rho g \Delta H}{\gamma \cos \theta} = \frac{\gamma \mu}{\gamma \cos \theta}
\]

(10)

where \( k \) is the intrinsic permeability, \( g \) is gravitational acceleration, \( \Delta H \) is the hydraulic head gradient, \( v \) is the velocity, \( \mu \) is the viscosity, \( \theta \) is the contact angle, and \( \gamma \) is the interfacial tension (Dawson, 1997). The \( N_{ca} \) evaluates the potential for NAPL to become mobilized due to velocities of groundwater, which may be applicable to a groundwater pumping remediation system. However, Larson et al. (1981) found that NAPL displacement began at \( N_{ca} \) of \( 2 \times 10^{-5} \), which can be considered high for most groundwater systems.

Bond number represents the ratio of gravitational forces to viscous forces that affect fluid trapping and mobilization. In fact, the bond number is the ratio of the gravitational force to the capillary force (Morrow and Chatzis, 1981). The bond number \( N_{bo} \) can be calculated from:
where \( \Delta \rho \) is the density difference between the immiscible fluids, \( g \) is gravitational acceleration, \( k \) is the intrinsic permeability, and \( n \) is the porosity (Dawson, 1997). Increases in \( N_{Bo} \) relate to increased potential for NAPL vertical mobilization due to gravitational forces.

The total trapping number \( (N_T) \) combines the entire force balance evaluated in the \( N_{ca} \) and \( N_{Bo} \) number analysis. Pennell et al. (1996) produced a general equation for \( N_T \) that may be used to evaluate the potential for NAPL mobilization in all flow directions:

\[
N_T = \left( N_{ca}^2 + 2N_{ca}N_{Bo} \sin \alpha + N_{Bo}^2 \right)^{0.5}
\]  

(12)

where \( \alpha \) is the angle the flow makes with the horizontal (counter-clockwise). Pennell et al. (1996) also conducted laboratory experiments to evaluate the forces required to mobilize trapped NAPL. They found that PCE mobilization began when \( N_T \) values were between \( 2 \times 10^5 \) and \( 5 \times 10^5 \), and complete displacement was observed as \( N_T \) reached approximately \( 1 \times 10^3 \).

Hydraulic conductivity is a measure of the ability of a media to transmit fluid that is dependent on the properties of the fluid and the media. If the fluid properties are known, then the media properties can be estimated from the hydraulic conductivity. NAPL mixture hydraulic conductivities may be calculated from density and viscosity variations, based on
estimates of hydraulic conductivity for water. The intrinsic permeability \( k \) can be calculated from the hydraulic conductivity \( K \):

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

The NAPL-mixture hydraulic conductivity could then be calculated for variations in density and viscosity due to compositional changes. Fluid specific conductivities are variable in multiphase systems. Some NAPLs such as PCE have greater densities and lower viscosities than water, which means that they have a greater conductivity than water for a given porous media (Mercer and Cohen, 1990). Relative permeabilities may be calculated as a fraction of the phase-saturated permeability. In general, the relative permeability for each phase decreases with that phase’s saturation. In multiphase systems, the permeability is less than it would be for the single phase flow.

The previous sections discussed the constitutive relationships that describe NAPL distribution, the physical processes that lead to NAPL mobility, and the physical properties that affect the distribution and mobilization of NAPL. This leads to the discussion of how the variations in composition impact the NAPL bulk physical properties that determine the NAPL distribution and mobility potential.

1.3.1.4. NAPL Physical Property Changes with Composition

The NAPL physical properties that impact the mobilization based on the calculations
of Bond and Capillary Numbers are the density, viscosity, interfacial tension, and contact angle (Dawson, 1997). The density of any material is simply the mass divided by the volume, and as previously mentioned some NAPLs are more dense than water and others are less dense than water (Mercer and Cohen, 1990). NAPL densities tend to differ from water by 10 to 50% (Mercer and Cohen, 1990), and Mackay et al. (1985) found that density differences of approximately 1% could influence fluid flow in the subsurface. Densities can also vary with temperature (Sleep and Ma, 1997). For NAPL mixtures, the mass will change depending on the NAPL composition. Therefore, the density is, by definition, dependent on the composition. Different pure NAPLs, such as PCE and TCE, have variations in density. As a multicomponent NAPL changes composition, its density must change, as well (Pfeiffer et al., 2005). Roy et al. (2002) observed remobilization of a pool of NAPL due to compositional changes associated with dissolution.

Ramsburg et al. (2004) recently described the development of a method for displacing NAPL through the modification of NAPL physical properties by altering the chemical composition of the NAPL. Previous research has suggested the application of alcohols to mobilize NAPL. Ramsburg et al. (2004) have suggested (and tested) the application of alcohol to modify the NAPL density and then a surfactant (a chemical added the aqueous solution that partitions to the NAPL-water interface) to reduce interfacial tensions. PCE is a dense (more dense than water) nonaqueous phase liquid (DNAPL). The paper shows that as the alcohol (lighter than water) partitions into the NAPL, the NAPL transitions from a DNAPL to an LNAPL. However, a significant concentration of alcohol
is required to immobilize the NAPL only through density manipulation. Therefore, a surfactant was also applied to reduce the interfacial tension of the NAPL/water, which facilitates NAPL displacement (Ramsburg et al., 2004). We can see from the previous research that changes in NAPL mixture composition can change the bulk NAPL phase density, which can impact the potential for mobilization of NAPL during aging or remediation.

Interfacial tension is the strength (force per unit length) of the film separating two immiscible fluids, which is dependent on the attractive forces between molecules within the liquids (Mercer and Cohen, 1990). Therefore, interfacial tension between NAPL and groundwater tends to vary between NAPLs of different composition and water of different compositions. Interfacial tensions exist at each interface between two immiscible fluids, and surface tension is the term used for the interfacial tension between a liquid and its vapor (Mercer and Cohen, 1990), which is the immiscible gas phase fluid at equilibrium. The surface tension of water at 25 degrees Celsius is 72 dyn/cm. The values for NAPL-water interfacial areas are generally lower (between 15 and 50 dyn/cm). The interfacial tension of NAPLs with groundwater tends to decrease with increasing temperature, and it can also vary with changes in water pH and amounts of gas dissolved in the water (Mercer and Cohen, 1990).

The interfacial tension and contact angle are related by Young’s Equation (Cohen and Mercer, 1993):

\[
\sigma_{s_f_1} = \sigma_{s_f_2} + \sigma_{f_1_f_2} \cos \theta
\]  

(14)
where $\sigma$ represents the interfacial tensions between the solid ($s$) and two fluids ($f_1$ and $f_2$), and the $\theta$, or contact angle (Cohen and Mercer, 1993). Different NAPLs have different interfacial tension values due to the internal chemical structure and forces that are specific to each NAPL compound. Therefore, mixtures of NAPLs with variable compositions have variable interfacial tensions and contact angles.

Previous research has begun to evaluate the behavior of the NAPL-water interface. Barranco et al. (1997) evaluated the variability in NAPL saturation and interfacial tension with changes in aqueous pH and ionic strength, and observed changes up to 10% in capillary pressure due to changes in ionic strength. Ramsburg and Pennell (2002) observed interfacial tension modifications due to butanol dissolution that lead to NAPL mobilization. Additionally, Harrold et al. (2003) found that the modification of NAPL composition (weathering or aging) during infiltration through soils caused changes in the interfacial tension.

Lord et al. (2005) and Seo and McCray (2002) describe interfacial tension and contact angle changes associated with NAPL mixture compositional changes. Lord et al. (2005) evaluated NAPLs containing organic acids and bases. NAPLs are generally considered hydrophobic due to the nonpolar nature of the compounds they contain. However, some NAPLs contain acids or bases, which have some polarity. Lord et al. (2005) found that the acid/base concentrations in the NAPL impacted the interfacial tensions (Lord et al., 2005). The increased concentrations of acid/base compounds decreased the hydrophobicity of the bulk NAPL, which decreased the tension between the NAPL and
water.

Seo and McCray (2002) measured interfacial tensions of chlorinated aliphatic NAPL mixtures as a function of the NAPL composition. Their research (Seo and McCray, 2002) shows the changes in NAPL/water interfacial tensions (and 3 different model predictions) with NAPL composition for trichloroethene (TCE) and tetrachloroethene (PCE) containing mixtures. The authors mention that these changes affect the two and three phase capillary pressure versus saturation relationships, as well as, the NAPL surface area, which has implications for mass transfer between phases during remediation. These previous researchers have shown that the interfacial tension between NAPL and water or NAPL and gas significantly impact the phase distributions, how the saturations change with changes in pressure, and the potential mobilization of trapped NAPL during remediation.

The absolute viscosity is the resistance of a fluid to displacement when a shear stress is applied. Mercer and Cohen (1990) define it as an internal friction derived from molecular attraction within a fluid that creates a resistance to flow. This physical characteristic of liquids tends also be variable for different NAPLs since it is dependent on the molecular attractions. Therefore, the viscosity also changes as different NAPL compounds are mixed together in variable compositions.

A low viscosity NAPL will tend to migrate further than a high viscosity NAPL since it is one of the fluid properties that controls the hydraulic conductivity. Viscous fingering has been observed for NAPLs in unstable displacement systems (Miller et al., 1998). Lunn and Kueper (1999) used a series of alcohol flushes to modify a pooled NAPL’s composition,
density, and viscosity for remediation by mobilization. Jain and Demond (1999) observed viscosity changes in PCE due to surfactant partitioning. Jarsjo et al. (1997) observed compositional affects on the viscosity of Kerosene, and Feja and Rice (1981) also observed changes in viscosity of a NAPL mixture due to composition. In NAPL-water multiphase systems, differences in viscosity can create nonuniform flow systems and phase distributions.

NAPL mixtures (one NAPL phase made up of more than one compound) are commonly encountered at environmental sites. NAPL mixtures may have compositional variations spatially throughout the NAPL distribution (McCray and Brusseau, 1999; Seo and McCray, 2002). Additionally, NAPL mixtures may change in chemical composition through time (Powers et al., 1996). The spatial variability may decrease over time due to diffusion within the NAPL. Otherwise, the NAPL composition may change over time due to various physiochemical processes that alter the NAPL composition such as biodegradation. Also, partitioning of compounds from the NAPL into other phases (air, water, and sorbed solid) tend to decrease concentrations. Remedation processes employed at a site may preferentially remove specific compounds or groups of compounds (McCray and Brusseau, 1999). These changes in composition decrease the concentration of the compound that leave the NAPL and increase the relative concentration of all other compounds left in the NAPL, and these changes may tend to alter not only the chemical but also the physical nature of the bulk NAPL phase (Seo and McCray, 2002). The previous research clearly demonstrates the need for an increased understanding of how multicomponent NAPL composition impacts the
NAPL physical properties and the mobilization potential during remediation.

1.3.2. Multicomponent NAPL Dissolution Processes

1.3.2.1. Introduction to Remediation by NAPL Dissolution

The previous sections describe the entrapment and potential for mobilization of NAPL in porous media, and previous research has confirmed that residual saturations of NAPL require unusually high hydraulic gradients to remediate through multiphase displacement (Wilson and Conrad, 1984; Lake, 1989; Pennell et al., 1996). Therefore, pump and treat remediation designs have been used to control the spread of contamination and remove NAPL constituent mass through dissolution into groundwater. However, the application of pump and treat to clean up NAPL source zones has been found to be extremely ineffective (Begley, 1997; NRC, 1994; Palmer and Fish, 1992).

NAPL source zones can take decades to remediate by dissolution into groundwater through a pump and treat system. Palmer and Johnson (1989) calculated cleanup times for TCE entrapped at a residual saturation of 20% with a soil porosity of 35%, a source zone of 1 cubic meter, and groundwater flow rate of 1.7 cm/day. They found that it would take 15 years with equilibrium dissolution, which suggests much longer cleanup times with rate-limited dissolution. In general, it has been observed that a relatively small amount of NAPL can contaminate large volumes of groundwater, and the resulting cleanup times based on conventional pump and treat methods can be very long (Mackay et al., 1985; Mackay and Cherry, 1989).
1.3.2.2. The Local Equilibrium Assumption

Most attempts to model NAPL-contaminated subsurface systems treat NAPL dissolution into the aqueous phase as an equilibrium inter-phase partitioning process (Abriola and Pinder, 1985; Corapcioglu and Bear, 1987). Design of pump-and-treat remediation systems traditionally assume that predictions for removal of organic pollutants from an aquifer may be based on the principle of equilibrium dissolution (Zheng et al. 1991; Higgens and Byers, 1989). The conceptualization of equilibrium mass transfer is called the “local equilibrium assumption” (LEA), which implies that thermodynamic equilibrium assumed to be instantaneous if the rate of NAPL-groundwater mass transfer is significantly greater than the transport of the dissolved NAPL compounds with groundwater away from the NAPL interface (Pinder and Abriola, 1986; Powers et al., 1994; Chyriskopoulos, 1999). The LEA has traditionally been applied to NAPL dissolution in groundwater systems, because the rate of natural groundwater flow and solute transport is generally considered to be relatively small. There is some previous research to support the applicability of the LEA for NAPL-groundwater remediation systems (Borden and Kao, 1992; Borden and Piwoni, 1992; Brusseau et al., 2000; Brusseau et al., 2002).

However, field data frequently show that groundwater concentrations of NAPL constituents are well below their respective aqueous solubilities (Mackay et al., 1985; Geller and Hunt, 1989; Mackay and Cherry, 1989; Mercer and Cohen, 1990). During pump and treat remediation, contaminant concentrations usually decrease rapidly after initiation of
pumping, then level off at some approximately constant concentration (U.S. EPA, 1989; Harvey et al., 1994). Generally, the approximately constant, or slowly decreasing, concentrations are above remediation limits prohibiting the cleanup and closure of remediation sites. Various processes that can create this behavior and limit the efficiency of pump and treat remediation may include porous media heterogeneities and relative permeability effects, and rate-limited mass transfer between the aqueous and NAPL phases, and NAPL mixture composition effects on the equilibrium aqueous concentrations of the individual constituents (Mackay and Cherry, 1989; Powers et al., 1991).

Groundwater concentrations are rarely observed at, or close to, NAPL compound solubilities even in known source areas. Groundwater concentrations of approximately 10% of the NAPL compound’s aqueous solubility is generally a good indication of the presence of NAPL phase. The observed low concentrations are usually explained by nonuniform flow patterns, dilution by noncontaminated water, heterogeneity of the porous media, heterogeneity of the NAPL distribution, multicomponent NAPL effects, and the mass transfer rate-limitation between NAPL and groundwater at the pore scale (Powers et al., 1991; Powers et al., 1992; Pennell et al. 1993; Brusseau et al., 2000).

Low concentrations of NAPL compounds in groundwater that has been in contact with the NAPL phase suggests that mass transfer limitations impact the dissolution of NAPL compounds into groundwater. The mass transfer rate-limitation impacts on the dissolution of NAPL-ganglia or blobs has been examined by various researchers (Miller et al., 1990; Powers et al., 1991; 1992; 1994a; 1994b; Abriola et al., 1993; Geller and Hunt, 1993;
Illangasekare et al., 1995). Additionally, mass transfer dissolution from NAPL pools has been a topic of previous investigation (Johnson and Pankow, 1992; Chyrskopoulos et al., 1995; Holman and Javandel, 1996; Lee and Chyrskopoulos, 1998; Kim and Chyrskopoulos, 1998; Roy et al., 2002). NAPL pools are generally believed to have smaller surface areas per unit volume, which may increase the mass transfer limitation (Whelan et al., 1994).

1.3.2.3. Rate-Limited NAPL Dissolution

Several review papers have discussed previous NAPL dissolution research (Mercer and Cohen, 1990; Khachikian and Harmon, 2000; Miller et al., 1989). Conceptualization of NAPL contaminated subsurface systems in the past has assumed equilibrium NAPL dissolution (Abriola and Pinder, 1985). However, Pfannkuch (1984) developed a literature review of petroleum mass transfer limitation investigations in groundwater systems. Schwille (1988) and Anderson (1988) performed experiments to evaluate kinetic mass transfer from DNAPLs into groundwater. Additionally, field studies have indicated that concentrations of NAPL compounds are often below their solubilities at high velocities and low residual saturations (Powers et al., 1991). Field-scale processes causing this apparent rate-limited behavior may include heterogeneity, mass transfer between the phases (NAPL, aqueous, or vapor), and dilution effects (Brusseau et al., 2000; Rivett and Feenstra, 2005).

Many researchers have concluded that rate-limited mass transfer is important under certain conditions (Hunt et al., 1988; Brusseau, 1992; Powers et al., 1991; Imhoff et al., 1994). In particular, this appears to be the case when (1) groundwater velocities are high,
(2) NAPL saturations are low, (3) NAPL is distributed as large blobs filling several pores (Hunt et al., 1988; Miller et al., 1990; Powers et al., 1991). Additionally, rate-limited mass transfer may be significant for low mole fraction components of NAPL mixtures (Borden and Kao, 1992). For weathered or aged contaminants, the presence of semi-gelatinous films at the NAPL-groundwater interface may also limit mass transfer (Ramaswami et al., 1994). The overall rate of dissolution is typically determined by the slowest of the following three steps: diffusion of constituents through the NAPL phase, dissolution at the interface, diffusion away from the NAPL-water interface into the bulk water phase.

Powers et al. (1991) produced a theoretical evaluation of NAPL dissolution rates, which showed that the concentration of a contaminant decreases as the volume of the contaminant in the source zone is reduced. Additionally, previous laboratory investigations have observed NAPL dissolution mass transfer becoming rate-limited upon reduction of NAPL saturation during remediation of a contaminated source zone (Imhoff et al., 1994 and 1998; Powers et al., 1994). Zhu, and Sykes (2000) examined the influence of NAPL dissolution characteristics on field scale contaminant transport in subsurface with numerical simulations that demonstrated the significance of dissolution kinetics impacts on groundwater.

Powers et al. (1992) determined that the properties of the porous medium such as pore structure and pore size distribution also has an impact on NAPL dissolution mass transfer limitation. The porous media properties can impact the NAPL volumetric saturation and distribution, which controls the relative NAPL surface area. Additionally, the porous
media properties may impact the groundwater conductivity, flow rate, and velocity, which also impacts the mass transfer.

NAPL dissolution rate-limited mass transfer has also been shown to be dependent on the groundwater velocity. Powers et al. (1992) found that high groundwater flow velocities, which are common to pump and treat remediation systems, would not allow the groundwater and NAPL enough contact time to have mass transfer proceed to equilibrium. This suggests that increases in groundwater velocities due to increased pumping rates will tend to increase the severity of NAPL dissolution rate-limited mass transfer, which would translate into decreased mass removal benefit for a given increase in flow rate.

For rate-limited dissolution of NAPL, it is common to quantify dissolution by using correlations that relate mass transfer kinetics to physical porous-medium properties and aqueous phase advective and diffusive characteristics (Khachikian and Harmon, 2000). Several researchers have used these types of mass transfer correlations along with idealized NAPL blob geometries and distributions for simplified estimations of the NAPL-water interfacial area (Hunt et al., 1988; Powers, 1991; Geller and Hunt, 1993).

The kinetics of NAPL-water mass transfer have been also simulated with a Fick’s Law diffusion approach (Kim and Chrysikopoulos, 1999). Previous researchers have assumed that the mass transfer rates are limited primarily by diffusion of the NAPL constituents through a boundary layer from the immiscible liquid interface to the bulk aqueous phase, which is based on theories developed in the chemical engineering field (Sherwood et al., 1975; Khachikian and Harmon, 2000). Linear driving force mass-transfer
models that account for the diffusion of compounds from an immobile to a mobile zone are categorized as 2-site models (Borden and Kao, 1992). The fraction of mobile and immobile zones and lumped mass transfer coefficients must be estimated from observations (Brusseau, 1992; Hatfield et al., 1993).

Another kinetic mass transfer modeling approach conceptualizes NAPL blobs trapped in porous media by capillary forces to be shaped as spheres, which may be a significant over-simplification of the NAPL morphology (Powers et al., 1994a). However, it does allow for estimation of interfacial areas based on measurements of NAPL volumes. Powers et al. (1992) conducted experiments with the compound Styrene as the NAPL phase. Then it was polymerized to a solid, separated from the porous media, and characterized by grain size analysis. If the NAPL blob sizes can be estimated, then surface areas can also be estimated by assuming a spherical shape, which allows the actual mass transfer rates to be determined from the lumped mass transfer rates (Geller and Hunt, 1993). However, measuring the NAPL-water interfacial areas can be difficult at laboratory scale due to the nonuniform nature of natural porous media and NAPL shapes and distributions (Powers et al., 1991), and field scale determination of NAPL-water interfacial areas is even more of a challenge. Therefore, the lumped mass transfer rate coefficient is generally used (Miller et al., 1990; Imhoff et al., 1993; Powers et al., 1994b; Ji and Brusseau, 1998):

\[ k_L = k_f a_o \]  \hspace{1cm} (15)

where \( k_L \) is the lumped rate coefficient, \( k_f \) is the actual mass transfer coefficient, and \( a_o \) is the NAPL-water specific surface area. Powers et al. (1994b) conducted several experiments that
revealed that the $k_L$ parameter is correlated to a few known or commonly measured properties such as the NAPL volumetric fraction, $\theta_N$, as a surrogate for $a_0$. The lumped rate coefficient for NAPL dissolution also depends on the groundwater velocity (Imhoff et al., 1993), the NAPL distribution (Powers et al., 1992; Imhoff, 1994), properties of the porous medium (Powers et al., 1994b), and the diffusion coefficient of the NAPL constituent in water (Miller et al., 1990; Powers et al, 1992; Imhoff et al., 1993).

Various previous researchers have used empirical correlations of mass transfer coefficients and interfacial areas to measurable properties that are used to estimate changes in mass transfer kinetics over time during NAPL dissolution (Khachikian and Harmon, 2000). Miller et al. (1990) related the kinetics of mass transfer to a power law correlation that contained the dimensionless numbers called Sherwood (Sh), Reynolds (Re), and Schmidt (Sc):

$$S_h = \beta_0 \, R_e^{\alpha_1} \, \theta_N^{\alpha_2} \, S_c^{1/2}$$

where $\theta_N$ (saturation multiplied by the porosity) is the NAPL volumetric fraction and:

$$S_h = \frac{(k_L d_{50})^2}{D_L}$$

$$R_e = \frac{(\nu \rho_w d_{50})}{\mu_w}$$

$$S_c = \frac{\mu_w}{(\rho_w D_L)}$$

where $k_L$ is the lumped mass transfer rate coefficient, $D_L$ is the aqueous diffusion coefficient, $d_{50}$ is the average diameter of the porous media grains, $\nu$ is the pore water velocity, $\rho_w$ is the aqueous density, and $\mu_w$ is the aqueous viscosity.
Then Powers et al. (1992 and 1994b) similarly developed a mass transfer power law correlation based phenomenological model for steady state and then transient mass transfer from immobile residual source zones of NAPL into mobile groundwater. The transient correlation related the transient kinetics to the initial (steady state) mass transfer rate coefficient by the changes in NAPL volumetric fraction and pore water velocity (Powers et al., 1994b):

\[
S'_{h} = \alpha d_{e}^{\beta_{1}} \delta^{\beta_{2}} U_{i}^{\beta_{3}} \left( \frac{\theta_{n}}{\theta_{n0}} \right)^{\beta_{4}}
\]  

(20)

where \( U_{i} \) is the uniformity index \((d_{10}/d_{50}) \), \( \delta \) is a normalized grain size \((d_{60}/d_{m}) \) where \( d_{m} \) is 500 \( \mu \)m, \( \theta_{n0} \) is the initial (steady state) NAPL fraction, \( \theta_{n} \) is the transient NAPL fraction, and the coefficients \( \alpha, \beta_{1}, \beta_{2}, \) and \( \beta_{3} \) were fitted through a correlation for \( 0.012 < R_e < 0.2 \) flow systems (Powers et al., 1992). Then Powers et al. (1994b) estimated the \( \beta_{4} \) coefficient as an unknown by modeling the transient mass transfer kinetics during NAPL source zone dissolution. They discovered that \( \beta_{4} \) values were higher for graded sands than for more uniform soils, and \( \beta_{4} \) appeared to be correlated to the grain size distribution parameters \( \delta \) and \( U_{i} \). There have been various other Sherwood number correlations developed for a variety of specific velocity ranges and NAPL saturations for the dissolution kinetics of NAPL in groundwater systems (Khachikian and Harmon, 2000). However, these correlation equations are empirical models, and were developed for a specific set of conditions, and may have limited applicability beyond the specified conditions.
1.3.2.4. Remediation of Multicomponent NAPL by Dissolution

While some of the most widely studied immiscible liquids are composed of a single component (e.g. TCE), many others (e.g. gasoline, diesel fuel, coal tar, creosote, solvent mixtures) are multicomponent liquids. Knowledge of the dissolution behavior of multicomponent liquids is essential to the prediction of their impact on groundwater quality. The dissolution of NAPL mixture components into water is not only controlled by the aqueous solubility of each component but also the composition of the immiscible liquid. With single component NAPLs mass transfer kinetic rates change over time as the NAPL volume and surface areas change. For multicomponent NAPLs, each component will have a solubility that is dependent on the NAPL composition (McCray and Brusseau, 1998; 1999). Since the mass transfer driving force is dependent on the solubility, the multicomponent NAPL mass transfer rates for each compound may change over time due to the changes in NAPL volume, surface area, and composition (Powers et al., 1994; Borden and Kao, 1992; Priddle and MacQuarrie, 1994). Additionally, interactions between NAPL mixture compounds may create nonideality that would impact the mixture solubilities and rate coefficients (McCray and Dugan, 2001).

