

ENHANCED-SOLUBILIZATION OF MULTICOMPONENT DENSE IMMISCIBLE LIQUID
IN HOMOGENEOUS POROUS MEDIA

by

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ABSTRACT

Complex multi-component nonaqueous phase liquid (NAPL) mixtures can significantly limit the effectiveness of groundwater remediation. The use of enhanced-flushing technologies has emerged as a promising technique for the remediation of sites contaminated with NAPL. A series of one-dimensional column experiments was conducted to quantify the effectiveness of four flushing agents (also referred to “solubilizing agents” in this study) for the removal of a uniformly distributed multi-component NAPL source within a homogeneous porous medium. The columns were established with NAPL saturations (S_n) targeted between 10-20%, consisting of an equal 1:1:1 mole mixture of tetrachloroethene (PCE), trichloroethene (TCE), and cis-1,2-dichloroethene (DCE). The solubilization agents investigated included 5 wt.% solutions of two complexing sugars: hydroxypropyl- β -cyclodextrin (HPCD) and methyl- β -cyclodextrin (MCD), a 5 wt.% solution of a surfactant: sodium dodecyl sulfate (SDS), and a 50 wt.% solution of ethanol (EtOH). For comparison purposes, a water flush (pump-and-treat) experiment was also conducted as a control, representing the system by which no enhanced-solubilization occurred. In general, initial effluent NAPL concentrations were successfully predicted using Raoult's Law, with minimal deviation (error) between the observed and predicted concentrations. The experimental data were used to test the efficiency of each flushing agent by analyzing the normalized contaminant mass recovery, the mass ratio of contaminant removed to reagent used, and the mole ratio of contaminant removed to reagent used. Mass flux reduction analysis was also used to test the efficiency of the various flushing agents. The results of the analyses showed that EtOH was the most efficient flushing agent for removing the contaminants when evaluated based on a normalized mass recovery analysis, but was least efficient based on a mass-ratio and mole-ratio of contaminant to reagent evaluation method. SDS was most efficient for contaminant

removal when analyzed by mass-contaminant to mass-reagent recovered basis. Based on the moles-contaminant to moles-reagent recovered ratio efficiency evaluation, the MCD flushing agent was most effective at removing the contaminants from the system. The results of these experiments indicate that the addition of a chemical flushing agent greatly reduces the time needed to remove each NAPL component, compared to flushing with water alone (i.e., pump and treat). PCE showed the greatest relative solubility enhancement for all enhanced flushing agents tested. In terms of consistent concentrations (5 wt.%), MCD and SDS were the most effective flushing agents removing all three NAPL components (DCE/TCE/PCE) with the least number of pore volumes. The HPCD flush had no appreciable solubility enhancement effect for DCE and TCE; however, PCE did show a 5-fold enhancement in solubility for this experiment. In terms of mass flux reduction/mass removal (MFR/MR) evaluation, DCE (the highest solubility NAPL component) exhibited the greatest nonideal (inefficient) response during both the water and HPCD flushing experiments. MFR/MR behavior for the target contaminants was least ideal during the SDS flush compared to the other enhanced-flushing agents. In terms of contaminant removal efficiency, SDS surpassed all other flushing agents based on a contaminant-mass to reagent-mass recovery evaluation and MCD surpassed all other enhanced flushing agents based on contaminant-mole to reagent-mole recovery evaluation. In general, HPCD and MCD are more expensive than SDS and EtOH, and therefore may be less desirable choices for use at greater scales; however, their toxicities to microbial communities in the subsurface and potential concerns to human health and the environment are negligible compared to SDS and EtOH. Results from this study indicate that several criteria should be used to evaluate the removal effectiveness of flushing agents for multi-component NAPL systems. Due to the variety of remediation scenarios that could be encountered in the field, these findings will be helpful in

developing more efficient and effective remediation strategies and for enabling more accurate prediction of resulting NAPL concentrations to meet the needs of various contaminated sites impacted by chlorinated compounds such as PCE, TCE, and DCE.