In general, chemical compounds, especially organics, tend to distribute, or partition, themselves between different phases (Schwarzenbach et al., 1993). The chemical equilibrium partitioning behavior of a contaminant will indicate the magnitude and number of phases in which the chemical resides (Lee et al., 1998; Lee and Peters, 2004). Mercer and Cohen (1990) define aqueous solubility of a chemical as the maximum concentration that
will dissolve into pure water at a constant temperature, and aqueous solubilities of NAPL compounds vary widely for different chemicals. Observation of aqueous solubility in a water sample is a good indication of the presence of a NAPL phase in contact with the water phase, because the NAPL source allows enough mass to dissolve to attain the solubility (Mercer and Cohen, 1990). However, dissolution of compounds without NAPL can occur through desorption or phase partitioning from the gas phase (Mercer and Cohen, 1990; Schwarzenbach et al., 1993; Heyse et al., 2002; Wang et al., 2003; Broholm et al., 2005). In general, nonpolar, or hydrophobic, compounds have lower solubilities than polar, or hydrophilic, compounds (Schwarzenbach et al., 1993). Solubility may vary due to compound structure/size, temperature, other cosolutes in solution, aqueous salinity, and concentration of dissolved organic matter (Mercer and Cohen, 1990). Powers et al. (1999) provide a review of petroleum compound partitioning theory, cosolvency, and mixture solubility.

Phase partitioning, or solubility, can also be quantified through thermodynamic analysis. Chemical equilibrium is defined by the state where chemical potentials are equal for all components (Schwarzenbach et al., 1993). The chemical potential ($\mu_{i\beta}$) in the $\beta$ phase may be determined from:

$$\mu_{i\beta} = \mu_i^\circ + RT \ln \left( \frac{X_{i\beta} \gamma_{i\beta}}{\alpha} \right)$$

(21)

where $\mu_i^\circ$ is the chemical potential at a reference state, $T$ is the temperature, $R$ is the universal gas constant, $X_{i\beta}$ is the mole fraction of the $i$th compound in $\beta$ phase, and $\alpha_i$ is the
activity coefficient of the \( i \)th compound in \( \beta \) phase (Schwarzenbach et al., 1993). The activity coefficient accounts for potential molar excess free energy related to solute-solvent and solute-solute dissimilarities or interactions that contribute to nonideal effects (Schwarzenbach et al., 1993).

If we designate \( \beta \) with a \( N \) for NAPL and \( \beta \) with an \( A \) for aqueous phases, then chemical equilibrium of a multicomponent NAPL-groundwater system is defined by setting \( \mu_N = \mu_A \) for each compound in the system. Once the chemical potential equations are equated and rearranged, the aqueous mole fraction for each component of a NAPL mixture is:

\[
X_i^A = X_i^o \left( \frac{X_i^N \gamma_i^N \gamma_i^o}{X_i^o \gamma_i^N \gamma_i^A} \right)
\]  

(22)

where the “o” is the designation for the when the component is in its pure phase (single component) in contact with water (Burris and MacIntyre, 1985).

The above expression may be simplified by assuming ideal conditions. The low solubility of most hydrophobic NAPL containing compounds suggests the potential for aqueous phase interactions for the multicomponent system to be identical to the aqueous phase interactions for the single component system (\( \gamma_i^{oA} = \gamma_i^A \)). This assumption suggests that the dissolution of each component in the mixture has an identical effect on the aqueous system as the dissolution of each component from a single pure NAPL (Banerjee, 1984; Burris and MacIntyre, 1985). Due to the typically hydrophobic nature of most common NAPLs, the dissolution of water into NAPL is generally negligible, which allows the \( X_o^N \)
and \( \gamma_i^{oN} \) to both be equal to one, as well. These simplifications lead to:

\[
X_i^A = X_i^{oA} \left( X_i^N \gamma_i^N \right)
\]  

(23)

The aqueous mole fractions can then be converted to units of concentration by multiplying by the molecular weight and dividing by the molar volume of water:

\[
S_i^A = S_i^{oA} \left( X_i^N \gamma_i^N \right)
\]  

(24)

where the aqueous concentration of the ith mixture component at equilibrium with the NAPL is \( S_i^{A} \) and \( S_i^{oA} \) is the solubility, or maximum concentration of that component when dissolving from a pure NAPL composed only of the ith compound.

If the NAPL mixture is composed of chemicals that have a similar size, shape, and structure, then each component will behave as each other component and the bulk NAPL phase (McCray and Dugan, 2001). Additionally, there will be similar interactions between each component. Essentially, the phase partitioning behavior for each compound in the mixture will be identical to behavior when the NAPL is composed of just one compound, except the partitioning is also dependent on each compound’s mole fraction. In this case, the NAPL mixture is considered ideal, and the organic phase activity coefficient \( (\gamma_i^{N}) \) is equal to one for each component (McCray and Dugan, 2001). This assumption leads to the expression known as Raoult’s Law:

\[
S_i^A = S_i^{oA} X_i^N
\]  

(25)

which describes the equilibrium water concentration in contact with ideal NAPL mixtures (Banerjee, 1984; Burris and MacIntyre, 1985; McCray and Brusseau, 1998; 1999).
Raoult’s Law also implies that the more soluble components in a NAPL mixture would generally dissolve first (Lesage and Brown, 1994; Liang and Udell, 1999; McCray and Dugan, 2001; Eberhardt and Grathwohl, 2002). Less soluble components do not tend to undergo significant dissolution until the mole fractions of the highly soluble components are significantly reduced. At this time the mole fraction of the less soluble components increase, along with the component’s rate of mass removal. This multicomponent order of elution may be complicated by variations in the initial mole fraction and activity coefficients. Accurate risk assessments, using each component in the mixture’s toxicity, must depend on the ability to predict this order of elution behavior (Peters et al., 1996; Peters et al., 1996).

Several researchers have observed that, under certain conditions, equilibrium dissolution of components from a NAPL mixture proceeds according to Raoult's Law (Lee et al., 1992a; 1992b; Cline et al., 1991; Burris and MacIntyre, 1985). As mentioned previously, Raoult's Law states that the equilibrium aqueous concentration of a component in a NAPL mixture is the product of the mole fraction of the species in the mixture and the single-component solubility of the species. This law is based on the assumption that the organic-phase activity coefficients are equal to unity, or as discussed in the previous section, the mixture is assumed to be ideal. It is also assumed that the aqueous-phase activity coefficient of a component is not influenced by the presence of other cosolutes in the aqueous phase (Lee and Peters, 2004; Hussam et al., 2005). This is generally valid for dilute solutions (Banerjee, 1984; Lane and Loehr, 1995). The organic-phase activity coefficient
may differ from unity when the components of the mixture exhibit significant variations in hydrophobicity or molecular structure (Banerjee, 1984; McCray and Dugan, 2001). Mixtures of this type are considered non-ideal, and this non-ideality may cause the equilibrium aqueous concentrations of individual species to differ from that predicted by Raoult's Law (McCray and Brusseau, 1999; McCray and Dugan, 2001). Several researchers have noted that ideal behavior was considered to be a reasonable assumption if the groundwater concentrations of NAPL mixture components were predicted by Raoult's Law within a factor of two (Lee et al., 1992a, b; Cline et al., 1991; Mukherji et al., 1997).

There have been some previous investigations that have conducted laboratory experiments that suggest that some NAPL mixtures exhibit nonideal behavior (Lee, 1992b; Rostad et al., 1985; Lesage and Brown, 1991; Borden and Kao, 1992; Whelan et al., 1994). NAPL mixture component nonideality may occur for a variety of reasons. For example, nonideal mixtures may occur when the components of the mixture are significantly different (Banerjee, 1984). These differences could be size, shape, structure, or even chemical composition, and NAPL mixture component activity coefficients may differ from one and each other due to compound specific interactions between different molecules in the mixture and differences in the shapes and sizes of the components (Prausnitz, 1980; McCray et al., 2001). Larger and more hydrophobic molecules will tend to have more difficulty dissolving into the hydrophobic structure of water. Also, NAPL components that are more hydrophilic or have a partially charged functional groups (organic acids and bases) will more readily dissolve into water than hydrophobic compounds. Additionally, specific functional groups
may create interactions between different compounds within the NAPL phase that could impact dissolution. The low mole fraction compounds may have dissolution limitations related to the availability of those compounds in the NAPL, which should result in NAPL mixture activity coefficients that are greater than unity (Banerjee, 1984; Burris and MacIntyre, 1985; Borden and Piwoni, 1992). However, previous studies have not thoroughly investigated the temporal variation in non-ideality as the NAPL depletes, nor the effects of non-ideality on rate-limited mass transfer (Khachikian and Harmon, 2000).

NAPL dissolution experiments performed by several researchers (Borden and Kao, 1992; Borden and Piwoni, 1992; Lesage and Brown, 1994; Whelan et al., 1994; McCray and Brusseau, 1999; McCray and Dugan, 2001) confirm that some multicomponent NAPL mixtures may exhibit non-ideal behavior. For entrapped NAPL, the activity coefficients of individual components, the mole fractions, and even NAPL composition are seldom known. Thus, it is difficult to ascertain the equilibrium aqueous concentrations of any given NAPL component. In a groundwater remediation pumping scenario, with an initially equimolar mixture for example, we would expect the more soluble components to elute first (Lesage and Brown, 1994). Less soluble components may not undergo significant dissolution until the mole fractions of the highly soluble components are significantly reduced, which alters all of the mole fractions and increases mixture solubilities. This "order of elution" is complicated by variations in the initial mole fraction and activity coefficients. Because components in a mixture may exhibit different toxicities, a thorough and accurate risk assessment depends on the ability to predict this type of behavior.
Powers et al. (2001) provide an introduction to the estimation of multicomponent NAPL activity coefficients. The UNIFAC method predicts activities based on compound specific functional groups that make up each compound’s chemistry and structure (Schwarzenbach, Gschwend, and Imboden, 1993). The UNIFAC method may be used to provide a reasonable estimation of solubility in some multicomponent systems. Heermann and Powers (1998) compared three different modeling methods for gasoline component solubility. The comparison of predictions and observations showed that piece-wise linear-log-linear cosolvency model was more accurate than prediction with the UNIFAC method.

Previous research has mainly evaluated mass transfer from a single-component NAPL, even though many hazardous waste sites contain multiple-component NAPLs (Lee and Rao, 1996; Peters et al., 1999; McCray and Brusseau, 1999; Broholm et al., 2005; Tiruta, 2006). However, recent work indicates that multi-component NAPLs can exhibit non-ideal mass transfer, which may increase the rate-limitation (Garg and Rixey, 1999; McCray and Dugan, 2001). As the more soluble components in a mixture dissolve, their concentration in the NAPL mixture will decrease, and the driving force for diffusive mass transfer will also decrease (Powers et al., 1994).

For a NAPL mixture, factors in addition to those mentioned in the previous section may constrain the rate of dissolution. In particular, rate-limited dissolution of a particular component in a NAPL mixture may occur if the mole fraction of the component in the mixture is small (Borden and Kao, 1992; Priddle and MacQuarrie, 1994). The rate-limiting step for dissolution of NAPL is often assumed to be diffusion of an organic species away
from the NAPL-water interface into the bulk aqueous phase (Miller et al., 1990; Powers et al., 1992; 1994a; 1994b). However, for a mixture, it is possible that the diffusion of a constituent within the NAPL to the interface may also be important, especially for the more hydrophobic (or low solubility) constituents. Additionally, as the more soluble components in a mixture are dissolved into the groundwater, their concentration in the NAPL mixture will decrease and the driving force for mass transfer will also decrease (Powers et al., 1994), causing rate-limitations to be more severe. However, as the mole fraction of a NAPL component in a mixture decreases, the component’s activity coefficient may increase (since the mixture may be less ideal with respect to that component), causing an increase in the equilibrium solubility (McCray and Dugan, 2001). Thus, in this instance, the effect of rate-limitations on the aqueous phase concentration could be partially mitigated by the increased multicomponent nonideal equilibrium solubility. Similarly, a more hydrophobic component in the mixture could exhibit less severe rate-limitations due to increases in mole fraction as more soluble components partition to the aqueous phase.

Work conducted by Borden and Kao (1992) and Priddle and MacQuarrie (1994) suggests that there may be a correlation between the mass transfer coefficient and mole fraction, although no detailed work has been completed to determine the extent or importance of such a relationship (Khachikian and Harmon, 2000). It seems apparent that the extent of rate-limitation on dissolution will depend on mole fraction. However, two components with different hydrophobicities in an otherwise identical mixture (ideal mixture with equal mole fractions) may show different degrees of rate-limitations. As mentioned
previously, the effect of varying hydrophobicity between components is accounted for by the organic phase activity coefficients of the individual components (Schwarzenbach, Gschwend, and Imboden, 1993). Based on this discussion, it is possible that the mass transfer of a component in a NAPL mixture may be correlated to the activity coefficient for that component, as well as to mole fraction.

Mass transfer from residual NAPL is considered to be limited by boundary layer diffusion from the NAPL-water interface to the bulk water (Miller et al., 1990; Powers et al., 1992; 1994a; 1994b; Khachikian and Harmon, 2000). For multicomponent systems, the diffusion processes occurring during mass transfer include the boundary layer water diffusion and the NAPL phase diffusion within the bulk NAPL phase to the boundary (Ortiz et al., 1999; Heyse et al. 2002; Tolsche et al., 2003). The literature has not clearly elucidated which of these processes is the limiting step defining the kinetics of multicomponent NAPL dissolution mass transfer rates (Khachikian and Harmon, 2000).

As a multicomponent NAPL dissolves compounds into water, the composition of the NAPL constantly changes. Initially, the composition change may be small. However, over time the NAPL bulk phase may become limited with respect to the compound (Totsche et al., 2003), and the compound may need to diffuse through the bulk NAPL to reach the boundary prior to dissolving. This intra-NAPL diffusion increases with decreasing NAPL mixture mole fraction for the same volume NAPL and surface area, which should increase the bulk mass transfer limitation. However, as the bulk NAPL becomes depleted the volume of NAPL and surface area decrease. This potentially increases the bulk NAPL mass transfer...
limitation, but it may also decrease the intra-NAPL mass transfer limitation. Additionally, McCray and Dugan (2002) found that nonideal multicomponent NAPL dissolution may be enhanced relative to ideal dissolution. Therefore, nonideality of a NAPL mixture may decrease the rate-limitation of dissolution.

1.3.2.5. Remediation of NAPL with Enhanced Solubilization

Spilled nonaqueous phase liquids (NAPL), such as gasoline, tend to slowly dissolve in groundwater, providing a continual source for contamination and limiting the effectiveness of remediation. The currently used remediation alternatives such as pumping groundwater for contamination treatment at the ground surface merely serve to contain contamination to keep groundwater from continuing to migrate and spread contamination. However, groundwater cleanup to regulatory standards at sites containing NAPL may take several decades due to low solubilities and dissolution rates (Cohen and Mercer, 1993; Pankow and Cherry, 1996).

In order to overcome this slow dissolution clean-up limitation, alternative, or innovative, technologies for remediation of NAPL contamination are being developed (Khachikian and Harmon, 2000; Oostrom et al., 2006). In the past, the vast majority of groundwater contamination remediation systems were based on pump and treat (NCR, 1994; Begley, 1997). The limitations of pump and treat systems to attain remedial goals within a realistic time has lead to the development of improved methods for groundwater cleanup (Palmer and Fish, 1992; Grubb and Sitar, 1994; NCR, 1994).
One method involves enhancing (compared to water pump-and-treat) the remediation of groundwater contaminated by NAPL constituents is by flushing with enhanced solubilization agents (ESAs), such as surfactants (Abdul et al., 1990; Fountain et al., 1991; Pennell et al., 1993; Shiau et al., 1994; Adeel and Luthy, 1995; Jawitz et al., 1998; Schaelaekens et al., 2000), cosolvents (Brusseau, 1992; Farley et al., 1992; Milazzo, 1993; Brandes and Farel, 1993; Augustijn et al., 1994; Imhoff et al., 1995; Rao et al., 1997; Lunn and Kueper, 1997; Hofstee et al., 2003), natural organic matter (Johnson and Amy, 1995; Lesage et al., 1995; Rebhun et al., 1998), and cyclodextrins (Wang and Brusseau, 1993; Brusseau et al., 1994; Wang and Brusseau, 1995; Bizzigotti et al., 1997; McCray and Brusseau, 1998; McCray and Brusseau, 1999; McCray et al., 2000; Tick et al., 2003). ESA’s, by definition, are chemicals in the aqueous phase that increase the apparent aqueous solubility of NAPL compounds, which increases the concentrations in the groundwater, and allows increased NAPL mass to be extracted to the surface for treatment.

ESAs are chemicals such as surfactants, cosolvents, natural organic matter, and cyclodextrins, which increase NAPL component solubilities above those obtained in water (Khachikian and Harmon, 2000; Oostrom et al., 2006). Increases in NAPL compound solubility may be viewed as increases in groundwater contamination. However, the goal of ESA applications is generally to increase the rate of transfer of NAPL compounds from the immobile residual NAPL phase to the mobile groundwater phase. ESA injection may only be applicable to sites that already have a groundwater pump and treat systems in place that have sufficient hydraulic containment of groundwater flow and NAPL compound transport.
to the surface for treatment. When injected into source zones of contamination, the enhancement allows contaminant mass to be more readily extracted from the subsurface for treatment (NCR, 1997; Khachikian and Harmon, 2000; Oostrom et al., 2006).

The majority of previous studies have focused on evaluating the treatment alternative of using NAPL dissolution into groundwater for extraction to the surface, and they have considered mass transfer from a single-component NAPL into water or ESAs (Khachikian and Harmon, 2000; Oostrom et al., 2006). The presence and interactions of different compounds in NAPL systems complicate the dissolution process, which complicates the source zone remediation. However, many hazardous waste sites contain multiple-component NAPLs (Peters et al., 1999; McCray and Brusseau, 1998; 1999; Tiruta et al., 2006). An improved understanding of applicability and limitation can be critical to in-situ ESA flushing (Khachikian and Harmon, 2000). Although solubility increases for most NAPL compounds in the presence of ESAs, significant non-equilibrium dissolution of NAPL has been observed in some experiments (Boving and Brusseau, 2000; Schaelaekens et al., 2000). The non-ideal and compositional constraints on ESA flushing of multicomponent NAPL have not been thoroughly evaluated, and would significantly aid in the design of effective ESA remediation systems (Khachikian and Harmon, 2000; McCray et al., 2001).

In the presence of an ESA, the equilibrium solubility for a single component should be significantly enhanced. However, the enhancement will depend on the type of ESA used and vary among the components from the mixture compared to that in water alone (McCray and Brusseau, 1999). In addition, the previously discussed assumption of a dilute aqueous
phase may no longer be valid for dissolution of organic mixtures in the presence of ESAs. That is, the (enhanced) aqueous phase activity coefficient may be influenced by the increased concentration of cosolutes in the (enhanced) aqueous phase (McCray et al., 2001).

A cosolvent can be any organic solvent that is miscible with water (Schwarzenbach et al., 1993). Powers et al. (2001) review cosolvency in general and describe the impact of adding cosolvents to gasoline has on the enhancement of dissolution, transport, and fate of compounds contained in gasoline after leaks occur. Alcohols, such as methanol and ethanol, are the most common cosolvents used as ESAs for environmental remediation (Lee and Peters, 2004), and alcohols have also been suggested for enhanced oil recovery for petroleum production (Gatlin and Slobod, 1960; Holm and Csaszar, 1962; Wachmann, 1964). Several researchers have investigated the dissolution and mobilization of NAPL in porous media with cosolvents (Peters and Luthy, 1993; Roy et al., 1995; Imhoff et al.; Rao et al., 1997). The remediation of porous media contaminated by NAPL with the application of cosolvent solutions occurs both by solubilization and mobilization. The enhancement of NAPL component solubility will depend on the compound and the cosolvent. In elevated concentration solutions of cosolvents, the cosolvent compounds can break up the structure of water and decrease the solution polarity, which may significantly increase the apparent solubility of NAPL compounds (Schwarzenbach et al., 1993).

Cosolvents have also been shown to reduce the interfacial tension between groundwater and NAPLs (Hofstee et al., 2003). Some cosolvents also partition into NAPL, which induces swelling of the NAPL and can alter the physical properties (i.e. lower NAPL
density with increased alcohol concentrations) of the NAPL that control the NAPL distribution and mobilization (Hofstee et al., 2003; Palomino and Grubb, 2004; Ramsburg et al., 2004). Imhoff et al. (1995) observed an interfacial tension reduction of 44.5 to 11.9 dynes/cm for PCE and a solution after adding methanol (60% by volume), and they showed that the cosolvent removed the PCE through enhanced solubilization and emulsification. Cosolvents that preferentially partition into NAPL are generally used for NAPL remediation by mobilization, and cosolvents that remain in the aqueous phase are best suited for enhanced solubilization remediation applications (Hofstee et al., 2003). Generally, cosolvent applications are only used after hydraulic control and containment of the mobile groundwater phase at the site. For example, a cosolvent solution could be used to enhance an already existing pump and treat system. However, due to the complications of multiphase flow, the mobilization of NAPL is risky due to the potential for a loss of hydraulic control and the spread of contamination.

Yalkowsky and others (1976) developed the understanding of cosolvency in the pharmaceutical research to describe nonpolar drug solubilization in solutions containing cosolvents. The theory suggests that cosolvents break up the molecular structure of water, surround nonpolar drugs in water, and alter the polar nature of water, which increases the solubility of nonpolar molecules. The solubility enhancement in cosolvent solutions has been quantified by log-linear correlations (Yalkowsky, 1976):

$$\log S_B = \log S_A + c\gamma_c$$

(26)

where $S_A$ is the apparent solubility of the hydrophobic compound in the cosolvent solution,
$S_A$ is the aqueous solubility of the hydrophobic compound in cosolvent free water, $f_c$ is the volume fraction of the cosolvent in solution, and $\sigma$ is the cosolvency power parameter (Ji and Brusseau, 1998). The above equation can be rearranged to define the enhancement factor ($E$) for cosolvent solutions:

$$E = \frac{S_B}{S_A} = 10^{\sigma_f}$$

(27)

where $E$ is the ratio of the enhanced solubility relative to the aqueous solubility or enhancement factor (Ji and Brusseau, 1998; McCray and Brusseau, 1999).

Surfactants (or surface active agents) are chemicals that have both hydrophobic and hydrophillic moieties (Schwarzenbach, Gschwend, and Imboden, 1993). The hydrophillic structural group of the molecule may be anionic, cationic, nonionic, or zwitterionic (contain both positive and negative charges) (Rosen, 1989). Detergents are an example of commonly used surfactants. Surfactants in aqueous solutions will tend to accumulate at the water interfaces (air/water, NAPL/water, or even solid/water) oriented with the hydrophilic part of the molecule toward the bulk water phase. The accumulation of surfactants at the water interface disrupts the molecular structure of water and the NAPL at the interface, which tends to reduce the interfacial tension (Klaus et al., 2003; Ramsburg and Pennell, 2002).

At increased surfactant concentrations, surfactants tend to self-aggregate to form a variety of microstructures (Champion et al., 1995). Surfactants exist as monomers below the aqueous surfactant concentration threshold called the critical micelle concentration.
(CMC). When surfactant concentrations equal or exceed the CMC, surfactants form microstructures. The CMC is a surfactant specific property that can be dependent on the aqueous pH, surfactant concentration, surfactant structure, temperature, and aqueous ionic strength (Rosen, 1989). Micelles are the smallest surfactant aggregates, and they are a single layer of molecules oriented with the interior of the spherical structure containing the hydrophobic moieties, which increases the thermodynamic stability of the molecules in water. Other surfactant structures include vesicles and lamella that tend to be larger structures with multiple layered surfactants (Champion et al., 1995).

Previous research has been conducted to examine enhanced flushing of NAPL by surfactants (Pennell et al., 1993; Abriola et al., 1993; Okuda et al., 1996; Mason and Kueper, 1996; Sabatini et al., 1996; Boving and Brusseau, 2000; Schaerlaekens et al., 2000; McCray et al., 2001). Surfactants in groundwater below the CMC have little or no effect on the aqueous solubility of most NAPL compounds. However, at and above the CMC, a significant enhancement in NAPL compound solubilities are generally observed (Okuda et al., 1996; Sabatini et al., 1998; Boving and Brusseau, 2000; Schaerlaekens et al., 2000). The mechanism for surfactant solubilization is generally attributed to the partitioning of the NAPL compounds into the hydrophobic interior of the micelle structures (Kile and Chiou, 1989; Edwards et al., 1991). The apparent NAPL solubility (solubility of NAPL compound in ESA solution as opposed to the aqueous solubility without the ESA in solution) increases with increasing surfactant concentration (Rosen, 1989; Pennell et al., 1993; Schaerlaekens et al., 2000; McCray et al., 2001). Although various batch experiments have shown a
substantial solubility increase for NAPL compounds in the presence of surfactants, significant nonequilibrium surfactant enhanced solubilization of NAPL has been observed in column experiments (Pennell et al. 1993; Abriola et al., 1993; Grimberg et al., 1995; Mason and Kueper, 1996; Boving and Brusseau, 2000; Schaerlaekens et al., 2000; McCray et al., 2001). The nonequilibrium dissolution was attributed to a significant decrease of the mass transfer rate coefficient due to the slow diffusion of contaminant-laden micelles away from the NAPL-water interface (Grimberg et al., 1995).

For some surfactants, enhanced removal of NAPL can occur by bulk phase mobilization or the formation of NAPL micro/macro emulsions (mixing of multiple phases into one pseudo-phase). NAPL mobilization due to the presence of surfactant solutions may be classified as either dispersion or displacement (Bai et al., 1997). Dispersion occurs upon the formation of an emulsion between NAPL and water (Abdul and Gibson, 1991; Ang and Abdul, 1991), and displacement is the mobilization facilitated by a reduction in the interfacial tension between NAPL and water due to surfactant partitioning at the interface (Abdul and Gibson, 1991; Ang and Abdul, 1991).

Mobilization and formation of micro/macro emulsions can greatly increase the mass removal of NAPL compared to enhanced solubilization. However, it may not be desirable because the newly-mobilized NAPL could become difficult to control, and may escape from hydraulic containment (e.g. downward flux by gravity for DNAPL) and increase the extent of contamination (Fountain, 1992). Surfactants and cosolvents can be selected to promote solubilization with minimum mobilization and emulsification (Ramsburg and Pennell, 2002).
In addition to NAPL compounds partitioning into surfactant structures, surfactants may actually partition into the bulk NAPL phase. Partitioning of surfactants into NAPL will tend to limit their effectiveness for groundwater remediation, because lower concentrations of surfactants in the aqueous phase decreases the solubility enhancement. Thus, a larger surfactant concentration is required to achieve micellar solubilization than the surfactant CMC (Butler and Hayes, 1998; Crook et al., 1965; Harusawa et al., 1980), and increased surfactant concentrations will increase the cost of a remediation project.

The amount of NAPL enhanced solubilization into a surfactant solution is dependent on a variety of factors including the NAPL compound solubility, compound/surfactant micelle partitioning relationship, surfactant micelle aggregation, surfactant structure, micelle geometry, aqueous ionic strength, aqueous chemistry and temperature, and NAPL compound size (Attwood and Florence, 1983). Surfactant enhanced solubilities are generally linearly dependent on the concentration of micelle structures, or the concentration of surfactant molecules in solution above the CMC. Prediction of surfactant solution solubility enhancement of NAPL compounds at surfactant concentrations above the CMC can be estimated with the relationship:

\[ E = \frac{S_E}{S_A} = 1 + K_m (C_m - CMC) \]  

(28)

where \( S_E \) is the apparent solubility of the hydrophobic compound in the surfactant solution, \( S_A \) is the aqueous solubility of the hydrophobic compound, \( K_m \) is the micelle/water
partitioning coefficient (slope of $S_e$ versus $S_{eq}$), and $C_m$ is the concentration of the surfactant in solution (Ji and Brusseau, 1998).

Organic material is commonly a component of the soil solid structure and may occur due to natural or anthropogenic sources. Additionally, dissolved organic matter (DOM) can also be common in soil pore water and even groundwater. DOM can be created by the dissolution of soil organic material, landfill/sewage sludge or effluent, animal wastes, decaying biological materials, or even industrial wastes. Organic matter in soils can be structurally and chemically extremely complex and variable. However, DOM is generally conceptualized as a separate nonaqueous phase (i.e. similar to NAPL) that can facilitate the transport of hydrophobic chemicals that partition into the structure of the organic material (Chiou et al., 1986; McCarthy et al., 1989; Heyse et al., 2002).

Hydrophobic compounds partitioning into DOM is a process similar to the sorption and adsorption of hydrophobic compounds to soil surfaces, or suspended matter, containing solid organic matter (Heyse et al., 2002). Hydrophobic compounds are generally attracted to other hydrophobic materials. These compounds tend to have low aqueous solubilities that result from their thermodynamic instability in water, but hydrophobic compounds are more stable sorbed or partitioned into the hydrophobic organic material on soils or in DOM (Schwarzenbach et al., 1993). The partitioning into DOM is similar to the partitioning of compounds into the center of surfactant micelle structures, and the form of the solubility enhancement equation is also similar. The solubility enhancement factor for NAPL compounds partitioning into DOM is linearly related to the concentration of the DOM in the
solution:

\[
E = \frac{S_E}{S_A} = 1 + K_{DOM}C_{DOM} \tag{29}
\]

where \(S_E\) is the apparent solubility of the hydrophobic compound in the DOM solution, \(S_A\) is the aqueous solubility of the hydrophobic compound, \(K_{DOM}\) is the DOM/water partitioning coefficient (slope of \(S_E\) versus \(S_A\)), and \(C_{DOM}\) is the concentration of the DOM in solution.

Abdul et al. (1990) suggested that DOM might be applied to cleanup contaminated sites. Lesage et al. (1995) used humic acids to enhance the removal of aromatic hydrocarbons from a NAPL contaminated aquifer. An order of magnitude enhancement in the dissolution and facilitated transport of polycyclic aromatic hydrocarbons (PAHs) from a diesel fuel was observed. Also, Johnson and John (1999) obtained a factor of 3 PCE solubility enhancement with commercial humic acid, but they did observe NAPL mobilization.

Additionally, other ESAs, such as cyclodextrins (Wang and Brusseau, 1993; McCray and Brusseau, 1998; 1999; Tick et al., 2003) have been considered for source zone remediation, because they can significantly enhance the solubility of NAPL compounds with no significant change in NAPL-water interfacial tension, which results in minimal potential for NAPL mobilization. Cyclodextrins are toroidal-shaped polycyclic oligosaccharide molecules (sugar-based and similar to common corn starch) formed through the bacterial degradation of starch (Bender and Komiyama, 1978). The number of glucose units in the toroid defines the type of cyclodextrin, and the six (\(\alpha\)), seven (\(\beta\)), and eight (\(\gamma\)) are the most
commonly used forms. Structurally, cyclodextrins have a lamp-shade shape with nonpolar functional groups lining the interior of the lamp-shade, and the exterior of the molecule contains primarily polar functional groups (Figure 1). This dual nature of the polar and nonpolar surfaces is a function of the orientation of the anhydroglucose with the hydroxyl groups along the exterior of the molecule and the hydrogen atoms lining the interior of the cavity (Bender and Komiyama, 1978).

Figure 1. Cyclodextrin structure and apolar cavity diagram

The result of the molecular structure is that cyclodextrins tend to possess a hydrophobic interior cavity that facilitates the partitioning of nonpolar organic compounds and a hydrophilic exterior that allows cyclodextrins to have relatively high aqueous solubilities (Blanford et al., 2001). Partitioning of NAPL compounds into the cavities of cyclodextrin molecules allows more NAPL compounds to dissolve into the cyclodextrin and water solution, which results in an enhancement of NAPL compound solubility (Wang and Brusseau, 1993; 1994; 1995a; Boving et al., 1999; McCray and Brusseau, 1998; 1999; Tick
et al., 2003). Wang and Brusseau (1993) have reported the total volume of the cyclodextrin cavity is approximately 0.35 cubic nanometers, and the outer diameter of the cyclodextrin molecule is approximately 1.5 nanometers (Brusseau et al., 1994), which is large enough to contain most NAPL compounds including polycyclic aromatic hydrocarbons (Wang and Brusseau, 1995a). Wang and Brusseau (1993) also showed that the solubility enhancement in cyclodextrin solutions is proportional to the NAPL compound’s hydrophobicity and inversely proportional to the aqueous solubility. Although, the less-hydrophobic compounds have greater mass removal in cyclodextrin solutions, because they have higher initial solubilities.

The hydrophilic exterior structure allows cyclodextrins to have relatively high aqueous solubilities for the large size of the organic molecule (Bender and Komiyama, 1978). The hydroxypropyl-β-cyclodextrin (HPCD) has an aqueous solubility above 500 grams per liter (Blanford et al., 2001). The HPCD molecule can also range in molecular weight from 1326 to 1500 grams/mole depending on the degree of hydroxypropyl substitution. Brusseau (1998a) found that cyclodextrin has a negligible effect on the bulk aqueous chemical properties such as pH and ionic strength. The solubility enhancement capability of cyclodextrins seems to not be affected by the solution pH or ionic strength variability (Wang and Brusseau, 1995b). Cyclodextrins have also been observed to have little or no effect on the NAPL-water interfacial tension (Bizzigotti et al., 1997; Wang et al., 1998; McCray et al., 2000). This makes cyclodextrins unsuited for NAPL mobilization, which may be a desirable quality, as mentioned previously. Therefore, cyclodextrins can be
used for NAPL source zone enhanced solubilization without the concern of spreading the contamination through the mobilization of NAPL.

Cyclodextrins are also relatively stable in groundwater systems. Wang et al. (1998) found that they are generally resistant to biological decay for a period of at least a few months, and Bender and Komiyama (1978) have suggested that cyclodextrins have a half-life of 48 days while undergoing hydrolysis in extreme conditions (pH of 0 and temperature of 40 degrees C). However, cyclodextrins may be expected to degrade over the long-term. The simple sugar molecular structure should allow it to be degraded by most indigenous microbial populations. Additionally, cyclodextrin have negligible toxicity, because they are sugar-based (Wang et al., 1998).

The hydrophilic exterior of the cyclodextrin structure has other advantages for aquifer remediation besides facilitating a high aqueous solubility. Cyclodextrin molecules do not tend to partition into NAPL due to their hydrophobic nature (Brusseau et al., 1994; Wang and Brusseau, 1995; McCray, 1998; 1999; McCray et al., 2000). Therefore, every molecule of the cyclodextrin that reaches the NAPL source zone will enhance the NAPL compound’s solubilities and contribute to the remediation. The hydrophilic nature of cyclodextrin’s exterior allows the molecules to be transported in groundwater systems with little or no adsorption to the soil or aquifer solid surfaces (Brusseau et al., 1994; Sheremata, Hawari, 2000). Brusseau et al. (1994) and Hu and Brusseau (1995) observed negligible adsorption of cyclodextrin to soils. These properties increase the chances for cyclodextrin to reach the NAPL source zone and for cyclodextrin to be removed from the subsurface with
groundwater extraction after the NAPL compounds have been dissolved and partitioned into the cyclodextrin molecules.

The solubility enhancement of hydrophobic NAPL compounds in cyclodextrin solutions has been shown to be linearly proportional to the concentration of cyclodextrin compounds in solution (Wang and Brusseau, 1993; McCray et al., 2000), which is similar to DOM and surfactants. However, cyclodextrin and DOM solubility enhancement does not have a concentration threshold, such as the CMC for surfactants, that must be exceeded before NAPL component solubilities increase. The solubility enhancement factor for NAPL compounds in cyclodextrin solutions is:

$$E = \frac{S_E}{S_A} = 1 + K_{CW} C_{CD}$$  \hspace{1cm} (30)$$

where $S_E$ is the apparent solubility of the hydrophobic compound in the cyclodextrin solution, $S_A$ is the aqueous solubility of the hydrophobic compound, $K_{CW}$ is the cyclodextrin/water partitioning coefficient (slope of $S_E$ versus $S_A$), and $C_{CD}$ is the concentration of the cyclodextrin compounds in the solution (Ji and Brusseau, 1998).

Another side-effect of the solubility enhancement of NAPL compounds is an increase in biodegradation of NAPL compounds. Biodegradation can be limited by the low solubility of NAPL compounds, which are not considered bioavailable. Thus, increases in aqueous phase concentrations or apparent solubilities due to ESA application can lead to increases in bioremediation. Brusseau et al. (1994) showed that cyclodextrin solutions can be used to
enhance desorption of low solubility organic compounds. Cyclodextrins also have been shown to increase bioavailability and NAPL-water mass transfer, which increase the rate of biodegradation (Wang et al., 1998; Fara et al., 2003; Wang et al., 2005). Additionally, some forms of cyclodextrins can enhance the solubility of both organic and metallic contaminants (Wang and Brusseau, 1995b; Brusseau et al., 1997), which may aid in the remediation at some mixed waste sites.

The hydrophobic interior of cyclodextrins increases the solubility and desorption of hydrophobic compounds, which increases the ease with which hydrophobic compounds can be transported with groundwater flow. The hydrophillic exterior of the cyclodextrin compounds gives cyclodextrins a high aqueous solubility and makes cyclodextrin sorption to most soils and aquifers negligible, which also increases the ease with which the cyclodextrin (and partitioned NAPL compounds) can be transported with groundwater. Additionally, the increases in NAPL component solubility in cyclodextrin solutions are due to hydrophobic compounds partitioning into a cavity in another molecule. This type of a nonspecific attraction is generally instantaneous and completely reversible, which suggests the potential for separation and reuse of cyclodextrins after extraction from the subsurface (Tick et al., 2003; Boving et al., 1998).

1.3.2.6. Multicomponent NAPL Solubility Enhancement

The equilibrium aqueous concentration for each component from the dissolution of the multicomponent NAPL in the presence of an ESA can be expressed in a modified version
of Raoult’s Law (McCray and Brusseau, 1999):

\[ S_A = \gamma_N X_N S_A^o E \quad (31) \]

where \( \gamma_N \) is the component activity coefficient in the immiscible liquid, \( S_A \) is the equilibrium NAPL mixture component aqueous concentration, \( X_N \) is the mixture mole fraction, \( S_A^o \) is the pure NAPL equilibrium aqueous concentration, and \( E \) is the ESA solubility enhancement factor. The activity coefficient represents nonidealities associated with differences in size and structure between a component and the bulk mixture (Prausnitz et al., 1980; Banerjee, 1984). These factors may cause the equilibrium aqueous concentrations of individual species to differ from those predicted by Raoult’s Law.

Numerical models have been developed to predict groundwater flow and solute transport, which allow us to quantify physical and chemical processes that control flow and transport in porous media. Simulating the transport of organic contaminants in the subsurface involves the coupling of multiple, complex processes, such as advection-dispersion, adsorption, and NAPL dissolution (Abriola and Pinder, 1985; Corapcioglu and Baehr, 1987; Ji and Brusseau, 1998; Brusseau et al., 2002; Johnson et al., 2003). Dissolution of NAPLs is generally described by the first-order mass transfer model (Powers et al., 1992; 1994a; 1994b; Imhoff et al., 1994). As previously discussed, the difference between the compound's aqueous concentration and its aqueous solubility provides the driving force for dissolution, which is also a function of the mass transfer coefficient and the NAPL/water interfacial area (Ji and Brusseau, 1998). The mass transfer coefficient and the specific interfacial area are usually lumped as one parameter, the mass transfer rate coefficient,
because it is difficult to determine the two separately (Powers et al., 1992; 1994a). Through the process of NAPL dissolution, the interfacial area (and, thus, the mass transfer rate coefficient) decreases as the mass of NAPL is depleted, which increases the rate-limitation. Several investigators have established correlations relating the mass transfer rate coefficient to NAPL saturation based on experimental aqueous dissolution results (Miller et al., 1990; Powers et al., 1992; Imhoff et al., 1994; Powers et al., 1994), and some correlations have been developed for surfactant enhanced solubilization (Mayer et al., 1999; Schaerlaekens et al., 2000). Khachikian and Harmon (2000) provide a review of the development of the NAPL mass transfer correlations.

Some previous researchers have attempted to model multicomponent NAPL dissolution. In multicomponent NAPLs previous research, the mixture has been generally assumed to be ideal (Mackay et al., 1991; Borden and Piwoni, 1992; Gonullu, 1996; Garg and Rixey, 1999; Hamed et al., 2000; Eberhardt and Grathwohl, 2002; Lee 2002; Chrisikopoulos and Vogler, 2004; Abriola et al., 2004). Mackay et al. (1991) used an analytical solution to model the transport assuming Raoult’s Law ideal mixture dissolution for a simple synthetic mixture. Gonullu (1996) used a lumped parameter approach to model kinetic dissolution from a 2 component pool of a NAPL mixture assuming a uniform composition except for a unavailable portion of the pool that underwent first order rate-limited dissolution. Borden and Piwoni (1992) developed a Raoult’s Law model to describe rate-limited dissolution and transport of compounds from a motor oil NAPL mixture. The model accounted for nonideality by including the ratio of the NAPL and water phase
activities, but this ratio was kept constant even though the composition changes due to dissolution.

Borden and Kao (1992) and Augustijn (1993) developed equations describing the NAPL mixture activity coefficients using the UNIFAC method. The activity versus composition expressions were used within solute transport equations to simulate NAPL mixture dissolution. The models matched reasonably well with multicomponent groundwater concentrations with fitted mass transfer rate coefficients. Lee and Chrysikopoulos (1995) used a numerical model of 3D solute transport with a multicomponent NAPL pool, and the results suggested that changes in NAPL component activities would significantly affect the results. Chrysikopoulos and Lee (1998) produced another NAPL pool mixture model with a semi-analytical solution, and suggested that models should consider the nonideality of NAPL mixtures. Garg and Rixey (1999) used a model to simulate dissolution of benzene, toluene, xylene, and naphthalene from tridecane using a multi-region rate-limited mass transfer model that assumed Raoult’s Law behavior. The model was able to simulate experimental results, but required 5 NAPL regions (zones), which interestingly enough was the number of components in the mixture. Hamed et al. (2000) used a distributed-site model with a NAPL distribution based on a probability density function, and used the linear kinetic Raoult’s Law mass transfer approach to modeling dissolution. Lee (2002) developed a semi-analytical 3D model for NAPL mixture dissolution based on Raoult’s Law. Multicomponent NAPL dissolution kinetics is still not well understood. Additionally, little work has been done to develop models that consider
NAPL nonideality and its impact on the rate-limited dissolution of multicomponent NAPLs.

Mathematical models have even been developed to simulate the ESA enhanced solubilization process for specific agents (Ji and Brusseau, 1998). However, the majority of the models have focused on the enhanced removal of sorbed contaminant (Augustijn et al., 1994; Adeel et al., 1995; Johnson et al., 1995). Models which simulate enhanced solubilization of NAPL-contaminated soil are generally based on empirical relationships obtained from experimental results because little information is available on the effects of agents on the dissolution of NAPL phase (Abriola et al., 1993), especially for multicomponent NAPLs.

Pennell et al. (1993) and Abriola et al. (1993) modeled laboratory experiments of surfactant enhanced solubilization of single component NAPL with observed rate-limitation confirmed by concentration rebound during a flow interruption, and they found that surfactant dissolution had more of a mass transfer limitation than water dissolution. Roy et al. (1995) evaluated the dissolution kinetics of coal tar into cosolvent solutions using laboratory column experiments and modeling analysis of mass transfer rate-limitation. Additionally, the mass transfer correlations proposed Roy et al. (1995) were used by Ali et al. (1995) to evaluate cosolvent enhanced solubilization scenarios. Mason and Kueper (1996) modeled surfactant enhanced DNAPL pool solubilization, and estimated rate-limited mass transfer. Schaelaekens et al. (2000) modeled NAPL enhanced solubilization in a surfactant solution, and developed a correlation for the observed rate-limited mass transfer. Rathfelder et al. (2001) modeled NAPL enhanced dissolution in a surfactant solution by
assuming linear partitioning between phases, and Molson et al. (2002) modeled humic acid enhanced dissolution of 7 compounds from diesel.

NAPL-water dissolution mass transfer has been previously modeled with expressions that describe the diffusive mass flux through an aqueous boundary layer at the immiscible phase interface governed by Fick’s Law (Kim and Chrysikopoulos, 1998). Generally, the first order kinetic approach is used to represent interphase mass transfer flux of compounds between an immobile NAPL source and a mobile water phase (Miller et al., 1990; Powers et al., 1992; 1994a; Ji and Brusseau, 1998):

\[
\frac{\partial M_n}{\partial t} = -k_f a_s (S_A - C_A)
\]

(32)

where \(M_n\) is the mass concentration of NAPL, \(k_f\) is the mass transfer coefficient, \(a_s\) is the specific surface area for the mass transfer, \(S_A\) is the equilibrium aqueous phase concentration at the interface between the NAPL and water, and \(C_A\) is the bulk aqueous phase concentration. The specific surface area is not usually known, which requires the combination of \(a_s\) and \(k_f\) to form the lumped mass transfer rate coefficient, which is \(k_L\). This mass transfer model has typically been applied to single component NAPL source zones, because the concentration gradient (driving force) is assumed to be only in the aqueous phase (Imhoff et al., 1998).

A model used to quantify the effect of an ESA remediation flush on NAPL dissolution kinetic mass transfer has been developed to include the enhancement factor (E) in the driving force equation (Ji and Brusseau, 1998):
where $M_n$ is the mass concentration of NAPL, $k_t$ is the mass transfer coefficient, $a_n$ is the specific surface area for the mass transfer, $S_A$ is the equilibrium aqueous phase concentration at the interface between the NAPL and water, $E$ is the NAPL component enhancement factor, and $C_e$ is the bulk aqueous phase ESA enhanced concentration for that NAPL component. However, as NAPL is removed over time, the interfacial area decreases. The Ji and Brusseau (1998) model accounts for this change by modifying the rate coefficient from the initial value based on changes in the NAPL volumetric content, which has been correlated with interfacial area (Powers et al., 1994). The transient behavior of the mass transfer rate coefficient has been quantified as:

$$ \frac{\partial M_n}{\partial \tau} = -k_t a_n \left( S_A - \frac{C_e}{E} \right) $$ (33)

The model updates the transient rate coefficient for each component based on change in each component’s NAPL volume ($\theta_n$), which accounts for compound specific rate coefficient changes and interfacial area changes as they change with time during the dissolution process. A multicomponent NAPL blob may act as a shrinking core, with $\theta_n$ decreasing over time as that compound becomes depleted.

The enhancement factor in equation 33 for complexing agents such as cyclodextrins...
was defined above in equation 30 (Ji and Brusseau, 1998). As mentioned previously, the aqueous concentration for each component from the dissolution of the multicomponent NAPL in the presence of an enhanced agent has been developed from Raoult’s Law as shown in equation 31 (McCray and Brusseau, 1999), which couples the kinetic mass transfer driving force for each compound to the multicomponent solubility in the presence (or absence) of an ESA solution. Additionally, the model keeps track of the mass for each compound to update the total mass, NAPL volume, and each component’s mole fraction.

The modeling of NAPL dissolution with an ESA solution requires the solution of the transport equations for both the ESA solution and each of the compounds contained in the NAPL, with a source term that describes the dissolution mass transfer. The transport of cyclodextrin in solution can be described with the equation:

$$ \frac{\partial C_{CD}}{\partial t} = D \frac{\partial^2 C_{CD}}{\partial x^2} - v \frac{\partial C_{CD}}{\partial x} $$

(35)

where $C_{CD}$ is the HPCD concentration in the ESA solution, $D$ is the dispersion coefficient, and $v$ is the interstitial velocity. The transport of NAPL components dissolved in water (subscript A) is given by:

$$ \frac{\partial C_A}{\partial t} + \frac{\rho}{\theta} \frac{\partial C_A}{\partial x} + \frac{\rho}{\theta} \frac{\partial C_2}{\partial x} + \frac{1}{\theta} \frac{\partial M}{\partial x} = D \frac{\partial^2 C_A}{\partial x^2} - v \frac{\partial C_A}{\partial x} $$

(36)

or dissolved in an ESA solution (subscript E) is given by:
\[
\frac{\mathcal{X}_g}{\alpha} + \frac{\rho}{\theta} \frac{\mathcal{X}_1}{\alpha} + \frac{\rho}{\theta} \frac{\mathcal{X}_2}{\alpha} + \frac{1}{\theta} \frac{\mathcal{M}_2}{\alpha} = D \frac{\partial^2 C_g}{\partial x^2} - \nu \frac{\mathcal{X}_g}{\alpha}
\]

(37)

where \(C_A\) is the solubilized concentration of each NAPL compound in the aqueous, \(C_E\) is the solubilized concentration of each NAPL compound in the ESA solution, and \(S_1\) and \(S_2\) are the instantaneous and rate-limited sorbed concentration of the NAPL compounds. Using the well known two-domain sorption approach, the instantaneous and rate-limited sorption of the NAPL compounds are described as:

\[
S_1 = F K_D \frac{C_A}{E}
\]

(38)

and

\[
\frac{\mathcal{X}_2}{\alpha} = k_2 \left[ (1 - F) K_D \frac{C_A}{E} - S_2 \right]
\]

(39)

where \(K_n\) is the linear sorption partitioning coefficient, \(k_2\) is the desorption rate coefficient and \(F\) is the fraction of sorbent for which sorption is instantaneous. The above equations assume that the sorption of NAPL compounds to porous media is linear and rate-limited, and equation 35 assumes that cyclodextrin is transported as a nonreactive tracer with no sorption.

1.3.3. Additional Uncertainty and Needs for Future Research

The persistence of NAPL at many contaminated sites suggests that it is still a major limitation to groundwater remediation (NRC, 1997). Pore scale research has been used to
evaluate mass transfer rate-limitations for a variety of conditions, and several mass transfer correlations have been produced (Khachikian and Harmon, 2000). Additionally, some research has taken NAPL dissolution to the intermediate scale (Oostrom et al., 2006). Some researchers have even used ESA innovative remediation pilot testing to evaluate multicomponent or single component NAPL dissolution in the field (Fountain et al., 1996; McCray and Brusseau, 1998; 1999; Tick, Lourenso, Wood, and Brusseau, 2003).

However, there still is considerable uncertainty in the behavior of NAPL and groundwater dissolution processes that affect remediation. In addition, we still know very little about multicomponent ideal and nonideal impacts on rate-limited dissolution and the impacts of NAPL composition on rate-limited dissolution. Additionally, rate-limitations related to boundary layer and intra-NAPL diffusion are still unknown. The effects of ESA solutions on multicomponent NAPL solubilization during source zone remediation is an area of uncertainty. Also, the impact of NAPL composition changes on the NAPL physical properties, distribution, and potential mobilization of NAPL are still relatively unknown. All of these uncertainties may have significant impacts on the feasibility of source zone remediation. Therefore, the research presented in this document attempts to evaluate the effects of composition on the distribution, mobilization, and partitioning of multicomponent NAPL, the kinetic limitation processes of multicomponent NAPL, and impacts of a cyclodextrin ESA solution on the kinetic limitation of multicomponent NAPL dissolution.
1.4. Overview of Format

The format of this dissertation is the publication dissertation format. Chapter 1 provides the reader with an introduction and literature review for the body of research contained in the dissertation. Chapter 2 contains a summary of the results and significant findings developed through the research. The body of research that is presented in this dissertation is divided into three appendixes labeled A, B, and C, which contain complete manuscripts that are being submitted to peer review scientific journals for publication. Each of the manuscripts contains an independent piece of research. However, the three papers are linked in the common goal of improving our understanding of multicomponent NAPL behavior and solubilization in subsurface systems for the characterization and remediation of contaminated aquifers. A brief overview of each paper as well as contributions of different authors is provided below.

Appendix A provides experimental data of the physical properties and phase partitioning relationships for PCE-diesel multicomponent NAPL obtained from a contaminated aquifer in Tucson, Arizona. The NAPL was modified in the laboratory to create several NAPL mixtures with variable PCE concentrations, experimental measurements of NAPL physical properties and phase partitioning were performed on each of the mixtures, and the data were analyzed to understand the NAPL phase and chemical distribution. The data suggested that the NAPL would be relatively immobile based on Capillary and Bond Number calculations for each of the NAPL mixtures. The results of the research provided technical support to a local, active NAPL remediation project. Preparation
of the proposal, all physical property measurements and phase partitioning experiments, report and journal manuscript drafting were performed by the author. M. L. Brusseau oversaw and guided the project as research advisor.

Appendix B examines the dissolution behavior for a multicomponent NAPL in water and an ESA solution. A simple, ideal NAPL mixture of toluene, ethylbenzene, and butylbenzene was used to evaluate dissolution and enhanced solubilization processes without complicating nonideal effects. Laboratory experiments were conducted to observe the concentration changes due to dissolution of multicomponent NAPLs. Water flushing was used to evaluation the multicomponent dissolution behavior for a pump-and-treat remedial system, and an HPCD solution was used to evaluate the dissolution behavior with an enhanced solubilization remedial system. The HPCD and water concentration data were used to confirm the applicability of Raoult’s Law for aqueous and enhanced solubility for a NAPL mixture. The author conducted all except one of the experiments (was assisted by Asami Murao with chemical analysis and Guiyun Bai provided one unpublished column experiment data set) and drafted the journal manuscript. M. L. Brusseau supervised the project as research advisor.

Appendix C examines the mass removal effectiveness and dissolution kinetics for multicomponent NAPL in water and an HPCD solution. This manuscript uses a numerical model to simulate solute transport and NAPL solubilization from an immobile residual source zone in saturated soil columns. The model has been used to evaluate the mass transfer rate-limitation during dissolution of multicomponent NAPL in water and a 10% by
weight HPCD solution. The author developed all of the experimental data except for one experiment (Guiyun Bai provided one unpublished column experiment data set Appendix B), and worked with Zhuhui Zhang to modify the model’s FORTRAN code (added Raoult’s Law based multicomponent dissolution) originally developed by Wei Ji. M. L. Brusseau oversaw and guided the project as research advisor.
CHAPTER 2. PRESENT STUDY

The background and literature review sections provide a summary of the major advances in nonaqueous phase liquid (NAPL) occurrence, distribution, mobilization, dissolution kinetics, multicomponent NAPL dissolution, multicomponent NAPL ideality, enhanced solubilization agent (ESA) solution applications for innovative remediation, and NAPL mixture ESA dissolution modeling. The effect of NAPL composition on NAPL properties has been shown to impact the NAPL volumetric spatial distribution and potential for mobilization. Researchers have used chemical agents to manipulate the properties of NAPL to facilitate mobilization for remediation. The NAPL composition characterization may also be used to improve our understanding of contamination phase partitioning and potential for mobilization. NAPL dissolution in a pump and treat system has typically been the traditional method for remediation at sites where immobile residual NAPL creates source zones of contamination, which is generally limited by rate-limited mass transfer from NAPL to groundwater. The remediation limitation may also become exacerbated by lower mixture solubilities and nonideal effects with multicomponent NAPLs, because NAPL mixtures do commonly occur at groundwater contamination sites. ESA solutions applied to NAPL source zones may be a way to minimize rate-limited NAPL dissolution, but we still lack a thorough understanding of multicomponent NAPL dissolution in water and ESA solutions (Khachikian and Harmon, 2000).

The research conducted during the development of this document focuses on the characterization, dissolution, and enhanced solubilization of multicomponent NAPLs in
porous media. The methods, results, and conclusions of this investigation are contained in three independent manuscripts located in the appendices, which have been prepared for submission to peer-review journals for dissemination. The following is a summary of the most important findings of the investigation. Additionally, a discussion of the potential for future research is included. The research documented in the three papers covers a broad range of topics that fall under the general subject of multicomponent NAPL behavior in subsurface remediation systems. Multicomponent NAPL contamination has been found at a variety of sites and continues to be a significant challenge for remediation projects. One of the papers examines a NAPL mixture obtained from a floating product at a contaminated site in Tucson, Arizona. The site is currently undergoing remediation, and the results of the research have and will aid the project managers during the site cleanup. The other studies evaluated NAPL mixtures comprised of compounds that are common contaminants of concern from petroleum fuel spill sites. These are the most commonly occurring types of multicomponent NAPLs contaminating groundwater systems.

The first paper involves the characterization of a complex, field sampled NAPL mixture composition, and the determination of compositional changes on NAPL phase physical properties and interphase partitioning behavior. The NAPL mixture was a tetrachloroethene (PCE) and diesel mixture. A mixture of PCE (up to 20 weight %) and diesel fuel was discovered at a site in Tucson, Arizona. The initial NAPL was obtained from a floating free product sample collected from a monitoring well within the contaminated site in Tucson, Arizona. The contamination site was a dry cleaning facility where PCE was the
primary contaminant of concern. However, a previous diesel spill in the area had also created a LNAPL (light nonaqueous phase liquid) lense above a perched aquifer below the site. Samples of the LNAPL from monitoring wells showed 1 to 15 % by weight PCE in the diesel-PCE mixture, which indicated that PCE was partitioning into the diesel or infiltrating into the diesel as two NAPLs mixing together. The purpose of this study was to characterize NAPL mixture, measure the physical properties, evaluate the mobilization potential, and determine the phase-partitioning behavior for the diesel-PCE mixture as a function of the PCE concentration in the NAPL. In order to evaluate the effect of NAPL compositional changes due to the PCE mixing with the diesel, the field sampled PCE-diesel mixture was chemically analyzed, split into several subsamples, and altered by adding varying amounts of pure PCE to each subsample. The NAPLs with differing PCE compositions were then used for a variety of physical property and partitioning tests. Variations in the density, viscosity, surface tension, and interfacial tension were measured for diesel-PCE mixtures, and partitioning of PCE between NAPL, gas, and water was determined for the different diesel-PCE mixtures. The results suggest that the PCE composition does impact the physical properties and phase partitioning behavior of the diesel-PCE mixture. The sample that had the largest amount of PCE added was above the amount needed to convert the diesel from a LNAPL to a DNAPL (dense nonaqueous phase liquid). However, the changes observed in composition were not likely to create NAPL mobilization based on capillary and bond number calculations. Comparison of results obtained from batch phase-partitioning experiments to predictions based on Raoult’s Law indicates that the diesel mixture behaves
essentially as an ideal mixture even after significant increases of PCE concentration in the mixture.

The second of the three papers evaluated the behavior of single, two component, and three component mixtures dissolving into water and a 10 % by weight ESA solution of HPCD. Most research to date has focused on the impact of surfactant solutions on enhancing solubility and mobilizing single-component NAPLs. In the second paper, the influence of a sugar-based enhanced solubilization agent (cyclodextrin) on the dissolution and removal of a NAPL mixture is examined using batch and column laboratory experiments. The investigation used toluene, ethylbenzene, and butylbenzene as components mixed together in the NAPL phase. These compounds are potentially carcinogenic contaminants found in various petroleum fuels such as gasoline. These components are similar in chemical composition and structure, which reduces the chance of nonideal mixture effects. However, they have somewhat different solubilities, which demonstrates variable dissolution behavior.

The investigation evaluated steady state mass transfer and equilibrium solubility enhancement in cyclodextrin for multiple component NAPLs. Both static and steady state mass transfer experiments were used to observe the dissolution behavior of toluene, ethylbenzene, and butylbenzene in NAPL mixtures. Batch solubility experiments were used to observe the single, two component, and three component (equal volume) NAPLs in water and various concentrations of HPCD solutions. The results of the cyclodextrin early-time (steady state) dissolution experiments are compared to those obtained with early-time
dissolution into water for the single component (toluene) NAPL and three component NAPL mixture. Addition of the cyclodextrin in the flushing solution enhances the dissolution and removal of all three organic compounds due to an increase in the driving force (i.e. concentration gradient) and the mass transfer coefficient. The early part of dynamic column experiments were approximately at steady state mass transfer, prior to significant depletion of each component. The steady state dynamic enhancement compared reasonably well with the equilibrium enhanced apparent solubilities. The difference between the aqueous dissolution apparent solubilities for the single and multiple component NAPLs could be explained with Raoult’s Law assuming ideality. This was also the case for the HPCD (ESA) experiments, but it was not the case for the same NAPL mixture in contact with a surfactant (McCray et al., 2001). The results confirm the applicability of Raoult’s Law for dynamic systems assuming local equilibrium. Additionally, the results suggest that Raoult’s Law can be used with ideal NAPL mixtures to evaluate mixture solubility enhancement in cyclodextrin solutions.

The third of the three papers evaluated the transient mass transfer behavior of the single, two component, and three component NAPL mixture experiments by using a numerical solute transport model to simulate the rate-limited dissolution mass transfer into water and a 10 % solution of the HPCD. Ji and Brusseau (1998) developed a model (described in the previous section) to simulate the dissolution of single component NAPLs into water and various ESA solutions. The model has been modified to simulate multicomponent NAPL dissolution into water or various ESA solutions assuming Raoult’s
Law behavior. The effect of sorption of the NAPL compounds was evaluated and incorporated into the model to specifically evaluate rate-limited mass transfer limitations due to dissolution. The model was used to match the single and multicomponent column experiments to estimate and compare the mass transfer kinetic rate coefficients. The results suggest that the model could be used to simulate water and HPCD solution dissolution of single component and multicomponent NAPLs. However, the model revealed deviations from Raoult’s Law behavior in the three component NAPL mixture HPCD solubilization experiments. Overall, the lumped rate coefficients did not vary significantly with NAPL composition (number of components), but the rate-limitation was significantly decreased by the HPCD solution. Additionally, deviations of the model from observed data suggest the need to evaluated intra-NAPL diffusion and nonideal mixture dissolution, which may also affect NAPL mixture dissolution behavior.

The overall result of this research is the advancement of the understanding of multicomponent NAPL dissolution behavior and remediation feasibility. It has been shown that characterization of multicomponent NAPL aids in the understanding of NAPL distribution and mobility, prediction of phase partitioning, and quantification of mixture solubilities using Raoult’s Law. Raoult’s Law has been found to be applicable for the prediction of compound concentrations in contact with ideal NAPL mixtures in either aqueous or cyclodextrin solutions, assuming mass transfer rate-limitation can also be taken into account. It has also been shown that the remediation of NAPL mixtures is rate-limited, which significantly limits the remediation efficiency and feasibility. The lumped mass
transfer rate coefficients were not significantly NAPL composition dependent. However, application of cyclodextrins to a NAPL source zone, even a multicomponent NAPL zone, can significantly reduce rate-limitation, increase the mass removal rate, decrease remediation time, and allow feasible cleanup of a contaminated system. It is hoped that the results of this research will aid the successful application of ESA solutions to enhance the cleanup of multicomponent NAPL source zones, which will help remediate contaminated groundwater systems and protect the environment.
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APPENDIX A: Compositional Effects on the Physical Properties and Partitioning Behavior of a Diesel-PCE Nonaqueous Phase Liquid Mixture
Compositional Effects on the Physical Properties and Partitioning Behavior of a Diesel-PCE Nonaqueous Phase Liquid Mixture

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ABSTRACT

Complex mixtures of nonaqueous phase liquids (NAPL) have been found at many contaminated groundwater sites. A mixture of PCE (tetrachloroethene) and diesel fuel was discovered at a site in Tucson, Arizona. The partitioning of PCE into the residual diesel, observed with concentrations of PCE up to 15-20-weight %, has formed a complex NAPL mixture. The purpose of this study was to characterize the mobilization potential and phase-partitioning behavior of this mixture as a function of the PCE concentration in the NAPL mixture. Changes in the density, viscosity, surface tension, and interfacial tension were measured for diesel-PCE mixtures with variable amounts of PCE to examine the potential for NAPL mobilization. The results suggest that the PCE composition does impact the physical properties and phase partitioning behavior of the diesel-PCE mixture. However, the variations in composition within the range tested did not suggest the potential for NAPL mobilization based on capillary and bond number calculations. Additionally, the gas and aqueous phase partitioning were linearly dependent on the composition of the NAPL mixture. Comparison of results obtained from batch phase-partitioning experiments to predictions based on Raoult’s Law indicates that the diesel mixture behaves essentially as an ideal mixture even after significant increases of PCE concentration in the mixture.
INTRODUCTION

Nonaqueous phase liquids (NAPLs) introduced into the subsurface become trapped at residual saturations due to capillary forces, and are difficult to displace even with increased groundwater velocities under pumping conditions (NRC, 1994). The presence of NAPL constitutes a source for groundwater contamination, and is considered to be the most important factor limiting site cleanup of organic contaminants (NRC, 1994). The typically low solubilities (although generally above regulatory standards) of many NAPL compounds may require decades of remediation to attain clean-up targets. In order to design effective remediation operations, an understanding of the NAPL mixture composition and its impact on the remediation design must be obtained.

Previous studies have shown that NAPL mobilization in the subsurface is governed by viscous, gravitational, and capillary forces (Mercer and Cohen, 1990; Dawson and Roberts, 1997; Khachikian and Harmon, 2000). Residual NAPL will remain immobile as long as capillary forces are the dominating force acting on the NAPL. These forces are generally evaluated in terms of capillary and bond numbers (Larson et al., 1981; Oostrom et al., 2006). The capillary number is the ratio of the viscous force to the capillary force. The bond number is the ratio of the gravitational force to the capillary force. The physical parameter data necessary for this analysis include the NAPL-mixture density, viscosity, interfacial tension, and contact angle (Dawson and Roberts, 1997). Variations in the density, viscosity, surface tension, and interfacial tension of a chemical mixture may affect the potential for NAPL mobilization. NAPL mobilization occurs when gravitational forces
(dependent on the fluid density) dominate the capillary forces (dependent on interfacial tensions). However, multicomponent NAPLs may have composition dependent physical properties that can impact the phase distribution, and remedial actions may also alter NAPL mixture compositions through mass transfer between phases (Roy et al., 2002). Previous researchers have begun to evaluate the effects of NAPL mixture composition (Powers et al., 1996; Seo and McCray 2002; Lord et al., 2005; Pfeiffer et al., 2005). Additionally, researchers have been looking into manipulating NAPL composition to aid remediation (Ramsburg and Pennell, 2002; Ramsburg et al., 2004; Hofstee et al., 2005).

Equilibrium partitioning describes the mass transfer of compounds between phases at equilibrium, and the behavior of a contaminant will indicate the magnitude and number of phases in which the chemical resides. Several researchers have observed that, under certain conditions, equilibrium dissolution (or evaporation) of components from a NAPL mixture proceeds according to Raoult's Law (Burris and MacIntyre, 1985; Lee et al., 1992a; Cline et al., 1989; McCray and Brusseau, 1999; McCray and Dugan, 2001). Raoult's Law states that the equilibrium aqueous (or vapor) concentration of a component in a NAPL mixture is the product of the mole fraction of the species in the mixture and the single-component solubility (or vapor pressure) of the species. The following expression is derived from basic thermodynamic principles (Burris and MacIntyre, 1985; McCray and Brusseau, 1999):

\[
S_A = S_A^0 \left( \frac{x_n}{x_n^0} \right) \left( \frac{\gamma_n^0}{\gamma_n^0} \right) \left( \frac{\gamma_A^0}{\gamma_A^0} \right)
\]

where the subscripts A refer to aqueous phase and N refer to NAPL; superscript o signifies
the pure phase (single component); $S_A$ is the dissolved NAPL mixture component concentration; $S^0_A$ is the dissolved pure compound solubility; $x_n$ is the NAPL mixture component mole fraction; $\gamma_n$ is the NAPL-phase activity coefficient; $\gamma_A$ is the water-phase activity coefficient.

Generally, the partitioning of water into NAPL is negligible (Schwarzenbach et al., 1993), which suggests that $x_n^0$ and $\gamma_n^0$ can be assumed to be equal to one. Additionally, most typical NAPL mixture components have relatively low solubilities, and the dissolution of multiple components does not significantly impact the aqueous activity coefficients (Banerjee, 1984; Burris and MacIntyre, 1985), which supports the assumption that $\gamma_A$ is equal to $\gamma_A^0$ for each component in the mixture. Typically, NAPL compounds are not ideally mixed with water due to the polar nature of water. However, the nonideal behavior of NAPL compounds in water may be similar for compounds dissolved from a single or multiple component NAPL.

The NAPL component activity coefficients ($\gamma_n$) tend to be equal to or greater than one (McCray and Brusseau, 1999 and McCray and Dugan, 2001), and they are typically greater than one for compounds that are significantly different (size, structure, or chemical composition) from the other compounds in the mixture (Burris and MacIntyre, 1985), which is considered a nonideal mixture. NAPL mixtures are considered ideal when the NAPL activity coefficients are equal to unity, and ideal equilibrium dissolution is described by Raoult’s Law (Banerjee, 1984; Burris and MacIntyre, 1985; McCray and Dugan, 2001). Chemical mixtures at equilibrium are described by Raoult’s Law, which assumes ideality
Raoult’s Law has been used to predict aqueous concentrations of nonchlorinated hydrocarbon compounds for many NAPL mixtures (e.g. Cline et al., 1991; Lane and Loehr, 1992; Lee et al., 1992a; 1992b).

The competitive effects of the different components in a multicomponent system can be evaluated in terms of partitioning coefficients (Lee et al., 1998). A previous study has evaluated partitioning of compounds from diesel into water (Lee et al., 1992a). However, the partitioning behavior and ideality of PCE-diesel mixtures is not well understood. Previous research indicates that multicomponent NAPLs can exhibit non-ideal mass transfer, which may increase the rate-limitation (Garg and Rixey, 1999). As the more soluble components in a mixture dissolve, their concentration in the NAPL mixture will decrease, and the driving force for diffusive mass transfer will also decrease (Powers et al., 1994).

Remediation alternatives, such as groundwater or soil vapor extraction, rely on mass transfer from the NAPL to other phases (water or vapor) before removal from the subsurface. Mass transfer can be limited due to a variety of processes including diffusion (in NAPL, water, and vapor), heterogeneity (by-pass flow), and NAPL mixture non-ideality (Khachikian and Harmon, 2000). Water or vapor flushing will also alter the chemical composition of the NAPL mixture by preferentially extracting high solubility or volatile compounds, which could also change the density of the mixture, as well as alter other

\[ S_A = S_A^0 x_n \]

\( x_n^0, y_n, \) and \( y_A^0, \) equal one and \( y_A \) and \( y_A \) are equal):
physiochemical properties such as interfacial tension and viscosity (Roy et al., 2002). These changes could, in turn, modify the physical properties or even the ideality of the mixture (McCray and Brusseau, 1999; McCray and Dugan, 2001).

The purpose of this investigation was to increase our understanding of the behavior of the complex multicomponent NAPLs in groundwater systems to improve prediction capabilities and remedial action design. The investigation included the compositional characterization of a complex NAPL mixture, the assessment of PCE composition impacts on the NAPL mixture bulk physical and inter-phase partitioning properties, and the evaluation of NAPL mobilization and mixture ideality due to variable PCE composition within the NAPL. The multicomponent NAPL chosen for evaluation in the current study was a PCE-diesel mixture present at a remediation site in Tucson, Arizona. PCE resides in the soil-gas and groundwater beneath the Park-Euclid Arizona State Superfund Site, and PCE may be present as a separate NAPL phase at the site. Diesel fuel free product is also located near the top of the perched water-bearing unit at the site. The partitioning of PCE into the diesel has formed a complex NAPL mixture. The free product collected from site wells has been analyzed to have concentrations of PCE between 200 and 150,000 mg/Kg. The approach herein was to investigate changes in the physical properties and phase partitioning of the NAPL mixture with changes in the concentrations of PCE in the diesel-PCE NAPL.
MATERIALS AND METHODS

NAPL mixtures

A sample of the NAPL mixture present at the Park Euclid site was collected with a Teflon well bailer-sampling device. The NAPL was stored at 4 degrees Celsius in amber glass vials (VWR, Brisbane, CA) with Teflon lined caps. A portion of the field NAPL was subsampled to create mixtures of the field sampled NAPL with differing concentrations of PCE. One subsample of the original NAPL was sent to Transwest Geochem Laboratories (Scottsdale, AZ) for chemical analysis and characterization using GC-MS. The PCE concentration of the original NAPL was determined to be 72,000 mg/Kg, and this was used as the initial (lowest PCE concentration) NAPL mixture for the experiments. Four additional samples with larger PCE concentrations were then created by adding known amounts of PCE to subsamples of the original field sample. PCE (99% ACS Grade) was obtained from Acros Chemical Company (New Jersey). The PCE concentration in the field sampled NAPL mixture was increased from 7.2% to 32% by weight (72,000; 118,206; 169,360; 232,814; and 320,942 mg/Kg PCE in NAPL). These NAPL mixtures of increasing PCE concentration were used in the physical property and the partitioning experiments to investigate the effect of increased PCE concentration on the field sampled NAPL mixture.

A synthetic NAPL mixture was also created by mixing PCE and hexadecane to obtain a 15% PCE by weight mixture. The hexadecane (99% ACS Grade) was obtained from Acros Chemical Company (New Jersey). These synthetic NAPL mixtures with 15% PCE, as well as pure PCE (100% PCE) and pure hexadecane (0% PCE) were also used in
the physical property and partitioning experiments. The synthetic NAPL was created with PCE and hexadecane as a simple 2-component analog to the PCE-diesel mixture obtained from the field site. Diesel is composed of hundreds of compounds that are structurally varied. The simple 2-component synthetic NAPL was used to confirm that the experimental results were not a function of the chemical interactions of the various chemicals in the field sampled NAPL mixture. All NAPL mixtures were kept in amber glass containers with Teflon lined caps.

**Physical Property Measurements**

The physical property measurement experiments included density, viscosity, and interfacial and surface tension. All measurements were conducted at 25 degrees Celsius. All fluids were kept in a constant temperature bath. The laboratory room temperature was set to a constant 25 degree Celsius temperature and temperature monitoring confirmed stable temperatures during the measurements. The effect of temperature variation on NAPL physical properties has been previously studied and described in the literature (Sleep and Ma, 1997).

Density is determined by dividing the mass of a substance by the volume that the substance occupies. To measure density, known volumes were prepared in volumetric flasks and masses of the fluids were determined gravimetrically. Clean (washed with soap and water, and rinsed with Methanol and distilled water), dry, 5 ml volumetric vials (Kimble-Kontes, Bineland, New Jersey) were weighted empty using an analytical balance (Mettler
Toledo PG-S, Greifensee, Switzerland). Then, each NAPL mixture was taken out of the constant temperature bath. The volumetric vials were quickly filled with the NAPL using disposable glass pipettes (Fisherbrand Pasteur Pipettes flint glass, Fisher Scientific International, Inc., Atlanta, GA). The volumetric vials were then sealed and weighted again. The mass of NAPL per 5 ml was determined as the difference between the two weights. The density was then calculated by dividing the NAPL mass by the volume (5 ml). The temperature was monitored throughout the experiments to confirm the consistency of 25 degrees Celsius. These measurements were conducted in triplicate, and the density of distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water was also measured in order to confirm the accuracy of the method.

Viscosity is the internal friction or resistance to flow that exists within a fluid. The unit of viscosity is the poise (CGS system), which is equal to 1 g/(cm sec). Viscosity measurements were conducted using a Gilmont Instruments Size #1 Falling Ball Type Viscometer obtained from VWR (Brisbane, CA). The viscometer measures absolute viscosity of fluids between 0.2 and 10 centipoise. This method uses a vertical glass tube containing the liquid of interest and a steel ball falling through the liquid for a distance designated by fiduciary lines designated on the tube. Measurement of times required for a steel ball to drop in a column of the reference liquids in the instrument was used to determine the relationship between falling-ball time and viscosity.

The viscometer was cleaned (washed with soap and water, and rinsed with Methanol and distilled water) and oven dried prior to each use. The viscometer was quickly filled with
the NAPL using disposable glass pipettes (Fisherbrand Pasteur Pipettes flint glass, Fisher Scientific International, Inc., Atlanta, GA). Approximately 5 ml of the test liquid was required to fill the tube. The stainless steel ball was then added to the tube, and the cap was used to seal the viscometer without headspace. The viscometer was placed in the constant temperature bath for at least one hour, and the temperature was monitored throughout the measurements to confirm its constancy. Once prepared, the measurement was initiated, and the time of decent required for the ball to fall a specified distance between two sets of fiduciary lines imprinted on the viscometer tube was measured with a stop-watch. This procedure was then repeated up to five times in order to examine the variability in the measurements.

The viscosity of distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water and hexadecane were used to calibrate the instrument. The viscosity of water and hexadecane are 0.89 centipoise and 3.03 centipoise, respectively (Lide and Frederikse, 1995). Measurements were then made for the diesel-PCE NAPL mixtures with variable PCE concentrations. Viscosity measurements were then made using the synthetic NAPL with 15% PCE.

Surface tension is the force per unit length required to disrupt a liquid surface in contact with the gas phase. Interfacial tension is the force per unit length required to break the interface between two liquids. Surface and interfacial tension has units of dyn/cm, which is equal to g/sec^2. The surface tension (NAPL and air) and interfacial tension (NAPL and water) of the five NAPL mixtures was measured using a Fisher Surface Tensiomat Model.
The instrument uses the du Nouy ring-method that utilizes the principles of operation specified by the American Society for Testing Materials in Methods D-971 (interfacial tension of oil against water) and D-1331 (surface and interfacial tensions of detergents). In the du Nouy method, a platinum-iridium ring of precisely known dimensions is suspended from a counter-balanced lever-arm. The arm is held horizontal by torsion applied to a taut stainless steel wire, to which it is clamped. Increasing the torsion in the wire raises the arm and the ring, which carries with it a surface film of the liquid in which it is immersed. The force necessary to pull the test ring free from this surface film is measured. The Surface Tensiometer shows this surface or interfacial tension (the latter measured at the interface between two immiscible liquids) on a calibrated dial.

Clear glass 50 ml beakers (Kimble-Kontes, Vineland, New Jersey) that have been dedicated to the Tensiometer contained the samples. According to ASTM Method D-971, the glassware was cleaned according to a procedure designed for organic liquids. Any residual oil from the previous sample is removed from the sample containers with dichloromethane followed by several washes with acetone and distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water. After cleaning, the sample containers were immersed in an acid bath, washed with distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water, and oven dried. The platinum-iridium ring was cleaned first with dichloromethane (to remove hydrocarbons) and then with acetone, which was allowed to evaporate prior to each measurement. The
tensiomet was calibrated to the surface tension of distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water, which has a surface tension of 72 dynes/cm at 25 degrees Celsius. This calibration was conducted before every surface and interfacial tension measurement in order to confirm the accuracy of the dial reading.

Each surface tension measurement was conducted using the identical procedure. Measurements were made for the diesel-PCE NAPL mixtures with variable PCE concentrations. Also, surface tension measurements were obtained for the synthetic NAPL with 15% PCE, as well as pure PCE (100% PCE) and pure hexadecane (0% PCE). The cleaned platinum-iridium ring was first attached to the hook at the end of the lever arm. The liquid sample was transferred to the clean glass vessel using disposable glass pipettes (Fisherbrand Pasteur Pipettes flint glass, Fisher Scientific International, Inc., Atlanta, GA) and placed on the sample table. The sample table was then raised until the ring was immersed in the test liquid. The ring was beneath the surface so that the entire ring was wetted. About 1/8 inch immersion (~20 ml) was considered sufficient. The torsion arm was then released and the instrument adjusted to a zero reading. Then the ring was slowly raised vertically through the liquid by rotating the dial, which indicates the increasing force required to pull the ring from the liquid. The surface of the liquid became distended while the index was kept on the reference. The adjustments were continued until the distended film at the surface of the liquid broke and the ring became released from the surface of the liquid. The scale reading at the breaking point of the distended film was taken at liquid surface tension.
Each interfacial tension measurement was made using a procedure similar to the surface tension measurements. Measurements were made with distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water equilibrated with the NAPL in contact with the diesel-PCE NAPL mixtures with variable PCE concentrations. Also, surface tension measurements were obtained for the synthetic NAPL with 15% PCE, as well as pure PCE (100% PCE) and pure hexadecane (0% PCE) in contact with distilled-deionized NANOpure water equilibrated with the synthetic NAPL. The water was brought to equilibrium with NAPL by mixing distilled-deionized NANOpure water with excess NAPL in an amber glass vial (VWR, Brisbane, CA) with a Teflon lined cap for at least one week to ensure equilibration. Interfacial tension from a more dense liquid to a less dense liquid was made by exerting an upward force on the ring. The cleaning of the ring and sample containers was identical to the procedure explained above. The more dense liquid was transferred to the clean glass vessel using disposable glass pipettes (Fisherbrand Pasteur Pipettes flint glass, Fisher Scientific International, Inc., Atlanta, GA) and placed on the sample table. The sample table was then raised until the ring was immersed about 1/8 inch (~20 ml) and wetted by the heavier liquid. The torsion arm was then released and the instrument adjusted to a zero reading. The knob on the right side of the case was adjusted until the index and its image were exactly in line with the reference mark on the mirror. Then the knob beneath the main dial on the front of the case was turned until the vernier read zero on the outer scale of the dial.
In order to create the dual liquid interfacial surface system, the lighter liquid was drop-wise transferred onto the surface of the heavier liquid to a depth of about ¼ inch, with a disposable glass pipette (Fisherbrand Pasteur Pipettes flint glass, Fisher Scientific International, Inc., Atlanta, GA). The layer of lighter liquid was deep enough (~30 ml) so that the ring did not break through the upper surface of the lighter liquid before the interface film ruptured. Before proceeding with the actual measurement, a period of five minutes was allowed to pass in order to allow the surface to equilibrate. This time is greater than the ASTM D-971 standard method, which prescribes an aging period of only 30 seconds for an interface between oil and water. Then the ring was slowly raised vertically through the heavier liquid by rotating the dial, which indicates the increasing force required to pull the ring from the liquid. The interface between the two liquids became distended, but the index was kept on the reference. Once the distended film at the interface ruptured, the ring was transferred from the heavier liquid to the lighter liquid. The scale reading at the breaking point of the interfacial film was recorded as the interfacial tension.

**Partitioning Experiments**

The phase partitioning experiments were conducted in batch (static) systems at 25 (±2) degrees Celsius. VWR Trace-Clean 25 ml clear vials with open top caps and Teflon lined septa (Brisbane, CA) (batch reactor vials) were used to equilibrate the each of the different phases in the partitioning experiments. Known volumes of NAPL were extracted from the NAPL containers with a Gastight Hamilton Company syringe (Reno, Nevada), and
added to the batch reactor vials. Distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water and/or ambient air were added to the appropriate batch reactor vials. The mass of the water added to each batch reactor vial was measured with an analytical balance (Mettler Toledo PG-S, Greifensee, Switzerland). The experiments were conducted using each of the diesel-PCE NAPL mixtures with variable PCE concentrations in triplicate.

The partitioning and sorption reactors were then placed on a Orbit Model shaker table (Lab-Line Instruments, Inc., Melrose Park, Illinois) set to 200 RPM for 120 hours to ensure complete equilibration, and then centrifuged (Beckman GP Centrifuge, Palo Alto, CA) at 2000 RPM for 30 minutes to confirm phase separation. Then aqueous and gas phases from each of the partitioning vials were sampled separately with a Gastight Hamilton Company syringe (Reno, Nevada) through the Teflon septa of the partitioning vials. The sub-samples were analyzed for PCE. Statistical confidence intervals (95%) were calculated from the triplicates.

**Chemical Analysis**

Chemical analysis of the diesel mixture was conducted (Transwest Geochem Laboratory, Scottsdale, AZ) using gas chromatography-mass spectroscopy (GC-MS) for accurate characterization of the complex mixture. A headspace analysis using gas chromatography (GC) with flame ionization detection (FID) (Shimadzu, Japan) was used to determine the concentration of PCE. Analytical standard solutions were prepared from pure
PCE (99.9 % Aldrich), and analyzed before sample analysis. The quantifiable detection limit was approximately 0.06 mg/L. Reference samples were analyzed every 5-6 samples to monitor changes in the GC system. Aqueous phase samples were prepared by adding 5ml of the sample into empty headspace vial (Kimble) sealed with open caps and Teflon-faced septa. Gas phase sample vials were prepared by adding 5 ml distilled-deionized NANOpure water into 21-ml headspace vial (Kimble) sealed with open caps and Teflon-faced septa. The gas samples (1-ml) that were collected were injected into the prepared vials.

Data Analysis

Mobilization Potential

NAPL mobilization potential can be evaluated in terms of the capillary and bond numbers. The capillary number is the ratio of the viscous force to the capillary force (Ng et al., 1978; Morrow and Songran, 1981; Wilson and Conrad, 1984). The capillary number ($N_{ca}$) can be calculated from:

$$N_{ca} = \frac{k \rho g \Delta H}{\gamma \cos \theta} = \frac{\nu \mu}{\gamma \cos \theta}$$

where $k$ is the intrinsic permeability, $g$ is gravitational acceleration, $\Delta H$ is the hydraulic head gradient, $\nu$ is the velocity, $\mu$ is the viscosity, $\theta$ is the contact angle, and $\gamma$ is the interfacial tension (Dawson, 1997). The $N_{ca}$ evaluates the increased potential for NAPL to become mobilized with increased $N_{ca}$ due to velocities of groundwater, which may be
applicable to a groundwater pumping remediation system. However, Larson et al. (1981) found that NAPL displacement began at $N_{Ca}$ of $2 \times 10^{-5}$.

Bond number represents the ratio of gravitational forces to viscous forces that affect fluid trapping and mobilization. In fact, the bond number is the ratio of the gravitational force to the capillary force (Morrow and Chatzis, 1981). The bond number ($N_{Bo}$) can be calculated from:

$$N_{Bo} = \frac{\Delta \rho (k / n)}{\gamma \cos \theta}$$

where $\Delta \rho$ is the density difference between the immiscible fluids, $g$ is gravitational acceleration, $k$ is the intrinsic permeability, and $n$ is the porosity (Dawson, 1997). Increases in $N_{Bo}$ relate to increased potential for NAPL vertical mobilization due to gravitational forces.

The total trapping number ($N_T$) combines the entire force balance evaluated in the $N_{Ca}$ and $N_{Bo}$ number analysis. Pennell et al. (1996) produced a general equation for $N_T$ that may be used to evaluate the potential for NAPL mobilization in all flow directions:

$$N_T = \left( N_{Ca}^2 + 2 N_{Ca} N_{Bo} \sin \alpha + N_{Bo}^2 \right)^{0.5}$$

where $\alpha$ is the angle the flow makes with the horizontal (counter-clockwise). Pennell et al. (1996) also conducted laboratory experiments to evaluate the forces required to mobilize trapped NAPL. They found that PCE mobilization began when $N_T$ values were between
and complete displacement was observed as $N_r$ reached approximately $1 \times 10^{-3}$.

In order to make the calculations, assumptions were made about the system, including the water hydraulic conductivity at the site was 30.4 ft/day (obtained from an aquifer test report (Golder, 2001)). Then it was assumed that the density and viscosity of water were 0.99707 g/cm$^3$ and 0.008904 g/(cm sec), respectively (Logan, 1999). The hydraulic gradient at the site (0.0083) was also used to estimate the darcy flux of 0.5 cm/hr with an assumed water filled porosity was 0.3, which yielded a pore water velocity of 1.7 cm/hr.

**Partitioning and Raoult’s Law**

The results of the partitioning experiments were evaluated as equilibrium partitioning coefficients determined by linear regression of batch isotherm data. Then the partitioning results were also compared to phase partitioning concentrations predicted using Raoult’s Law. The analysis of the ideality of the mass transfer from the partitioning experiments was accomplished by comparison of observed concentrations from the experiments and the concentrations predicted from Raoult’s Law. The PCE-diesel NAPL mixture mole fractions for specific compounds must be estimated. To enable these calculations, the mole fractions ($x_{ni}$) for specific components of the experimental mixtures were calculated with:

$$x_{ni} = \frac{(C_i / mw_i)}{\sum(C_i / mw_i)}$$
where $C_i$ is the mass of a NAPL component per mass of sample, $mw_i$ is the molecular weight of each component (McCray and Brusseau, 1999). $C_i$ is obtained by a solvent extraction and GC-MS chemical analysis of the NAPL mixture as discussed below.

The diesel-PCE NAPL mixture differs from most diesels due to its high concentrations of PCE and TCE. For this study, an Arizona certified commercial laboratory, Transwest Geochem Laboratories (Scottsdale, AZ), conducted GC-MS analysis (EPA Methods 8260 and 8270 following extraction with hexadecane (Method 3585)) of the original field sampled NAPL mixture measured the concentrations of PCE and TCE in the original NAPL, as well as providing a “concentration” for groups of molecules with similar structures and molecular weights by integration of sections of the GC-MS chromatogram. These groups represent the molecules of increasing carbon chain length from 9 – 25 (with negligible concentrations besides PCE and TCE below 9 carbons and above 25). The concentrations based on the GC-MS NAPL analysis accounted for approximately 90% of the total NAPL. The remaining ~10% of the NAPL’s unknown or unidentified composition was approximated by the average molecular weight of diesel (227 g/mol), which has been measured and reported in the literature (Cline et al., 1991; Lee et al., 1992a; Lee et al., 1992b; Chen et al., 1994).

RESULTS AND DISCUSSION

The PCE additions to the original field sampled NAPL mixture created a series of NAPL mixtures that varied by the concentration of PCE in the NAPL phase. Analysis of the
original mixture and the addition of PCE only, facilitated the observation of compositional changes due to PCE in the diesel-PCE mixture. PCE was observed to be miscible with the NAPL mixture for the range of concentrations examined. The physical property experiments were conducted in order to examine the changes in the PCE-diesel mixture as a function of PCE concentration. Figure 1 contains the density results and shows the NAPL density increasing with increasing PCE concentration. It shows the density variation of the PCE-diesel NAPL mixtures with increasing PCE concentrations in the NAPL, and the measurements show the transition from LNAPL to DNAPL (less than 1 to greater than 1 g/cm³). The error bars were calculated from the 95% confidence intervals, and a linear regression equation is shown on each figure. The intercept of the regression equation in Figure 1 indicates that the estimated diesel with no PCE present has a density of 0.88 g/cm³, which is in the expected range for the density of diesel. The densities of PCE (1.6 g/cm³) and hexadecane (0.773 g/cm³) from the synthetic NAPL mixture were also accurate compared to published values (Lide and Frederikse, 1995). The experimental error (average standard deviation) was 0.0016 g/cm³.

The viscosity results are shown in Figure 2. The results confirm that viscosity decreases with increasing PCE concentration in both the PCE-diesel and the synthetic NAPL mixtures. Figure 2 suggests that the diesel-PCE NAPL viscosity would increase to 4.4 centipoise without any PCE based on the intercept of the linear regression equation, which was hither than the synthetic NAPL mixtures. The error bars were calculated from the 95% confidence intervals, and a linear regression equation is shown on the figure. The measured
viscosity of PCE (0.844 centipoise) was also found to be accurate compared to published values (Lide and Frederikse, 1995). The experimental error (average standard deviation) was 0.080672 centipoise.

The surface and interfacial tension results are shown in Figure 3. The NAPL surface tension increases with increasing PCE for both the diesel-PCE mixtures and the synthetic NAPL mixture. The interfacial tension decreases with increasing PCE in the NAPL for both systems, because PCE has a lower interfacial tension than hexadecane. However, the interfacial tension values for the diesel-PCE mixture are decreased compared to hexadecane (46 dyn/cm) and pure PCE (37 dyn/cm), and the diesel-PCE mixture interfacial tension decrease, with increasing PCE in diesel, was more significant than the difference between hexadecane and PCE, which may indicate interactions between PCE and other diesel NAPL mixture components. Anyhow, the results show that the effect of NAPL PCE concentration was greater on the interfacial tension than the surface tension. The error bars were calculated from the 95% confidence intervals, and a linear regression equation is shown on each figure. The measured surface tension of hexadecane (27 dyn/cm) was also found to be accurate compared to a published value (Lide and Frederikse, 1995) and similar to the y axis (pure diesel) for the diesel-PCE mixture. The experimental error for the surface tension measurements (average standard deviation) was 0.336 dyn/cm, and the experimental error for the interfacial tension measurements (average standard deviation) was 0.924 dyn/cm.

The effect of increased NAPL concentrations of PCE on the viscous, gravitational, and capillary forces has been quantified through calculation of capillary and bond numbers
for each of the NAPL mixtures with increased PCE concentrations. Figure 4 shows calculated capillary and bond numbers versus NAPL PCE concentrations for the PCE-diesel NAPL mixtures with variable PCE concentrations. The results show the calculated bond numbers increased with increasing PCE concentration, which suggests a relative increase in the gravitational force due to PCE. The NAPL with the highest PCE concentration became a DNAPL, and the Bond number became positive. Capillary numbers, in general, increased with increasing PCE concentrations, which suggests a relative increase in the viscous force compared to the capillary force. However, all of the calculated capillary numbers are below the threshold value ($2 \times 10^{-5}$) required to create displacement of residual oil (Larson et al., 1981).

The variation in PCE concentration in the PCE-diesel NAPL mixtures also altered the phase partitioning behavior. The vapor and aqueous partitioning from the PCE-diesel NAPL mixtures is shown in Figure 5. The concentrations in the aqueous and the gas phases increased with increasing NAPL concentrations. These partitioning relationships were represented by linear equations using regression analysis. The error bars were calculated from the 95% confidence intervals, and a linear regression equation is shown on each figure. However, the NAPL-water partitioning does show slight nonlinearity. The gas phase chemical analysis experimental error (average standard deviation) was 3.1 mg/L, and the water phase chemical analysis experimental error was 7.7 mg/L.

The NAPL compositional dependence on phase partitioning can also be related to Raoult’s Law. Figure 6 shows the PCE partitioning concentrations predicted from Raoult’s
Law compared to the measured concentrations in aqueous and gas phase in contact with the PCE-diesel NAPL mixtures of differing PCE concentrations. The NAPL mixture shows a deviation from ideal behavior as predicted by NAPL-gas and NAPL-water phase partitioning with Raoult’s Law. The structural differences between PCE and the other compounds in the diesel-PCE NAPL mixture seem to cause some slightly nonideal interactions in the NAPL phase. The diesel-PCE NAPL activity coefficients ranged from 0.96 to 1.1 for the water solubility experiments, and the gas partitioning NAPL activity coefficients ranged from 0.74 to 0.84 for the diesel-PCE mixtures. However, these deviations from Raoult’s Law were minor, which was unexpected. This analysis was also used for the field scale behavior comparison to ideal conditions. Figure 7 shows the observed aqueous-NAPL partitioning compared to predictions based on Raoult’s Law from the ADEQ Updated Site Conceptual Model 2001 (ADEQ, 2001). Several free product and water samples were analyzed from different wells at the site to examine the partitioning behavior, which corroborate the laboratory findings. These results suggest that the PCE-diesel NAPL mixture with increasing PCE concentrations is nearly an ideal mixture.

CONCLUSIONS

The results of this study have shown that PCE compositional changes in the PCE-diesel mixture does affect the physical properties and phase partitioning relationships. The density has been shown to increase with increasing PCE concentrations. The viscosity has been shown to decrease with increasing PCE concentrations. The results also show that the
surface tensions increase slightly with increasing PCE concentrations, and that the NAPL-water interfacial tensions decrease with increasing PCE concentrations in the NAPL phase. These results have been corroborated by the changes in physical properties of three synthetic NAPL mixtures, which were a distribution between hexadecane and PCE. The measured values for the various controls employed in this work are comparable to values previously reported in the literature, supporting the robustness of the measurements. The compositional effects on NAPL physical properties have been related to NAPL mobilization potential through capillary and bond numbers. However, the capillary numbers calculated were below the lower threshold for residual NAPL mobilization. The results of this study have also shown that the concentration of PCE in the PCE-diesel mixture does have an effect on the partitioning behavior of PCE to water and gas phases. The partitioning of PCE into water and gas phases was shown to be linearly dependent on the PCE concentration in the NAPL phase. The partitioning relationships were compared to the predicted partitioning relationships assuming ideal behavior using Raoult’s Law for both laboratory and field measurements, which suggested slightly nonideal behavior. However, both predictions had only small deviations from the observations. This suggests that the PCE-diesel NAPL mixture behaves as a relatively ideal mixture even with significant changes in PCE concentrations.

This study has used bench-scale laboratory experiments to characterize the complex PCE-diesel NAPL mixture and the effect of PCE composition on the NAPL physical properties and phase partitioning. The results of this study demonstrate that the chemical
composition of a NAPL can influence the physical and partitioning properties of that NAPL. However, the physical property variations did not cause the capillary numbers to increase above the threshold for residual NAPL mobilization. The effect of increased PCE concentration in the diesel-PCE multicomponent NAPL was observed through variations the phase partitioning behavior. PCE was shown to partition to each of the measured phases, which could serve as sources of contamination at the site, and the partitioning was dependent on the NAPL composition. The partitioning behavior exhibited slight deviations from Raoult’s Law. However, Raoult’s Law gave a reasonable approximation of the mixture component solubilities in both the gas and aqueous phases. The results of this research suggest that characterization of multicomponent NAPL composition is critical to understanding the NAPL distribution and mobility, phase partitioning, exposure and risk, and remediation feasibility.

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Figure 1. Diesel-PCE NAPL Mixture Density Results
Figure 2. Diesel-PCE NAPL Mixture Viscosity Results
Figure 3. Diesel-PCE NAPL Mixture Surface and Interfacial Tension Results
**Figure 4.** Diesel-PCE NAPL Mixture Capillary and Bond Numbers
Figure 5. Diesel-PCE NAPL Mixture Equilibrium Partitioning Behavior
Figure 6. Raoult's Law Prediction and Laboratory Scale PCE Partitioning from the Diesel-PCE NAPL Mixture
Figure 7. Raoult’s Law Prediction and Field Scale Aqueous Partitioning from the Diesel-PCE NAPL Mixture
APPENDIX B: Multicomponent NAPL Dissolution 1: Steady State Cyclodextrin Enhanced Solubilization and Raoult's Law Behavior
Multicomponent NAPL Dissolution 1: Steady State

Cyclodextrin Enhanced Solubilization and Raoult’s Law Behavior

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ABSTRACT

Nonaqueous phase liquid (NAPL) mixtures represent a long-term source of contamination that can significantly limit the effectiveness of groundwater remediation. One method of enhancing the rate of remediation of NAPL constituents, compared to water pump-and-treat, involves source zone treatment with enhanced solubilization agents (ESAs), such as cyclodextrins. Understanding applicability and limitations can be critical to successful application of ESA flushing of contamination source zones, and previous research has focused on surfactant and cosolvent solutions flushing single-component NAPLs. In this paper, equilibrium and steady state cyclodextrin enhanced solubilization of simple 1, 2, and 3 component NAPL mixtures were examined to evaluate the applicability of Raoult’s Law. The results suggest that Raoult’s Law may be used to estimate equilibrium and early-time dynamic groundwater concentrations in contact with ideal NAPL mixtures, and Raoult’s Law may also be used to estimate cyclodextrin enhanced groundwater concentrations for ideal NAPL mixtures. Solubility enhancement of NAPL compounds was a dependent on the HPCD solution concentration and independent of NAPL composition for an ideal mixture. Column experiments demonstrated the increased removal rates for single component and 3 component NAPL mixtures in the HPCD solution as compared to aqueous dissolution.
INTRODUCTION

Immiscible liquid saturation serves as a long-term source of pollution for groundwater. Conventional pump and treat remediation technology has been shown to be ineffective for remediating groundwater systems contaminated with immiscible liquids. The use of cosolvents, surfactants, and complexing agents (such as cyclodextrins) for enhancing the NAPL chemical constituent solubility during pump and treat have been proposed as an alternative, or innovative, method for removing the NAPL from groundwater contamination source zones (McCray and Brusseau 1998; 1999; Boving et al., 1999; Boving and Brusseau, 2000; McCray et al., 2001; Tick et al., 2003). The removal can be accomplished by enhancement of the apparent solubilities of NAPL constituents by solubilization or by mobilization of the entrapped residual NAPL, but mobilization may not be desirable in some situations due to the potential to increase the extent of contamination (McCray et al., 2001; Tick et al., 2003).

Multicomponent NAPLs containing several chemical compounds are common to groundwater contamination sites (Mercer and Cohen, 1990; Lee et al., 1992a; McCray and Brusseau, 1998; 1999; McCray, 2001; McCray and Dugan, 2002). NAPL chemical composition is generally not considered in subsurface contamination research, but multicomponent NAPLs may significantly complicate groundwater remediation (McCray and Brusseau, 1998; 1999). Mixtures of NAPL compounds with similar structures at equilibrium are assumed to follow Raoult’s Law for ideal mixtures (Banerjee, 1984; Burris and MacIntyre, 1985, Lee et al. 1992a), but some mixtures may be nonideal or
may become nonideal due to compositional changes during remediation (McCray and Brusseau, 1998; 1999; McCray and Dugan, 2002). Additionally, NAPL components that behave ideally when dissolving in water can become nonideal when dissolving in ESA solutions, such as biosurfactants (McCray et al., 2001). Previous research indicates that NAPL components dissolving ESA solutions can become rate-limited (Boving et al., 1999; Pennell et al., 1993; Johnson, et al., 2003), which can significantly limit mass removal rates and increase time associated with remediation.

Research has recently been conducted to study cyclodextrin and other enhanced solubility agent (ESA) dissolution processes for environmental applications (Wang and Brusseau, 1993; McCray and Brusseau, 1998; 1999; Boving et al., 1999; Boving and Brusseau, 2000; McCray et al., 2001; Tick et al., 2003). ESAs, such as surfactants, cosolvents, and cyclodextrins, increase the solubility of NAPL mixture compounds, which increases the rate of mass removal (McCray and Brusseau, 1998). Hydroxypropylbetacyclodextrin (HPCD), the ESA evaluated in this paper, is a glucose based molecule that allows NAPL compounds to partition into a hydrophobic cavity, which increases the apparent solubility (McCray and Brusseau, 1998; 1999; Boving et al., 1999; Boving and Brusseau, 2000; Tick et al., 2003). Most laboratory cyclodextrin and flushing studies have considered only single-component immiscible liquids (Khachikian and Harmon, 2000; Oostrom et al., 2006). McCray and Brusseau (1998; 1999) used cyclodextrin to enhance the solubility of a complex multicomponent NAPL at a field site, but specific dissolution behavior into cyclodextrin was complicated by the
complexity of the NAPL (nearly 50 components) and heterogeneous field conditions (McCray et al., 2001). Thus, little information is available regarding enhanced flushing of multicomponent immiscible liquids (e.g., gasoline, coal tar), which are prevalent at many contaminant sites. In a multicomponent system, many factors influence the feasibility and effectiveness of in-situ enhanced solubilization, such as apparent solubility/partition preference, potential intraphase nonideality, and the interphase mass-transfer behavior of each component (McCray et al., 2001). Understanding the impact of cyclodextrin solutions on the behavior of multicomponent NAPL source zones is essential to successful implementation of in-situ enhanced remediation systems. There is a need to evaluate the dissolution behavior of NAPL mixtures and to evaluate cyclodextrin solubilization of compounds from NAPL mixtures to evaluate the applicability of cyclodextrin as an ESA for source zone remediation.

This paper investigates the dissolution of an ideal NAPL mixture into water and a HPCD solution in order to evaluate the flushing solution’s potential to remediate the groundwater contamination source zones. The objectives of this study are to investigate the effect of an ESA on the removal of residual multicomponent NAPL from porous media, and to test the applicability of Raoult’s Law for the prediction of solubilized component concentrations during static and steady state mass transfer experiments of ideal NAPL mixture dissolution into water and HPCD solutions. The utilization of simple 1, 2, and 3 component combinations for experimental NAPL mixtures was
selected to eliminate compositional uncertainties to develop an improved fundamental understanding of ideal multicomponent NAPL solubilization in water and HPCD.

**MATERIALS AND METHODS**

**Materials**

HPCD (90% average molar mass of 1363 g/mol from Cerastar USA, Inc., Hammond, Indiana, Lot #F8028) and distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water was used in the experiments. Toluene, ethylbenzene, and butylbenzene (properties referenced in McCray et al., 2001), common constituents of gasoline, were selected as representative aromatic constituents of an immiscible liquid, and were obtained from Aldrich Chemical Company ((greater than 99% purity) Milwaukee, WI). The multicomponent NAPL was prepared with approximately equal volume fractions for 1, 2, and 3 component mixtures NAPL with toluene, ethylbenzene, and butylbenzene as the NAPL components. Stainless-steel chromatography columns (with stainless-steel tubing), with dimensions of 5 cm length and 2.54 cm diameter, were used in this study (Alltech). Each column was packed with a quartz sand of 0.3 to 0.42 mm diameter (Accusand of 40/50 mesh size, North Kato Supply, MN). The Accusand clean, fine grained quartz sand was used as the aquifer material to minimize sorption of organic compounds. All materials and solutions were autoclaved before each experiment.
**Experimental procedures**

NAPL component solubilities and enhancement factors were determined by batch (equilibrium) experiments at 25 (+/-2) degrees Celsius. Single component and equal volume 2 and 3 component NAPL (toluene, ethylbenzene, and butylbenzene) mixtures were prepared and injected into reactor vials with water or various concentrations of HPCD (10, 15, and 20 % by weight). The experiments were conducted using each of the NAPL mixtures with each HPCD solution concentrations in triplicate. VWR Trace-Clean 25 ml clear vials with open top caps and Teflon lined septa (Brisbane, CA) (batch reactor vials) were used as reactors for phase equilibration. Known volumes (5 ml) of NAPL were injected into 20 ml of distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water or HPCD solutions in the reactor vials with a Gastight Hamilton Company syringe (Reno, Nevada), and sealed without headspace. The masses of the water and/or NAPL added to the batch reactor vials were measured with an analytical balance (Mettler Toledo PG-S, Greifensee, Switzerland). The reactor vials were placed on a Orbit Model shaker table (Lab-Line Instruments, Inc., Melrose Park, Illinois) set to 200 RPM for 72 hours to ensure complete equilibration (as previously determined experimentally), and then centrifuged (Beckman GP Centrifuge, Palo Alto, CA) at 1500 RPM for 30 minutes to confirm phase separation, and the aqueous or HPCD solutions were sampled with a Gastight Hamilton Company syringe (Reno, Nevada) through the Teflon septa of the reactor vials, and sealed in headspace.
vials for immediate chemical analysis. Statistical confidence intervals (95%) were calculated from the triplicates.

Water and cyclodextrin-enhanced dissolution of the single and 3 component immiscible liquid were studied using column experiments. Single component and equal volume, 3 component NAPL (toluene, ethylbenzene, and butylbenzene) mixtures were prepared and injected into columns to obtain a uniform distribution of residual NAPL (residual was established by flushing mobile NAPL with NAPL equilibrated water). The columns were packed incrementally with air-dried Accusand to establish a consistent porosity (0.4) and bulk density (1.8 kg/L). After the completion of column packing, the immiscible liquid was emplaced in the column using the following procedure. First, about 80 pore volumes de-aerated water were pumped through the column from the bottom to saturate the column. Second, 10 ml of the immiscible liquid were introduced into the column from the top to maintain stable displacement with a syringe pump (Sage Instruments Model 335) at 0.02 cm³/min. At the end of this step, the immiscible liquid occupied about 90% of the total pore space. Third, NAPL mixture equilibrated water was introduced into the column from the bottom to displace the mobile NAPL. The water was pumped at the equivalent pore-water velocity of 8.5 cm/hr for 1 hour and 45 minutes (about 2 pore volumes), followed by a pore-water velocity of 85 cm/hr for another 45 minutes (about 10 pore volumes). The residual saturation of NAPL was determined by measuring the volume of water and mobile NAPL displaced during this procedure, which resulted in a consistent residual saturation (approximately 20%).
the establishment of residual saturation, the column was flushed (Shimadzu LC-10AS piston pump, Japan) in an upward direction with either water or cyclodextrin (10% by weight) at a pore-water velocity of 10 cm/hour (mobilization of NAPL was not observed during the experiments). The effluent solution was sampled through time with a Gastight Hamilton Company syringe (Reno, Nevada) and sealed in headspace vials for immediate chemical analysis.

The chemical analysis was performed on headspace vials samples with by gas chromatography (Hewlett-Packard 5890) with flame-ionization detection (Shimadzu GC-17A, Japan) connected to a headspace autosampler (Tekmar 7000) for analysis of toluene, ethylbenzene, and butylbenzene. Aqueous and HPCD samples were prepared by adding 5 ml of the sample into empty headspace vial (Kimble) sealed with open caps and Teflon-lined septa. Standards prepared in distilled-deionized NANOpure water and HPCD solutions depending on the sample matrix were used for quantification, and the quantifiable detection limit was approximately 0.005 mg/L for each compound.

**Data Analysis**

*Solubilization of NAPL mixtures in water*

Equilibrium solubilization of chemical mixtures may be developed from thermodynamic analysis (Burris and MacIntyre, 1985). The aqueous concentration of each component of a NAPL mixture can be determined from:

\[
S_A = S_A^0 \left( x_n / x_n^0 \right) \left( y_n / y_n^0 \right) \left( y_A / y_A^0 \right)
\]
where the subscript A refers to aqueous phase and N refers to NAPL; superscript o signifies the pure phase (single component); $S_A$ is the dissolved NAPL mixture component concentration; $S_A^0$ is the dissolved pure compound solubility; $x_n$ is the NAPL mixture component mole fraction; $\gamma_n$ is the NAPL-phase activity coefficient; $\gamma_A$ is the water-phase activity coefficient.

Generally, the partitioning of water into NAPL is negligible (Schwarzenbach et al., 1993), which suggests that $x_n^0$ and $\gamma_n^0$ can be assumed to be unity. Additionally, most typical NAPL mixture components have relatively low solubilities, and the dissolution of multiple components does not significantly impact the aqueous activity coefficients (Banerjee, 1984; Burris and MacIntyre, 1985), which allows the applicability of the assumption that $\gamma_A$ is equal to $\gamma_A^0$ for each component in the mixture.

The NAPL component activity coefficients ($\gamma_n$) tend to be equal to or greater than one (McCray et al., 2001), and they are typically greater than one for compounds that are significantly different (size, structure, or chemical composition) from the other compounds in the mixture (Burris and MacIntyre, 1985), which is considered a nonideal mixture. NAPL mixtures are considered ideal when the NAPL activity coefficients are equal to unity, and ideal equilibrium dissolution is described by Raoult’s Law (Banerjee, 1984; Burris and MacIntyre, 1985; McCray and Dugan, 2002). Chemical mixtures at equilibrium are described by Raoult’s Law, which assumes ideality ($x_n^0$, $\gamma_n$, and $\gamma_n^0$ equal one and $\gamma_A^0$ and $\gamma_A$ are equal):
which has been used to predict aqueous concentrations of nonchlorinated hydrocarbon compounds for many NAPL mixtures (e.g. Cline et al., 1991; Lee et al., 1992a, 1992b; Lane and Loehr, 1995).

Enhanced solubilization of NAPL mixtures in Cyclodextrins

The enhancement of single component NAPL solubilities has been defined as:

$$E^o = \frac{S^o_E}{S^o_A}$$

where the superscript $o$ signifies single component; $E$ is the enhancement factor; $S^o_E$ is the pure compound enhanced (apparent) solubility; $S^o_A$ is the dissolved pure compound solubility. The enhancement factor has been defined for a variety of ESA source zone flushing solutions (Ji and Brusseau, 1998). For cyclodextrin solutions, the enhanced equilibrium solubility is a function of the HPCD concentration:

$$S^o_E = S^o_A (1 + K_{cw} C_{CD} ) = S^o_A E^o$$

where $C_{CD}$ is the aqueous concentration of HPCD, and $K_{cw}$ is the partitioning coefficient between for each compound between the HPCD and water. Thus, the enhanced flushing factor ($E$) can be expressed as a function of the HPCD concentration and the compound specific partitioning coefficient:
\[ E^o = 1 + K_{\text{CMF}} C_{\text{CD}} \]

A nonideal expression can also be developed for NAPL mixtures in equilibrium with HPCD:

\[ S'_A = S'^o_A x_n \gamma_n (\gamma'^o_A / \gamma_A) E^o = S'^o_A x_n \gamma_n E^o \]

where the \( \gamma_A \) and the \( \gamma'^o_A \) are the single and multicomponent activity coefficients for the compound in the HPCD solution (McCray and Brusseau, 1999). If the ESA and NAPL mixture behave ideally, the enhanced solubility Raoult’s Law expression becomes:

\[ S'_A = S'^o_A x_n E^o \]

which was developed by McCray and Brusseau (1999) to evaluate multicomponent NAPL solubility enhancement with HPCD. Alternatively, nonidealities related to solubilization may be lumped into a mixture specific enhancement factor:

\[ \lambda = \frac{E}{E^o} \]

where E is the specific to each compound in each mixture and \( E^o \) is only specific to each compound (McCray et al., 2001), but for ideal enhanced dissolution \( \lambda \) is equal to unity.

The measured concentrations in water and HPCD solutions for this investigation have been used to calculate E and \( E^o \) values for each mixture for comparison.
RESULTS AND DISCUSSION

Equilibrium solubilization

The observed, average, apparent solubilities of pure phase toluene, ethylbenzene, and butylbenzene in water and HPCD solutions are presented in Figure 1. As expected, the apparent solubilities increase linearly with increasing HPCD concentration, and the results of linear regression analysis are also shown. The range of concentrations shows that the order of aqueous solubility (i.e. toluene, ethylbenzene, and butylbenzene) remains consistent through the range of solubility enhancement. The NAPL compounds are dissolved and partition to the interior of the HPCD, which enhances the overall solubility of each compound as is expected. Table 1 presents the average enhancement factors and the 95% confidence interval (C.I.) ranges for the 1 component (Table 1a), 2 component (Table 1b), and the 3 component (1c) batch experiments, which show that solubility enhancement is dependent on the chemical being solubilized and the HPCD concentration.

Figure 2 shows the enhancement factor change with variable concentration of HPCD in solution for each of the three single component NAPLs. Figures 2a, 2b, and 2c contain the toluene, ethylbenzene, and butylbenzene enhancement, respectively. Figure 3 presents the enhancement factor versus HPCD concentration for the 2 component NAPL mixture. Figures 3a, 3b, and 3c contain the toluene-ethylbenzene, toluene-butylbenzene, and ethylbenzene-butylbenzene mixture enhancement, respectively. Figure 4 shows the enhancement factor with variable HPCD concentration for the various combinations of 3
component NAPL mixtures. The results of linear regression analysis are shown, and the error bars show the 95% statistical confidence intervals for each of the equilibrium enhancement plots.

The slope of the enhancement versus HPCD concentration, which is the partitioning coefficient for the compound into HPCD solution, is comparable for specific compounds for each plot regardless of which other compounds are in the mixture. For example, the butylbenzene slope for the single component NAPL is 11 (Figure 2c), the two component butylbenzene slopes for the 2 component NAPL mixtures were 12 (Figure 3b) and 11 (Figure 3c), and the 3 component butylbenzene slope is also 11 (Figure 4). This suggests that HPCD solubility enhancement for a compound in an ideal mixture is independent of the NAPL composition. We can also observe that the order of enhancement factor magnitude (i.e. butylbenzene, ethylbenzene, and toluene) is opposite of the order of aqueous solubility (i.e. toluene, ethylbenzene, and butylbenzene) for all experiments. The enhancement factor is independent of the NAPL composition, but it is compound specific and does depend on the HPCD concentration.

Steady State Solubilization

The dissolution of toluene as a single component NAPL in water is illustrated in Figure 5a. The majority of the toluene was removed from the single component NAPL after approximately 250 pore volumes. The initial dissolution concentration is approximately equal to the single component solubility (554 mg/L), which suggests that
the local equilibrium assumption may be applicable for the initial phase of dissolution in a source zone with residual NAPL. However, researchers have shown that steady state rate-limitations can be observed for increased velocities (Powers et al., 1992). Powers et al. (1992) showed that the early period in residual NAPL dissolution undergoes steady state mass transfer with water at a constant velocity. During this early-time dissolution, when NAPL saturation is relatively high, there may be negligible change in the NAPL-water interfacial area compared to the late-time dissolution when NAPL saturation decreases. At a constant velocity, NAPL volume, and interfacial area are the primary factors contributing to the steady state dissolution. At higher velocities, dissolved chemicals are transported away from the source zone at a higher rate relative to the diffusive mass transfer, which results in a larger concentration gradient. The amount of molecules transferred from the NAPL-water interface to the water phase is proportional to the interfacial area. However, if these variables are constant in time, then steady state mass transfer occurs.

The effluent concentration of the column experiment with the equi-volume 3 component NAPL mixture dissolving into water is presented in Figure 5b. As expected, toluene was removed first due to its higher solubility, with a majority of the toluene removed after approximately 600 pore volumes of flushing. Although there was less toluene mass in the mixture experiment compared to the single component toluene experiment (similar volume NAPL but less toluene due to mixture), it took additional pore volumes of flushing to remove from the column. The increased removal time is, in
part, related to the reduced solubility associated with the NAPL mixture. For this NAPL mixture experiment, as toluene was depleted, the concentrations of ethylbenzene and butylbenzene increased due to their increasing mole fractions, which demonstrates that Raoult’s Law may be applied to dynamic systems, also.

The average initial aqueous concentrations of the three compounds (207 mg/L for toluene, 56 mg/L for ethylbenzene, 3.3 mg/L for butylbenzene) were close to that expected based on predictions by Raoult’s Law. In addition, the estimated immiscible-liquid phase mole fractions, calculated using the measured aqueous concentrations, sum to unity. These results indicate that the initial dissolution process can be approximated as instantaneous and the local equilibrium assumption may be applicable for low velocity dissolution of ideal mixtures. However, the local equilibrium is dependent on the rate of diffusive mass transfer being relatively high compared to the rate of fluid flux.

The influence of the cyclodextrin solution on the enhanced solubilization of the same single component NAPL and 3 component NAPL mixture was also compared. Figures 6a and b show the solubility enhancement factor through time during the dissolution of the single component toluene NAPL (Figure 6a) and the three compounds being dissolved from the 3 component mixture (Figure 6b) in a 10% by weight HPCD solution. The majority of the toluene was removed from the single component NAPL after approximately 150 pore volumes, and in the 3 component experiment the toluene was removed first due to its higher enhanced solubility, with a majority of the toluene removed after approximately 100 pore volumes of flushing. The reduction in
remediation time due to cyclodextrin solubility enhancement is evident from these experiments. The transient nature of rate-limited NAPL mixture dissolution and HPCD enhance solubilization are evaluated in Appendix C.

The apparent mixture solubility and also the enhancement factor for each component can be calculated using the respective average effluent concentrations measured for the early-time (steady state) dissolution experiment. These values, which represent the solubility enhancement affected by the HPCD solution during flushing, can be compared to the enhancement factors determined from the steady state column data and the results of the batch experiments. As was the case with the batch experiments, the steady state enhancement for single component toluene was equal to the toluene enhancement factor for the 3 component experiment. Comparison shows that the enhancement factors measured for the three-component batch experiment match the values determined from the column experiment. These results indicate that the initial dissolution process during the HPCD flushing experiment can be considered as instantaneous. Furthermore, the consistency of results from two different types of experiments suggests that the preferential solubility enhancement observed for the more hydrophobic compounds is real, and not an experimental artifact. The fact that the phenomenon is observed in both batch and column experiments indicates that the causative mechanism is associated with a thermodynamic, rather than a kinetic (e.g., rate-limited), process.
Evaluation of Raoult’s Law Behavior

The applicability of the local equilibrium assumption for dissolution of the 1, 2, and 3 component NAPL mixture was examined. Tables 2, 3, and 4 compare the equilibrium single, 2 component, and 3 component mixture equilibrium and initial steady state dynamic dissolution concentrations and enhancement factors for the 10 % by weight concentration of HPCD. There is some slight variability in each chemical’s enhancement factor. However, in general the equilibrium concentrations, if evaluated in terms of Raoult’s Law, and the enhancement factors are comparable. The enhancement factor for toluene ranges from about 6.5 to 8 with an average of 7. The ethylbenzene enhancement factor ranges from 14.6 to 18 with an average of 15. The enhancement factor for butylbenzene ranges from 112.5 to 118.5 with an average of 115.

Table 2 presents the single component NAPL equilibrium concentrations in water and 10 % by weight HPCD solution. Table 3 displays the 2 component NAPL equal volume mixture equilibrium concentrations in water and 10 % by weight HPCD solution. Table 4 contains the 3 component NAPL equal volume mixture equilibrium concentrations in water and 10 % by weight HPCD solution. The tables also contain the mole fractions for each component in each mixture, and the calculated enhancement factors (for 10% by weight HPCD) for each component of the NAPL mixtures and pure liquids.

The tables also contain the early-time, steady state dissolution concentrations for comparison to the batch equilibrium data. The initial dynamic data also tend to follow
Raoult’s Law, and have enhancement factors that are comparable to the batch equilibrium values. This suggests that the local equilibrium assumption may be valid for the initial dynamic dissolution, and that Raoult’s Law may be applied to dynamic NAPL mixture dissolution, as long as rate-limited mass transfer can be accounted for separately.

The “estimated” solubilities in each table are estimated concentrations from experimental data using Raoult’s Law for single component from multiple component data and vice versa. For example, Table 2 contains single component solubilities for the measured data, but it also contains the estimated mixture component solubilities for the 3 component system assuming the mole fractions from Table 4. The estimated mixture solubilities from Table 2 are comparable to the measured solubilities in Table 4 in both water and 10 % HPCD, and a similar comparison has been made for the 2 component data. These results suggest that Raoult’s Law is applicable for both aqueous and HPCD dissolution for each component in any combination of 1, 2, or 3 component mixtures, and in the case of the simple ideal mixture used in these experiments the $E$ and $E^\circ$ values were almost the same for each mixture.

The mixtures were nearly ideal for each of the 1, 2, and 3 component mixtures through the change in number of compounds and mole fraction. Although, the low mole fraction range, where nonideal effects have been observed in another simple NAPL mixture (McCray and Dugan, 2002), was not tested in these experiments. McCray et al. (2001) also observed that toluene, ethylbenzene, and butylbenzene in 2 and 3
component mixtures were ideal in water. However, they observed nonideal enhanced solubilization of the mixtures with biosurfactant solutions (McCray et al., 2001).

CONCLUSIONS

Cyclodextrin flushing of groundwater contamination source zones with residual NAPL was evaluated for the enhanced solubilization and removal of organic compounds from the simple 3 component NAPL mixture. Both equilibrium and steady state mass transfer experiments were performed to observe the dissolution behavior with variations in NAPL composition during water and HPCD flushing to compare traditional pump and treat remediation to ESA source zone remediation with pump and treat. The solubility enhancement was significant for each of the NAPL components, and the overall mass removal rate was significantly increased with the application of 10% HPCD, which may be reasonable for field applications (McCray et al., 1989; 1999). The three chemicals were combined into 1, 2, and 3 component mixtures to evaluate the compositional effects on NAPL dissolution and HPCD solubility enhancement. The results indicate that HPCD increases solubilities for each component in a manner that was independent of the NAPL composition and proportional to the HPCD concentration without preferential partitioning associated with multiple compounds dissolving from the NAPL. The enhanced, or apparent, solubilities, as well as the aqueous solubilities, had only minor deviations from Raoult’s Law for each of the combinations of NAPL mixtures used, which suggests that Raoult’s Law may be used to predict ideal mixture dissolution in
water and HPCD. These results have developed an improved understanding of multicomponent NAPL dissolution and cyclodextrin solubilization of NAPL mixtures. We expect the results of this research to be applicable to a variety of sites contaminated with ideal NAPL mixtures. However, NAPL mixture dissolution behavior may be highly dependent on the nature of the compounds and the NAPL composition. Additionally, dissolution rate-limitations may significantly impact the feasibility of remediation projects.

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REFERENCES


Table 1a. Single Component NAPL Enhancement Factors (E) from Batch Experiments

<table>
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<tr>
<th>HPCD (wt. %)</th>
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<th>Butylibenzene (E (95% C.I. Range))</th>
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*Note: 95% C.I. refers to the statistical confidence intervals*
### Table 1b. Two Component NAPL Enhancement Factors (E) from Batch Experiments

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*Note: 95% C.I. refers to the statistical confidence intervals*
### Table 1c. Three Component NAPL Enhancement Factors (E) from Batch Experiments

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<th>Toluene</th>
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<td>E (Ave.)</td>
<td>E (95% C.I. Range)</td>
<td>E (Ave.)</td>
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*Note: 95% C.I. refers to the statistical confidence intervals*
Table 2. Single Component NAPL Aqueous and Cyclodextrin Enhanced Concentrations (mg/L) and Enhancement Factors (-) from Batch and Column Experiments

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<td>112.3</td>
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<tr>
<td>E (-)</td>
<td>Column</td>
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<td>15.1</td>
<td>116.7</td>
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**Table 3.** Two Component NAPL Aqueous and Cyclodextrin Enhanced Concentrations (mg/L) and Enhancement Factors (-) from Batch Experiments

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<table>
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<td>E (-)</td>
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<td>117.7</td>
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Table 4. Three Component NAPL Aqueous and Cyclodextrin Enhanced Concentrations (mg/L) and Enhancement Factors (-) from Batch and Column Experiments

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<td>Butylbenzene</td>
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<td>E (-)</td>
<td>Column</td>
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<td>18.2</td>
<td>112.5</td>
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Figure 1. Single Component NAPL Solubility Enhancement with HPCD
Figure 2a. Toluene Single Component Enhancement Factor versus HPCD Concentration
Figure 2b. Ethylbenzene Single Component Enhancement Factor versus HPCD Concentration

\[ y = 1.12x + 1.43 \]

\[ R^2 = 0.989 \]
Figure 2c. Butylbenzene Single Component Enhancement Factor versus HPCD Concentration

\[ y = 10.99x + 0.94 \]

\[ R^2 = 0.999 \]
Figure 3a. Toluene-Ethylbenzene Two Component Mixture Enhancement Factor versus HPCD Concentration
Figure 3b. Toluene-Butylbenzene Two Component Mixture Enhancement Factor versus HPCD Concentration
Figure 3c. Ethylbenzene-Butylbenzene Two Component Mixture Enhancement Factor versus HPCD Concentration
Figure 4. Toluene-Ethylbenzene-Butylbenzene Three Component Mixture Enhancement Factor versus HPCD Concentration
Figure 5a. Toluene Single Component NAPL Aqueous Dissolution Concentration versus time
Figure 5b. Toluene, Ethylbenzene, and Butylbenzene Three Component NAPL Mixture Aqueous Dissolution Concentration versus time
Figure 6a. Toluene Single Component NAPL 10% HPCD Enhanced Dissolution Concentration versus time
Figure 6b. Toluene, Ethylbenzene, and Butylbenzene Three Component NAPL 10% HPCD Enhanced Dissolution Concentration versus time
APPENDIX C: Multicomponent NAPL Dissolution 2: Transient Mass Transfer Limitation and Cyclodextrin Enhanced Solubilization
Multicomponent NAPL Dissolution Behavior 2: Transient
Mass Transfer Limitation and Cyclodextrin Enhanced
Solubilization

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2Department of Soil, Water, and Environmental Science
University of Arizona, Tucson, AZ 85721

*Corresponding author
ABSTRACT

In this paper, the influence of a cyclodextrin on the dissolution and removal of a simple 1, 2, and 3 component nonaqueous phase liquid (NAPL) (toluene, ethylbenzene, butylbenzene) mixture has been examined using laboratory experiments to enhance our understanding of the kinetic limitations on dissolution of ideal, multiple-component, NAPLs in subsurface systems. Dynamic laboratory experiments and numerical modeling were used to evaluate the dissolution behavior of NAPL mixtures in water and an enhanced solubilization agent (ESA) solution of hydroxypropylbetacyclodextrin (HPCD) to estimate mass transfer rates and removal efficiencies. The aqueous multicomponent dissolution followed Raoult’s Law, and the model estimated lumped rate coefficients, which were shown to be independent of the NAPL composition. Addition of the HPCD enhanced the dissolution and removal of all three organic compounds from immobile residual NAPL due to an increase in the driving force (i.e. concentration gradient) and the mass transfer coefficient. The model results suggest that Raoult’s Law is applicable for ideal NAPL mixture dissolution in water, but potential nonideality was observed and caused the model to deviate from the dissolution behavior for the 3 component HPCD solubilization experiment. HPCD dissolution experiments were less rate-limited than aqueous dissolution, and the mass transfer coefficients were quantified through calibration of the numerical model. The results of the model suggest that NAPL mixture nonideality and intra-NAPL diffusion may also impact enhanced dissolution behavior.
INTRODUCTION

Contamination of soil and groundwater by immiscible liquids has become a major problem for most industrial countries. Immiscible liquid saturation serves as a long-term source of pollution in groundwater. NAPL requires unreasonably high hydraulic gradients to remediate through multiphase displacement (Wilson and Conrad, 1984; Lake, 1989; Pennell et al., 1996). Therefore, pump and treat remediation designs have been used to control the spread of contamination and remove NAPL constituent mass through dissolution into groundwater. However, the application of pump and treat to clean up NAPL source zones has been found to be extremely ineffective (Begley, 1997; NRC, 1994; Palmer and Fish, 1992; McCray and Brusseau, 1998, 1999; Boving et al., 1999; Tick et al., 2003).

The use of cosolvents, surfactants, and complexing agents (such as cyclodextrins) for enhancing the nonaqueous phase liquid (NAPL) solubility during pump and treat has been proposed as an alternative method for removing the NAPL from the subsurface (McCray and Brusseau 1998; 1999; Boving et al., 1999; Boving and Brusseau, 2000; Khachikian and Harmon, 2000; McCray et al., 2001; Tick et al., 2003; Oostrom et al., 2006). The removal can be accomplished by enhancement of the apparent solubilities of NAPL constituents by solubilization or by mobilization of the entrapped NAPL. While mobilization may greatly increase the mass removal of a NAPL compared to solubilization, it would not be desirable in some situations because the newly mobilized NAPL may escape from hydraulic control (e.g., downward flux by gravity for dense
immiscible liquid) and increase the extent of contamination (McCray et al., 2001; Tick et al., 2003).

Previous research has concluded that rate-limited mass transfer during NAPL dissolution is significant under certain conditions (Hunt et al., 1988; Brusseau, 1992; Powers et al., 1991; Imhoff et al., 1994). This generally appears to be the case when (1) groundwater velocities are high, (2) NAPL saturations are low, (3) NAPL is distributed as large blobs filling several pores (Hunt et al., 1988; Miller et al., 1990; Powers et al., 1991). Additionally, rate-limited mass transfer may be significant for low mole fraction components of NAPL mixtures (Borden and Kao, 1992). For weathered or aged contaminants, the presence of semi-gelatinous films at the interface may also limit mass transfer (Ramaswami et al., 1994). Low concentrations of NAPL compounds in groundwater that has been in contact with the NAPL phase suggests that mass transfer limitation impacts the dissolution of NAPL compounds into groundwater. Mass transfer rate-limitation impacts on the dissolution of NAPL-ganglia or blobs has been the focus of previous investigations (Miller et al., 1990; Powers et al., 1991 and 1992; Abriola et al., 1993; Geller and Hunt, 1993; Illangasekare et al., 1995).

Mass transfer from residual NAPL is considered to be limited by boundary layer diffusion from the NAPL-water interface to the bulk water (Powers et al., 1992). For multicomponent systems, the diffusion processes occurring during mass transfer include the boundary layer water diffusion and the NAPL phase diffusion from the bulk NAPL phase to the boundary (Heyse et al. 2002). As a multicomponent NAPL dissolves
compounds into water, the composition of the NAPL constantly changes. Initially, the composition change may be small. However, over time the NAPL bulk phase may become limited with respect to a compound, and the compound may need to diffuse through the bulk NAPL to reach the boundary prior to dissolving. This intra-NAPL diffusion limitation increases with decreasing NAPL mixture mole fraction, which increases the bulk mass transfer limitation. However, as the bulk NAPL becomes depleted the volume of NAPL and surface area decrease. This potentially increases the bulk NAPL mass transfer limitation, but it may also decrease the intra-NAPL mass transfer limitation. Additionally, McCray and Dugan (2002) found that nonideal multicomponent NAPL dissolution may be enhanced relative to ideal dissolution. Therefore, nonideality of a NAPL mixture may affect the rate-limitation of NAPL dissolution.

Research has been conducted that supports the applicability of cyclodextrin and other enhanced solubility agents (ESA) for NAPL source zone remediation (McCray and Brusseau, 1998; 1999; Boving et al., 1999; Boving and Brusseau, 2000; McCray et al., 2001; Tick et al., 2003). ESAs, such as surfactants, cosolvents, and cyclodextrins, increase the solubility of NAPL mixture compounds, which increases the rate of mass removal (Ji and Brusseau, 1998; Boving and Brusseau, 2000). Hydroxypropyl-β-cyclodextrin (HPCD), the ESA evaluated in this paper, is a glucose based molecule that allows NAPL compounds to partition into a hydrophobic cavity, which increases the apparent solubility (McCray and Brusseau, 1998; 1999; Boving et al., 1999; Boving and
Previous laboratory cyclodextrin and flushing studies have considered only single-component immiscible liquids (Boving et al., 1999; Boving and Brusseau, 2000). However, McCray and Brusseau (1998; 1999) used cyclodextrin to enhance the solubility of a complex multicomponent NAPL at a field site, but specific dissolution behavior into cyclodextrin was hindered by the complexity of the NAPL (nearly 50 components) and heterogeneous field conditions (McCray et al., 2001).

Multicomponent NAPLs containing several chemical compounds are common to groundwater contamination sites (Mercer and Cohen, 1990; Lee et al., 1992a; McCray and Brusseau, 1998; 1999; McCray, 2001; McCray and Dugan, 2002). NAPL chemical composition is generally not considered in subsurface contamination research, but multicomponent NAPLs may significantly complicate groundwater remediation (McCray and Brusseau, 1998; 1999). Mixtures of NAPL compounds with similar structures at equilibrium are assumed to follow Raoult’s Law for ideal mixtures (Banerjee, 1984; Burris and MacIntyre, 1985, Lee et al. 1992a). Previous research indicates that NAPL dissolving in water and ESA solutions can become rate-limited (Boving et al., 1999; Pennell et al., 1993; Johnson, et al., 2003), which can significantly limit mass removal rates and increase time and costs associated with remediation. However, little information is available regarding enhanced flushing of multicomponent immiscible liquids (e.g., gasoline, coal tar), which are prevalent at many contaminant sites (Khachikian and Harmon, 2000). Understanding the impact of cyclodextrin solutions on the behavior of multicomponent NAPL source zones is essential to successful
implementation of in-situ enhanced remediation systems. There is a need to quantify the
dissolution kinetics of NAPL mixtures and to evaluate HPCD solubilization of
compounds from NAPL mixtures to evaluate the applicability of HPCD as an ESA for
source zone remediation (Khachikian and Harmon, 2000).

Mathematical models have been developed to simulate the NAPL dissolution and
solute transport with groundwater and also ESAs, such as surfactants, cosolvents, natural
organic matter, and complexing agents (Ji and Brusseau, 1998). Pennell et al. (1993) and
Abriola et al. (1993) modeled laboratory experiments of surfactant enhanced
solubilization of single component NAPL with observed rate-limitation confirmed by
concentration rebound during a flow interruption, and they found that surfactant
dissolution had more of a mass transfer limitation than water dissolution. Roy et al.
(1995) evaluated the dissolution kinetics of coal tar (considered as one chemical
component) into cosolvent solutions using laboratory column experiments and modeling
analysis of mass transfer rate-limitation. Additionally, NAPL-water dissolution mass
transfer has been previously modeled with expressions that describe the diffusive mass
flux through an aqueous boundary layer at the NAPL interface governed by Fick’s Law
(Kim and Chrysikopoulos, 1999). However, few investigations have provided numerical
modeling evaluations of multicomponent NAPL dissolution, especially in ESA solutions
(Khachikian and Harmon, 2000; Oostrom et al., 2006).

This paper investigates the transient kinetic dissolution of a NAPL mixture into
water and a HPCD solution in order to evaluate each flushing solution’s potential to
reduce mass transfer limitation and remediate the NAPL mixture. The objectives of this study are to model the effect of an ESA on the removal of residual multicomponent NAPL from porous media, and to predict dissolution and transport of solubilized components during NAPL mixture dissolution into water and a HPCD solutions. The utilization of simple 1, 2, and 3 component combinations for experimental NAPL mixtures was selected to develop an improved fundamental understanding of ideal multicomponent NAPL solubilization in water and HPCD. The dynamic column dissolution experiments were designed to focus on solubilization as the removal mechanism. A mathematical model is used to quantify the magnitude and rate of dissolution in the presence and absence of the flushing agents.

MATERIALS AND METHODS

Materials

Hydroxypropyl-β-cyclodextrin (HPBC) (90 % with an average molar mass of 1,363 g/mol from Cerastar USA, Inc., Hammond, Indiana, Lot #F8028) and distilled-deionized NANOpure (Series 550, Barnstead Thermolyne Corp., Dubuque, Indiana) water was used in each experiment. Toluene, ethylbenzene, and butylbenzene (properties referenced in McCray et al., 2001), common constituents of gasoline, were selected as representative aromatic constituents of an immiscible liquid, and were obtained from Aldrich Chemical Company ((greater than 99% purity) Milwaukee, WI). The three component NAPLs were prepared with approximately equal volume fractions for
toluene, ethylbenzene, and butylbenzene as the components. A two component mixture was created by adding toluene (1:1000 volume mixture) into a matrix of hexadecane for a low mole fraction mixture. Another equal volume three component mixture of chlorophenol, chlorobenzene, and dichlorobenzene was prepared. Stainless-steel chromatography columns (with stainless-steel tubing), with dimension listed in Tables 1 and 2, were used in this study (Alltech). Each column was packed with a uniform, fine to medium grained, quartz sand (Accusand of 40/50 or 20/30 mesh size, North Kato Supply, MN). The Accusand was used to minimize sorption of organic compounds. Before each experiment, all materials and solutions were autoclaved, and the columns were packed in a sterile hood (HEPA filtered forced air) to avoid biodegradation during experiments.

**Experimental procedures**

NAPL component solubilities and HPCD solution enhancement factors were determined by batch (equilibrium) experiments (as described in Appendix B). Water and cyclodextrin-enhanced dissolution of the single and 3 component NAPL mixture was studied using column experiments. Single component and equal volume, 3 component NAPL (toluene, ethylbenzene, and butylbenzene) mixtures were prepared and injected into columns to obtain a uniform distribution of residual NAPL (residual was established by flushing mobile NAPL with NAPL equilibrated water). The columns were packed incrementally with air-dried Accusand to establish a consistent porosity and bulk density. After the completion of column packing, a three component aqueous tracer test was used
to evaluate adsorption of the NAPL compounds in the porous media used for the NAPL dissolution experiments. Rate-limited sorption of NAPL compounds has been shown to have a tailing behavior that may complicate the characterization of NAPL dissolution (Johnson et al., 2003), and the sorption experiment was used to elucidate the effects of NAPL dissolution and sorption on the effluent concentrations, and to estimate sorption behavior modeling parameters. All miscible-displacement experiments were conducted at 25(±2)°C. A pulse of a non-reactive tracer, ACS grade pentafluorobenzoic acid (Aldrich Chemical Co., Inc., Milwaukee, WI) (PFBA) solution was injected for several pore volumes (Table 1), after which the tracer-free water was injected to elute the tracer solution from the column. The PFBA solution from the column effluent was analyzed with a flow-through Shimadzu UV-VIS Spectrophotometer (Japan) using a 254 nanometer wavelength. A similar tracer experiment was conducted with a solution containing toluene, ethylbenzene, and butylbenzene (Table 1). The 3 component solution was prepared in NANOpure water, injected into the saturated column, and then eluted by switching the injection solution to tracer-free NANOpure water. A flow interruption of 24 hours was also conducted toward the end of the elution, which involved stopping flow, starting flow after a known amount of time, and collecting additional samples to observe potential concentration rebound. Samples for the 3 component sorption experiment were collected from column effluent and the injection solution during the experiment with a Gastight Hamilton Company syringe (Reno, Nevada) and sealed in
headspace vials for immediate chemical analysis. The column was cleaned and repacked prior to each experiment (sorption and NAPL dissolution).

Several NAPL dissolution experiments were conducted after completion of the tracer experiments, and experimental properties are listed in Table 2 (the parameters are numbered for the compounds in each experiment [Tol for toluene, EB for ethylbenzene, and BB for butylbenzene]). The immiscible liquid was emplaced in the column using the following procedure. First, about 80 pore volumes de-aerated, NAPL mixture equilibrated water were pumped through the column from the bottom to saturate the column. Second, 10 ml of the NAPL were introduced into the column from the top to maintain stable displacement with a syringe pump (Sage Instruments Model 335) at 0.02 cm$^3$/min. At the end of this step, the immiscible liquid occupied about 90% of the total pore space. Third, an aqueous solution saturated with the three NAPL components was introduced into the column from the bottom to displace the mobile NAPL. The water was pumped at the equivalent pore-water velocity of 8.5 cm/hr for 1 hour and 45 minutes (about 2 pore volumes), followed by a pore-water velocity of 85 cm/hr for another 45 minutes (about 10 pore volumes). The residual saturation of NAPL was determined by measuring the volume of water and mobile NAPL displaced during this procedure (Table 2). After the establishment of residual saturation, the column was flushed (Shimadzu LC-10AS HPLC piston pump, Japan) in an upward direction with either water (Table 2a) or cyclodextrin (Table 2b) solution (10% by weight) at a pore-water velocity of 10 cm/hour, and Table 2c contains the experimental setup for the NAPL dissolution.
experiments conducted at increased pore-water velocities. For each experiment, the effluent solution was sampled through time with a Gastight Hamilton Company syringe (Reno, Nevada) and sealed in headspace vials for immediate chemical analysis.

The chemical analysis was performed on headspace vials samples with by gas chromatography (Hewlett-Packard 5890) with flame-ionization detection (Shimadzu GC-17A, Japan) connected to a headspace autosampler (Tekmar 7000) for analysis of toluene, ethylbenzene, and butylbenzene. Aqueous and HPCD samples were prepared by adding 5 ml of the sample into empty headspace vial (Kimble) sealed with open caps and Teflon-lined septa. Standards prepared in NANOpure water and 10% by weight HPCD solutions depending on the experiment were used for quantification, and the quantifiable method detection limit was approximately 0.005 mg/L for each compound.

DATA ANALYSIS

Solubilization of NAPL mixtures in water:

Quantification of equilibrium solubilization of chemical mixtures has been developed from thermodynamic analysis (Burris and MacIntyre, 1985). NAPL mixtures comprised of compounds with similar size and functional groups are considered ideal, and ideal equilibrium dissolution is described by Raoult’s Law (Banerjee, 1984; Burris and MacIntyre, 1985; McCray and Dugan, 2002):

\[ S_A = S_A^0 x_n \]
where the subscript A refers to aqueous phase and N refers to NAPL; superscript o signifies the pure phase (single component); $S_A$ is the equilibrium dissolved NAPL mixture component concentration; $S_N^o$ is the equilibrium dissolved pure compound solubility; and $x_n$ is the NAPL mixture component mole fraction. Raoult’s Law has been used to predict aqueous concentrations of nonchlorinated hydrocarbon compounds for many NAPL mixtures (e.g. Cline et al., 1991; Lee et al., 1992a, 1992b; Lane and Loehr, 1995).

**Enhanced solubilization of NAPL mixtures in Cyclodextrins:**

The ESA solution enhancement of single component NAPL solubilities has been defined as:

$$E^o = \frac{S_N^o}{S_A^o}$$

where the superscript o signifies single component; E is the enhancement factor; $S_N^o$ is the pure compound enhanced (apparent) solubility. The enhancement factor has been defined for a variety of ESA source zone flushing solutions (Ji and Brusseau, 1998). For cyclodextrin solutions, the enhanced equilibrium solubility is a function of the cyclodextrin (HPCD) concentration:

$$S_N^o = S_A^o (1 + K_{cw} C_{CD}) = S_A^o E^o$$
where $C_{CD}$ is the aqueous concentration of HPCD, and $K_{cw}$ is the partitioning coefficient between for each compound between the HPCD and water. Thus, the enhancement factor (E) can be expressed as a function of the HPCD concentration and the compound specific partitioning coefficient:

$$E^0 = 1 + K_{cw} C_{CD}$$

If the ESA and NAPL mixture behave ideally, the enhanced solubility Raoult’s Law expression becomes:

$$S_A = S_A^0 X_n E^0$$

which was developed by McCray and Brusseau (1999) to evaluate multicomponent NAPL solubility enhancement with HPCD.

**Mathematical Model:**

A mathematical model (Ji and Brusseau, 1998) was previously published that simulates NAPL dissolution and dissolved-phase transport (with sorption to porous media) of organic contaminants in porous media. This model was also developed to consider the enhanced solubilization of NAPL with various ESAs. The Ji and Brusseau model was modified for this investigation to incorporate ideal multicomponent immiscible liquids. The model now has the ability to simulate a number of different compounds that make up a multicomponent NAPL trapped in a porous medium at residual saturation. The dissolution of the multicomponent NAPL constituents into
water, or an ESA, is quantified as was previously done for single components, except the NAPL components dissolving into the flushing solution have apparent solubilities that follow Raoult’s Law.

This multicomponent NAPL dissolution and enhanced solubilization and transport numerical model was used to simulate the effluent data from the NAPL column experiments, and NAPL dissolution lumped mass transfer rate coefficients were quantified. The, commonly used, first order kinetic approach was used to represent interphase mass transfer flux of compounds between an immobile NAPL source and a mobile water phase (Miller et al., 1990; Powers et al., 1994; Ji and Brusseau, 1998):

$$\frac{\partial M_n}{\partial t} = -k_f a_o (S_A - C_A)$$

where $M_n$ is the mass concentration of each NAPL component, $k_f$ is the mass transfer coefficient, $a_o$ is the specific surface area for the mass transfer, $S_A$ is the equilibrium aqueous phase concentration at the interface between the NAPL and water, and $C_A$ is the bulk aqueous phase concentration. The specific surface area is not usually known, which requires the use of the lumped mass transfer rate coefficient $k_L$, which is a combination of $a_o$ and $k_f$. This mass transfer model has typically been applied to single component NAPL source zones, because the diffusive mass transfer limitation is assumed to be the transport of molecules from the NAPL-water interface into the bulk aqueous phase (Imhoff et al., 1998). If a multicomponent NAPL is depleted with respect to a compound
at the NAPL-water interface, intra-NAPL diffusion from the bulk NAPL to the interface may constitute a significant diffusive mass transfer rate-limitation as well. The use of the simple first order approach will result in lumped mass transfer rate coefficient that combines the impact of both mass transfer processes.

The model was also developed to quantify the effect of an ESA remediation flush on NAPL dissolution kinetic mass transfer by including the enhancement factor (E) in the driving force equation (Ji and Brusseau, 1998):

$$\frac{dM_n}{d\alpha} = -k_f \alpha_0 \left( S_A - \frac{C_E}{E} \right)$$

where $C_E$ is the bulk aqueous phase ESA enhanced concentration for that NAPL component.

As NAPL is removed over time, the interfacial area decreases. The Ji and Brusseau (1998) model accounts for this change by modifying the rate coefficient from the initial value based on changes in the NAPL volumetric content, which has been correlated with interfacial area (Powers et al., 1994). The transient behavior of the mass transfer rate coefficient is expressed as:

$$k_L(t) = k_{L0} \left( \frac{\theta_n(t)}{\theta_{n0}} \right)^{\eta_k}$$
The model updates the transient rate coefficient for each component based on the change in each component’s NAPL volume ($\theta_{ni}$), which accounts for compound specific changes in interfacial area with time during the dissolution process. A single multicomponent NAPL sphere may be conceptualized to have a shrinking core for each compound within the NAPL matrix, with a compound specific $\theta_{ni}$ decreasing over time as that compound becomes depleted. The model was setup to update the total NAPL $\theta_n$ and the $\theta_{ni}$ for each compound at each time step to change the rate coefficient for each compound. As mentioned previously, the aqueous concentration for each component from the dissolution of the multicomponent NAPL in the presence of an enhanced agent has been developed from Raoult’s Law (McCray and Brusseau, 1999), which couples the kinetic mass transfer driving force for each compound to the multicomponent solubility in the presence (or absence) of an ESA solution.

The modeling of NAPL dissolution with an ESA solution requires the coupled solution of the transport equations for both the ESA compound and each of the compounds contained in the NAPL, with a source term that describes the dissolution mass transfer (with the driving force equation). The transport of cyclodextrin in solution can be described with the equation:

$$\frac{\partial c_{CD}}{\partial t} = D \frac{\partial^2 c_{CD}}{\partial x^2} - \nu \frac{\partial c_{CD}}{\partial x}$$
where $D$ is the dispersion coefficient, and $v$ is the interstitial velocity. The transport of each NAPL component dissolved in water (subscript A) is given by:

$$\frac{\partial C_A}{\partial t} + \rho \frac{\partial \frac{\partial C_A}{\partial x}}{\partial x} + \rho \frac{\partial \frac{\partial F C_A}{\partial x}}{\partial x} + \frac{1}{\theta} \frac{\partial \frac{\partial M_x}{\partial x}}{\partial x} = D \frac{\partial^2 C_A}{\partial x^2} - v \frac{\partial C_A}{\partial x}$$

or dissolved in an ESA solution (subscript E) is given by:

$$\frac{\partial C_E}{\partial t} + \rho \frac{\partial \frac{\partial C_E}{\partial x}}{\partial x} + \rho \frac{\partial \frac{\partial F C_E}{\partial x}}{\partial x} + \frac{1}{\theta} \frac{\partial \frac{\partial M_x}{\partial x}}{\partial x} = D \frac{\partial^2 C_E}{\partial x^2} - v \frac{\partial C_E}{\partial x}$$

where $C_A$ is the concentration of each NAPL compound in the aqueous solution, $C_E$ is the concentration of each NAPL compound in the ESA solution, and $S_1$ and $S_2$ are the instantaneous and rate-limited sorbed concentrations of the NAPL compounds. Using the well known two-domain sorption approach, the instantaneous and rate-limited sorption of the NAPL compounds are described as:

$$S_1 = F K_D \frac{C_A}{E}$$

and

$$\frac{\partial S_2}{\partial t} = k_2 \left[ (1 - F) K_D \frac{C_A}{E} - S_2 \right]$$

where $K_D$ is the linear sorption partitioning coefficient, $k_2$ is the desorption rate coefficient and $F$ is the fraction of sorbent for which sorption is instantaneous. The
above equations assume that the sorption of NAPL compounds to porous media is linear and rate-limited, and the transport equation for the ESA assumes that cyclodextrin is transported as a nonreactive tracer with no sorption.

Application of this model to simulate a particular flushing process requires knowledge of several parameters. Experimental properties were typically measured independently and are presented in Tables 1 and 2. The initial tracer test with the nonreactive tracer (PFBA) was used to estimate the mechanical dispersion, the 3 component tracer sorption experiment was used to determine compound specific retardation coefficients and sorption rate coefficients, and batch experiments (Appendix B) were used to measure single component and NAPL mixture solubilities in water and the HPCD solution. Standard temporal moment analysis was used to calculate the mass balance and the retardation factor for all tracer experiments (e.g., Valocchi, 1985). The 0th moment (integration of eluted concentration) was compared to the measured injected mass to calculate mass recovery, which was nearly complete for each tracer. The mean travel time was calculated using the normalized 1st moment. The ratio of the NAPL compound and non-reactive tracer travel times was used to calculate the retardation factor (Table 1).

The mass transfer rate coefficients were compared to previous empirical mass transfer correlations for the Sherwood number (Sh) and Reynolds number (Re) (Powers et al., 1994b). The Reynolds number is defined as:
where \( \rho_w \) is the density of the water phase, and \( \mu_w \) is the viscosity of water, and the Sherwood numbers were calculated from the initial mass transfer rate coefficients:

\[
Re = \frac{\nu \rho_w d_{50}}{\mu_w}
\]

\[
k_L = \frac{S_h D_L}{d_{50}^2} = k_f a_0
\]

where \( D_L \) is the bulk water diffusion coefficient for the NAPL compounds.

**RESULTS AND DISCUSSION**

**Sorption Evaluation**

Table 1 contains the sorption experimental and transport modeling parameters. Both toluene and ethylbenzene had travel times similar to the nonreactive tracer, but butylbenzene did exhibit minor retardation. Figure 1 presents the 3 component tracer experiment elution data with a flow interruption at the end of the elution. The concentrations of each compound increased during the interruption, which suggests rate-limited sorption. All three compounds exhibited concentration elution tailing related to rate-limited sorption mass transfer.

Sorption linearity was evaluated by comparing the shapes of the arrival and elution waves for each breakthrough curve (e.g., Hu and Brusseau, 1998; Carroll et al.,
When nonlinear sorption significantly affects transport, the arrival wave exhibits self-sharpening behavior while the elution wave exhibits spreading behavior (for concave-downward isotherms), and the arrival and inverted elution curves are, therefore, different. The arrival and inverted elution waves are compared for each of the 3 components during the tracer experiment in Figure 2. The coincident nature of the two sets of curves for each solute indicates that nonlinear sorption had minimal impact on transport. Thus, it appears that rate-limited, linear sorption is responsible for the nonideal transport observed.

The model was used to evaluate the solute transport of the nonreactive tracer and toluene, ethylbenzene, and butylbenzene sorption. Figure 3 shows the observed data and simulated breakthrough curves. The model was able to match the observed transport by calibrating to the sorption kinetic parameters (i.e. $F$ and $k_2$). Table 1 contains the results of sorption modeling parameter estimation, and the sorption properties also were considered in the NAPL dissolution modeling.

**NAPL Solubilization Experiments**

The effluent concentration results from dissolution of toluene as a single component NAPL are illustrated in Figure 4a. The majority of the toluene was removed from the single component NAPL after approximately 200 pore volumes, but then mass transfer rate-limitation tailing occurs. The initial aqueous concentration is similar to the single component solubility, which suggests that the local equilibrium assumption may
be a reasonable approximation for the initial phase of dissolution for this system. Appendix B provides additional discussion regarding early-time dissolution and steady state mass transfer. However, researchers have shown that rate-limitation also can be observed with concentration tailing over time as the residual NAPL, or components within the NAPL, become depleted, which indicates transient rate-limited dissolution. The concentration tail observed in the toluene single component NAPL experiment (Figure 4a) is a significantly higher concentration (3 orders of magnitude) than what was observed for the rate-limited sorption tailing (Figure 1).

Figure 4b shows the results of aqueous concentrations resulting from dissolution of toluene from a 2 component mixture. The initial mixture was 0.05 ml toluene in 50 ml hexadecane, and hexadecane’s solubility is negligible compared to toluene. Essentially, the total NAPL volume, and presumably the NAPL/water interfacial area, remained constant over the experiment. The initial toluene concentration (1.75 mg/L) is significantly lower than its pure phase aqueous solubility (583 mg/L), but the initial concentration compares favorably with the NAPL mixture solubility for toluene estimated from Raoult’s Law (583 mg/L multiplied by mole fraction of 0.003 equals 1.75 mg/L). After approximately 50 pore volumes, the toluene concentrations decrease, and transient rate-limited mass transfer occurs. However, the slope of the curve was relatively constant with no concentration tail in contrast to the single component experiment (Figure 4a).
The effluent concentrations of the column experiment with the equi-volume 3 component NAPL mixture dissolving into water is presented in Figure 4c. The initial aqueous concentrations for each of the three components were significantly lower than the aqueous solubilities, but they were similar to the concentrations predicted by Raoult’s Law when each component’s mole fraction (Table 2) was multiplied by the compound’s solubility. As expected, toluene was removed from the NAPL first due to its higher solubility, with a majority of the toluene removed after approximately 600 pore volumes of flushing. The order of elution was, in part, related to the reduced concentration of ethylbenzene and butylbenzene associated with the NAPL mixture composition. As toluene was depleted, the concentrations, and removal rate, of ethylbenzene and butylbenzene increased due to their increasing mole fractions. The 3 component NAPL toluene elution curve was similar to the 2 component toluene experiment (Figure 4b) without concentration tailing.

The difference between single and multicomponent toluene NAPL dissolution behavior may be attributed to a variety of factors including differences in NAPL-water interfacial area between experiments, mixture solubility and composition impacts, or intra-NAPL diffusion through the NAPL matrix prior to boundary layer mass transfer. Mixture solubility and NAPL composition may impact rate-limited dissolution by altering the aqueous phase concentrations (and dissolution concentration gradient). The single component NAPL solubility (and concentration gradient) may be constant (assuming constant velocity), but the multicomponent concentration gradient can change
with the NAPL composition. Secondly, changes in interfacial areas may be different for single and multiple component NAPLs. The order of elution dissolution behavior of multicomponent dissolution suggests that components are depleted while the bulk NAPL phase continues to be present, which suggests that changes in interfacial areas will be different from single component NAPLs. The magnitude of interfacial area is directly proportional to the magnitude of mass transfer. Thirdly, intra-NAPL diffusion may create differences in the dissolution behavior between single and multiple component systems. Single component systems will not undergo intra-NAPL diffusion, but multiple component systems will tend to develop NAPL composition variability during depletion of the NAPL with respect to a specific compound. As a mixture component is dissolved, the NAPL concentration decreases for that compound, and mass transfer occurs at the interface, which can create a concentration gradient within the NAPL toward the interface if dissolution is rapid relative to the diffusion of compounds in the mixture. If mixture compositional variability occurs, it suggests that diffusion of depleted compounds from the interior of NAPL to the interface could limit mass transfer.

Figure 4a shows toluene exhibiting a concentration tail due to rate-limited dissolution from the single component NAPL, but toluene did not have a concentration tail when dissolving from the multicomponent NAPL experiments (Figures 4b and c). The multicomponent experiments did not exhibit concentration tailing, because the NAPL-water interfacial area was not significantly reduced during the time of the toluene dissolution. For the toluene-hexadecane experiment, the change in area was most likely
negligible during the entire experiment, but it was also not likely to have changed significantly during the 3 component experiment due to the significant volumes of ethylbenzene and butylbenzene remaining. For the single component experiment that exhibited dissolution tailing during NAPL removal, the magnitude of $k_i$ decreased with time (increasing rate-limitation) given that it incorporates the NAPL-water specific interfacial area, which decreases as dissolution proceeds. Changes in specific interfacial area are generally assumed to be non-linearly related to NAPL volume (Powers et al., 1994). Therefore, changes in $k_i$ due to decreasing NAPL volume will have a more significant affect on mass transfer than linear changes in the concentration gradient. Additionally, if intra-NAPL diffusion or multicomponent mixture solubility changes affecting the concentration gradient were responsible for the differences in dissolution behavior, we would expect to observe the change to occur as a function of the NAPL mole fraction. The effect of mixture solubility on rate-limitation should be a function of the mole fraction, because the mixture solubility is dependent on the mole fraction. Also, the amount of intra-NAPL diffusion should be a function of NAPL composition (or variability in NAPL composition), which changes with the mole fraction. However, toluene dissolution tailing was not observed in the multicomponent NAPL experiments as a function of mole fraction.

Additional experiments examined the influence of a 10 % by weight cyclodextrin complexing agent solution (using HPCD) on the enhanced solubilization of the same single and 3 component NAPL mixtures. Figure 5a presents the column effluent
concentrations for a single component (toluene) NAPL enhanced solubilization experiment. The initial concentration in the column matched the aqueous solubility for toluene. After one pore volume, the concentrations increased to the enhanced apparent solubility, which is the product of the enhancement factor and the aqueous solubility (Table 2 and 3). The single component toluene ESA experiment (Figure 5a) had a similar initial NAPL saturation as the single component toluene water experiment (Figure 4a). However, the HPCD enhanced dissolution experiment removed the majority of NAPL in significantly less time (approximately 100 pore volumes) than the aqueous dissolution (approximately 200 pore volumes).

Figures 5b and 5c show the single component NAPL enhanced solubilization with 10% by weight HPCD for ethylbenzene and butylbenzene, respectively. The results for all three single component ESA experiments are comparable. Concentrations increase after one pore volume from aqueous solubility to the enhanced (apparent) solubility for the HPCD solution. An initial steady state mass transfer period is observed for each experiment followed by a steep decrease in concentrations and concentration tailing, which suggests rate-limited mass transfer. An early-time steady state mass transfer period and rate-limited concentration tailing was observed for all 3 single component HPCD enhanced solubilization experiments (Figures 5a, b, and c).

The effluent concentration of the column experiment with the equi-volume 3 component NAPL mixture dissolving into the same 10% HPCD solution is presented in Figure 5d. The 3 component ESA experiment had initial concentrations were near the
aqueous NAPL mixture solubilities for each component based on Raoult’s Law, and the enhanced concentrations had a small steady state period where the enhanced concentrations was approximately the product of the enhancement factor and the NAPL mixture component aqueous solubility (similar to the batch results from Appendix B). The reduction in remediation time, compared to the aqueous experiments, due to cyclodextrin solubility enhancement is evident from these experiments. However, long-term concentration tailing due to rate-limited solubilization was observed in each of the HPCD solubilization experiments.

**NAPL Dissolution Simulation**

The numerical model was used to simulate the dissolution and solute transport observed in each of the experiments. Figure 6 presents the comparison of the observed elution data with the model simulated column elution concentrations resulting from residual NAPL rate-limited aqueous dissolution and solute transport with rate-limited sorption. The model results compare favorably with the observed data. The total mass removed matched the experimentally determined removal, and the model seems to capture both the steady state and transient dissolution behavior for the 1, 2, and 3 component aqueous dissolution experiments. Additionally, the model does capture the multicomponent order of elution, and it shows an increase in NAPL component concentrations with mole fractions over time (Figure 6c). Table 3a presents the results of the modeling including estimation of the dissolution mass transfer kinetics, mole
fractions, Re numbers, and Sh numbers for each experiment. As with Table 2, the parameters are numbered for each of the compounds (Tol for toluene, EB for ethylbenzene, and BB for butylbenzene). The results for the aqueous dissolution show that the lumped rate coefficients ($k_L$) vary from 8.8 for single component NAPL to 10.4 hr$^{-1}$ for the 3 component NAPL. The difference in $k_L$ values between experiments is minor, which suggests that NAPL composition did not have a significant effect on $k_L$ values. For example, the single component NAPL (toluene $x = 1$) had a $k_L$ value of 8.8 hr$^{-1}$ and the toluene-hexadecane mixture (toluene $x = 0.003$) had a $k_L$ value of 9.9 hr$^{-1}$.

Simulated elution curves for cyclodextrin enhanced dissolution are presented in Figure 7, and the modeling results are listed in Table 3b. The simulations match the observed data relatively well. As was the case for water flushing, the HPCD-enhanced dissolution was, in general, rate-limited. However, similar to the water flushing data, the local equilibrium assumption was valid during the early steady state stage of the experiments and modeling. The total mass removed matched the experimentally determined removal, and the model seemed to capture both the steady state and transient HPCD enhanced dissolution behavior for the single component column experiments.

The 3 component NAPL mixture HPCD solubilization experiment and model comparison is presented in Figure 8a. The model does match the toluene elution data. However, it shows significant deviation from the observations of ethylbenzene and butylbenzene. The model predicts the initial aqueous concentrations, the increased concentrations to the enhanced apparent solubilities, and even shows increases of
concentrations of NAPL components with changing mole fraction. However, the increases in ethylbenzene and butylbenzene concentrations due to changes in mole fraction in the model were delayed relative to the observed changes in concentration. It is possible that the NAPL mixture became nonideal, which would create deviations from the Raoult’s Law based model.

Figures 8b and 8c contain the estimated NAPL mole fractions for each component through time for the 3 component NAPL aqueous (Figure 8b) and HPCD solubilization experiments (Figure 8c). The mole fractions in the NAPL were estimated using Raoult’s Law by dividing the observed concentrations by the aqueous or apparent (for HPCD) solubilities. The sum of the mole fractions is plotted as well. The results suggest that the mixture remained ideal throughout the aqueous experiment, because the sum of the mole fractions remained at approximately one (Figure 8b). However, the results presented in Figure 8c suggest that the 3 component NAPL mixture may have become nonideal during the HPCD solubilization experiment due to the deviations from unity in total mole fraction. Previous research examining surfactant enhanced dissolution of the same 3-component NAPL found the mixture to be ideal dissolving in water and nonideal dissolving in the surfactant solution (McCray et al., 2001). However, equilibrium dissolution of the NAPL mixture into HPCD followed Raoult’s Law during batch experiments (Appendix B), which suggests that the deviation may be due to transient non-ideality or intra-NAPL diffusive mass transfer behavior.
One possible explanation for the deviation from Raoult’s Law is nonideality created from dissolution mass transfer and intra-NAPL diffusion from the interior of the NAPL to the interface, which was not specifically accounted for in the model. The observations show both ethylbenzene and butylbenzene concentrations increasing while toluene was still dissolving, which may potentially be related to NAPL mole fraction changes due to toluene depletion near the NAPL-water interface (mole fraction variability within the NAPL). Decreases in toluene within the NAPL would be expected to occur at the interface. If mass transfer is rapid relative to intra-NAPL diffusion, a toluene concentration gradient would occur within the NAPL. The change in mole fraction near the NAPL-water interface could locally increase the mixture solubilities of the other compounds. However, the cause of HPCD enhanced solubilization of multicomponent NAPL nonideality remains uncertain.

**Evaluation of Rate-Limitation**

The lumped mass transfer rate coefficients determined for cyclodextrin flushing were significantly larger than the values determined for water flushing (Table 3). The $k_L$ values for the HPCD experiments varied from 26 hr$^{-1}$ for single component toluene to 145 hr$^{-1}$ for single component butylbenzene, which was between 3 and 15 times the aqueous dissolution $k_L$ coefficients. The lumped rate coefficients increased with increasing solubility enhancement. This results suggests that the HPCD solution significantly reduces the NAPL dissolution mass transfer rate-limitation. The removal
times were not only decreased by the increased concentrations, but the rates of mass transfer were increased, as well. This result suggests that groundwater source zone NAPL remediation may be significantly improved (relative to pump and treat technology) through the application of HPCD solutions.

As noted previously, variability in velocity may have a significant impact on rate-limited mass transfer (Powers et al., 1992; 1994). Figure 9 and Table 3c present the results of 4 experiments and simulations conducted at increased velocities (relative to the previously described experiments) to evaluate the effect of velocity on multicomponent NAPL dissolution and HPCD enhanced solubilization. Figure 9a shows the observed and simulated effluent concentrations from the high velocity toluene single component NAPL dissolution experiment, which may be compared to the lower velocity experiment and model results in Figure 6a. The high velocity experiment shows a decreased concentration within the steady state, early-time dissolution, which is most likely a result of the increased velocity. Also, the transition period of decrease in concentration takes longer for the high velocity experiment, and the experiment had a lower concentration tail. Figure 9b presents the results from the high velocity 3 component aqueous dissolution experiment and simulation, which is comparable to the lower velocity 3 component experiment and model results shown in Figure 6c. The high velocity aqueous experiment shows the Raoult’s Law behavior similar to the low velocity experiment. Conversely, the high velocity 3 component NAPL enhanced solubilization experiment (Figure 9c) does not follow the Raoult’s Law behavior, which is similar to the low
velocity HPCD solubilization experiment (Figure 8a). The Raoult’s Law based model was not able to match either 3 component NAPL cyclodextrin flush experiment. Additionally, Figure 9d presents the observations and modeling results of a 3 component DNAPL mixture aqueous dissolution experiment. Chlorophenol (CphOH), chlorobenzene (CB), and dichlorobenzene (DCB) created an ideal equal volume mixture that illustrates the applicability of Raoult’s Law and the numerical model to the remediation of other types of mixtures. CphOH has a very high solubility compared to the other compounds, and it was removed rapidly from the mixture. However, the mixture followed Raoult’s Law, and the model was able to simulate the dissolution behavior.

Figure 10 presents a comparison of some of the previously published NAPL dissolution mass transfer correlations as a Sherwood Number versus Reynolds Number plot, which is a typical dimensionless number comparison for relative mass transfer versus flow system (Khachikian and Harmon, 2000). The plot contains NAPL dissolution mass transfer correlations for both aqueous and surfactant flushing, and the results of the current investigation have been plotted on the figure. The results suggest that the mass transfer kinetics for the NAPL aqueous dissolution experiments were within the range of results that have been previously reported. However, the HPCD enhanced NAPL solubilization experiments showed increased mass transfer compared to the previous investigations. Additionally, the aqueous experiments were all grouped even though the experiments had different NAPL compositions (1, 2, and 3 components),
but the HPCD enhanced dissolution experiments showed some variability in mass transfer with different NAPL compositions. These results support the previously mentioned results that aqueous ideal multicomponent NAPL dissolution rate-limitation was independent of the NAPL composition.

**CONCLUSIONS**

In summary, cyclodextrin flushing enhanced the removal of organic compounds from the NAPL mixtures. Dissolution was generally rate-limited when flushing with or without the cyclodextrin solutions, but the rate-limitation was reduced in the presence of the flushing agent. The NAPL mixtures appear to be ideal for each of the 1, 2, and 3 component mixtures used through the change in number of compounds and mole fraction for aqueous dissolution. However, the 3 component NAPL solubilized in HPCD solution deviated from Raoult’s Law behavior, which may be related to nonideality as previously observed in surfactant solutions (McCray et al., 2001).

Cyclodextrin flushing of groundwater contamination source zones with residual NAPL was evaluated for enhanced solubilization and removal of organic compounds from the simple 3 component NAPL mixture. Dynamic experiments were performed to observe the dissolution behavior with variations in NAPL composition during water and HPCD dissolution to compare traditional pump and treat to ESA remediation of NAPL source zones. The solubility enhancement was significant for each of the NAPL components, and the general mass removal rate was significantly increased with the
application of 10% HPCD, which may be a reasonable concentration for field applications (McCray and Brusseau, 1989; 1999). The numerical simulation of single and multiple component NAPL dissolution and HPCD solubilization was used to estimate mass transfer rate coefficients and predict the dissolution behavior. Toluene dissolution rate-limitation in water was independent of variability in NAPL composition. The model estimated rate coefficients were comparable to previous correlations for the aqueous experiments, and HPCD solubilization rate coefficients were increased (lower rate-limitation) compared to the aqueous rate coefficients. The modeling results also suggest that nonideality and intra-NAPL diffusion should be included in the simulations to test the effects on NAPL mixture rate-limited dissolution.

ACKNOWLEDGMENTS

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REFERENCES


Table 1. Miscible displacement solute transport and adsorption experiment and modeling results

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<th>Parameter(^a)</th>
<th>PFBA Nonreactive Tracer</th>
<th>Toluene Reactive Tracer</th>
<th>Ethylbenzene Reactive Tracer</th>
<th>Butylbenzene Reactive Tracer</th>
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<td>100</td>
<td>99</td>
<td>101</td>
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<td>7.05</td>
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\(^a\) Parameters are defined in text. Ranges represent 95% confidence intervals.

\(^b\) A refers to the column cross sectional area and L refers to the column length.

\(^c\) \(T_i\) refers to the time of tracer injection (other parameters are defined in text).
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<th>Parameter</th>
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### Table 2b. NAPL cyclodextrin enhanced solubilization experimental parameters

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Table 2c. NAPL high velocity dissolution experimental parameters

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<td>(CpOH=1; CB=2; DCB=3)</td>
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<td>ρn-3</td>
<td>g/l</td>
<td>Component Density</td>
<td>-</td>
<td>860.1</td>
<td>860.1</td>
<td>1306</td>
</tr>
<tr>
<td>Vn</td>
<td>L</td>
<td>Initial NAPL Vol.</td>
<td>2.82E-03</td>
<td>3.29E-03</td>
<td>2.10E-03</td>
<td>2.34E-03</td>
</tr>
<tr>
<td>x-1</td>
<td>-</td>
<td>Component Mole Frac.</td>
<td>1.00E+00</td>
<td>4.00E-01</td>
<td>4.00E-01</td>
<td>2.57E-01</td>
</tr>
<tr>
<td>x-2</td>
<td>-</td>
<td>Component Mole Frac.</td>
<td>-</td>
<td>3.40E-01</td>
<td>3.70E-01</td>
<td>4.37E-01</td>
</tr>
<tr>
<td>x-3</td>
<td>-</td>
<td>Component Mole Frac.</td>
<td>-</td>
<td>2.60E-01</td>
<td>2.30E-01</td>
<td>2.64E-01</td>
</tr>
<tr>
<td>Sn</td>
<td>-</td>
<td>Initial Mixture Resid. Sat.</td>
<td>3.07E-01</td>
<td>3.58E-01</td>
<td>2.28E-01</td>
<td>2.46E-01</td>
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<tr>
<td>Ccc (Co)</td>
<td>g/l</td>
<td>HPCD Injection Conc.</td>
<td>0.00E+00</td>
<td>0.00E+00</td>
<td>1.11E+02</td>
<td>0.00E+00</td>
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Table 3a. NAPL aqueous dissolution modeling parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Parameter</th>
<th>1 Component - Water (Tol=1)</th>
<th>2 Component - Water (Tol=1; Hexadecane=2)</th>
<th>3 Component - Water (Tol=1; EB=2; BB=3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>cm2/hr</td>
<td>Dispersion Coeff.</td>
<td>5.26E-01</td>
<td>5.11E-01</td>
<td>5.15E-01</td>
</tr>
<tr>
<td>D_t-1</td>
<td>cm2/hr</td>
<td>Component Diffusion Coeff.</td>
<td>3.42E-02</td>
<td>3.42E-02</td>
<td>3.42E-02</td>
</tr>
<tr>
<td>D_t-2</td>
<td>cm2/hr</td>
<td>Component Diffusion Coeff.</td>
<td>-</td>
<td>3.10E-02</td>
<td>3.24E-02</td>
</tr>
<tr>
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<td>cm2/hr</td>
<td>Component Diffusion Coeff.</td>
<td>-</td>
<td>-</td>
<td>3.10E-02</td>
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<tr>
<td>E-1</td>
<td>-</td>
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<td>1</td>
<td>1</td>
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<tr>
<td>E-2</td>
<td>-</td>
<td>Component Enhancement</td>
<td>-</td>
<td>1</td>
<td>1</td>
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<tr>
<td>E-3</td>
<td>-</td>
<td>Component Enhancement</td>
<td>-</td>
<td>-</td>
<td>1</td>
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<tr>
<td>K_cw-1</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
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<td>0</td>
<td>0</td>
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<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
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<td>T</td>
<td>PV</td>
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<td>448</td>
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<td>-</td>
<td>Reynolds Number</td>
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<td>1.0E-02</td>
<td>1.0E-02</td>
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<tr>
<td>Sh-1</td>
<td>-</td>
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<td>2.7E-01</td>
<td>3.0E-01</td>
<td>2.7E-01</td>
</tr>
<tr>
<td>Sh-2</td>
<td>-</td>
<td>Sherwood Number</td>
<td>-</td>
<td>-</td>
<td>1.8E-01</td>
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<tr>
<td>Sh-3</td>
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<td>Sherwood Number</td>
<td>-</td>
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<tr>
<td>k_s-1</td>
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<td>8.8</td>
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<td>l/hr</td>
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Table 3b. NAPL cyclodextrin enhanced solubilization modeling parameters

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<th>Symbol</th>
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<th>Parameter</th>
<th>1 Component - HPCD</th>
<th>1 Component - HPCD</th>
<th>1 Component - HPCD</th>
<th>3 Component - HPCD</th>
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<tr>
<td></td>
<td></td>
<td>(Tol=1)</td>
<td>(EB=2)</td>
<td>(BB=3)</td>
<td>(Tol=1; EB=2; BB=3)</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>cm²/hr</td>
<td>Dispersion Coeff.</td>
<td>5.14E-01</td>
<td>5.37E-01</td>
<td>5.39E-01</td>
<td>5.38E-01</td>
</tr>
<tr>
<td>D₁₋₁</td>
<td>cm²/hr</td>
<td>Component Diffusion Coeff.</td>
<td>3.42E-02</td>
<td>-</td>
<td>-</td>
<td>3.42E-02</td>
</tr>
<tr>
<td>D₁₋₂</td>
<td>cm²/hr</td>
<td>Component Diffusion Coeff.</td>
<td>-</td>
<td>3.24E-02</td>
<td>-</td>
<td>3.24E-02</td>
</tr>
<tr>
<td>D₁₋₃</td>
<td>cm²/hr</td>
<td>Component Diffusion Coeff.</td>
<td>-</td>
<td>-</td>
<td>3.10E-02</td>
<td>3.10E-02</td>
</tr>
<tr>
<td>E₁</td>
<td>-</td>
<td>Component Enhancement</td>
<td>7.7</td>
<td>-</td>
<td>-</td>
<td>8.0</td>
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<tr>
<td>E₂</td>
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<td>Component Enhancement</td>
<td>-</td>
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<tr>
<td>E₃</td>
<td>-</td>
<td>Component Enhancement</td>
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<td>-</td>
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<td>124.3</td>
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<tr>
<td>Kₑₑ⁻¹</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
<td>6.03E-02</td>
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<td>6.30E-02</td>
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<tr>
<td>Kₑₑ⁻²</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
<td>-</td>
<td>1.69E-01</td>
<td>-</td>
<td>1.65E-01</td>
</tr>
<tr>
<td>Kₑₑ⁻³</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
<td>-</td>
<td>-</td>
<td>1.38E+00</td>
<td>1.11E+00</td>
</tr>
<tr>
<td>t</td>
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<td>Total Experiment Time</td>
<td>224</td>
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<td>484</td>
<td>1030</td>
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<td>T</td>
<td>PV</td>
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<td>1.06E-02</td>
<td>1.05E-02</td>
<td>1.05E-02</td>
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<tr>
<td>Sh₁</td>
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<td>Sherwood Number</td>
<td>7.95E-01</td>
<td>-</td>
<td>-</td>
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<td>Sherwood Number</td>
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<td>2.13E+00</td>
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<tr>
<td>Sh₃</td>
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<td>Sherwood Number</td>
<td>-</td>
<td>-</td>
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<td>kₑ₁</td>
<td>1/hr</td>
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<td>26.06</td>
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<td>-</td>
<td>26.66</td>
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<tr>
<td>kₑ₂</td>
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<td>-</td>
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<td>-</td>
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<tr>
<td>kₑ₃</td>
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232
Table 3c. NAPL high velocity dissolution modeling parameters

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<th>Parameter</th>
<th>1 Component - Water (Tol=1)</th>
<th>3 Component - Water (Tol=1; EB=2; BB=3)</th>
<th>3 Component - HPCD (Tol=1; EB=2; BB=3)</th>
<th>3 Component - Water (CpOH=1; CB=2; DCB=3)</th>
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<tr>
<td>D</td>
<td>cm²/hr</td>
<td>Dispersion Coeff.</td>
<td>2.40E+00</td>
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<td>4.35E+00</td>
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<td>D_e-1</td>
<td>cm²/hr</td>
<td>Component Diffusion Coeff.</td>
<td>3.42E-02</td>
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<td>3.42E-02</td>
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</tr>
<tr>
<td>D_e-2</td>
<td>cm²/hr</td>
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<tr>
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<td>cm²/hr</td>
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<td>-</td>
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<td>3.10E-02</td>
<td>4.32E-02</td>
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<td>1.0</td>
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<td>1.0</td>
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<tr>
<td>K_{cw-1}</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
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<td>0.00E+00</td>
<td>5.85E-02</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>K_{cw-2}</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
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<td>1.61E-01</td>
<td>0.00E+00</td>
</tr>
<tr>
<td>K_{cw-3}</td>
<td>l/g</td>
<td>Component HPCD Partition Coeff.</td>
<td>-</td>
<td>0.00E+00</td>
<td>1.86E+00</td>
<td>0.00E+00</td>
</tr>
<tr>
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<td>626</td>
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<td>T</td>
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<td>1.49E+00</td>
</tr>
<tr>
<td>k_{e-1}</td>
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<td>k_{e-3}</td>
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<td>Component Lumped Rate Coeff.</td>
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<td>90.15</td>
<td>299.43</td>
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Figure 1. Three Compound Sorption Break Through Curve with Interruption
Figure 2a. Toluene Sorption Comparison of Arrival and Elution
Figure 2b. Ethylbenzene Sorption Comparison of Arrival and Elution
Figure 2c. Butylbenzene Sorption Comparison of Arrival and Elution
Figure 3. Three Component Sorption Experiment and Simulation Results
Figure 4a. Single Component NAPL Aqueous Dissolution Experimental Results
Figure 4b. Two Component NAPL Aqueous Dissolution Experimental Results
Figure 4c. Three Component NAPL Aqueous Dissolution Experimental Results
Figure 5a. Single Component NAPL Cyclodextrin Enhanced Dissolution Experimental Results
Figure 5b. Single Component NAPL Cyclodextrin Enhanced Dissolution Experimental Results
Figure 5c. Single Component NAPL Cyclodextrin Enhanced Dissolution Experimental Results
Figure 5d. Three Component NAPL Cyclodextrin Enhanced Dissolution Experimental Results
Figure 6a. Single Component NAPL Aqueous Dissolution and Simulation Results
Figure 6b. Two Component NAPL Aqueous Dissolution and Simulation Results
Figure 6c. Three Component NAPL Aqueous Dissolution and Simulation Results
Figure 7a. Single Component NAPL Cyclodextrin Enhanced Dissolution and Simulation Results
Figure 7b. Single Component NAPL Cyclodextrin Enhanced Dissolution and Simulation Results
Figure 7c. Single Component NAPL Cyclodextrin Enhanced Dissolution and Simulation Results
Figure 8a. Three Component NAPL Cyclodextrin Enhanced Dissolution and Simulation Results
Figure 8b. Three Component NAPL Mole Fraction During Aqueous Dissolution
Figure 8c. Three Component NAPL Mole Fraction During Cyclodextrin Enhanced Dissolution
Figure 9a. High Velocity Single Component NAPL Aqueous Dissolution and Simulation Results
Figure 9b. High Velocity Three Component NAPL Aqueous Dissolution and Simulation Results
Figure 9c. High Velocity Three Component NAPL Cyclodextrin Enhanced Dissolution and Simulation Results
Figure 9d. High Velocity Three Component DNAPL (Chlorophenol, Chlorobenzene, and Dichlorobenzene) Aqueous Dissolution and Simulation Results (inset shows lower concentration range)
Figure 10. Comparison of Dissolution Mass Transfer Correlations