LIST OF ABBREVIATIONS AND SYMBOLS

cm Centimeter

β Beta

hr hour

I.D. Inner diameter

L Liter

min Minute

mg Milligram

mL Milliliter

nm Nanometer

NAPL Nonaqueous Phase Liquid: also known as an immiscible liquid (with water)

S_n NAPL saturation: Ratio of NAPL volume to void volume

q Darcy's velocity (L/T)

T Time

UV Ultraviolet: wavelengths shorter than light but longer than X-rays

v_p Linear pore velocity

wt.% Weight percent

% Percent

> Greater than

\pm Plus or Minus

Σ Summation: The arithmetic operation of calculating the sum of two or more numbers

= Equal to

x Mole fraction

- E* Enhancement Factor: Ratio of maximum enhanced-flushing concentration to maximum aqueous-concentration (during water flushing)
- n* Porosity: Ratio of the volume of void space in a unit volume of earth material to the total volume of material including both voids and solids

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CHAPTER 1: INTRODUCTION AND OBJECTIVES

Introduction

Contamination of soil and groundwater by hazardous organic immiscible liquids poses significant risks to human health and the environment, across the U.S. and worldwide. A large fraction of the impacted sites are contaminated by mixed-waste contaminants and chemicals, commonly including nonaqueous phase liquids (NAPLs), also referred to as immiscible liquids. Immiscible liquids are defined as any liquid that is not miscible or does not readily mix in water. Immiscible liquids exist as a separate liquid phase from that of water and typically must rely on rate-limited dissolution kinetics to dissolve in water, thus making them difficult to remediate via pump-and-treat methods in feasible time periods. The typically low solubility limits associated with many immiscible liquids inhibit the remediation process, and are often a limiting factor preventing complete removal of the contaminants from groundwater within reasonable time periods. The presence of immiscible liquids in the subsurface is the single most important factor limiting cleanup of soil and groundwater (NRC 1994, 1997, 1999, 2000, 2005; USEPA 2003). Chlorinated solvents, such as tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE), are ubiquitous at many contaminated sites. Chlorinated solvents are persistent in the environment due their low solubility limits and tendency to reside as trapped pure phase in the pore spaces of the subsurface. Many of these chemicals have been classified as carcinogens or suspect carcinogens and have been shown to cause a variety of human health issues, including respiratory problems and birth defects. In fact, TCE was recently upgraded from suspect carcinogen to known carcinogen (USEPA, 2011; OMB Watch, 2011; LA Times, 2011).

Hazardous waste disposal sites and many other contaminated sites commonly contain various compounds ranging from light nonaqueous phase liquids (LNAPLs) and petroleum hydrocarbon derivatives (i.e. decane), to dense nonaqueous phase liquids (DNAPLs) such as chlorinated solvents (i.e. TCE), and mixtures of both immiscible liquids and miscible liquids (e.g., McCray and Dugan, 2002; Rao et al., 1997; McCray and Brusseau, 1998; McCray et al., 2011). Very little research has been conducted on the dissolution and enhanced removal of mixed waste systems, in particular, multi-component chlorinated immiscible liquid systems. It is therefore critical to understand the dissolution, mass flux, and mass removal relationships of these mixed waste systems under both pump-and-treat and under enhanced remediation scenarios.

Objectives

The purpose of this research is to evaluate the effectiveness of a variety of enhanced-solubilization flushing agents (e.g., complexing sugars, co-solvents, and surfactants) for the removal of multi-component immiscible liquid within physically homogeneous porous media. One aspect of this research was to evaluate contaminant mass removal efficiency using various metrics including: normalized mass recovery; contaminant-mass to reagent-mass recovery; and contaminant-mole to reagent-mole recovery. This research was also conducted to test the behavior of the contaminants under enhanced flushing conditions, to see whether the dissolution processes initially behave ideally according to equilibrium partitioning relationships as predicted by Raoult's Law. This research also examines the mass flux reduction behavior for each target contaminant and whether distinct differences in mass flux behavior occur as a result of the specific enhanced-flushing agent itself.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

Background

Chlorinated solvents such as PCE, TCE and DCE are some of the most pervasive and persistent chemicals found at sites contaminated by immiscible liquids. These highly toxic contaminants have been proven to be carcinogenic in lab animals. Consequently, even small amounts of these substances in aquifers can render large volumes of groundwater unsuitable for use, posing serious health risks to humans through drinking water supplies (Connor, 1988). In addition, these chlorinated solvents are commonly found together at contaminated industrial waste disposal sites where chemicals used in manufacturing, processing, and treatment, are degraded, as PCE breaks down to TCE, and TCE breaks down to DCE, via anaerobic reductive dechlorination. The solubility limits are 170 mg/L for PCE, 1,200 mg/L for TCE, and 3,500 mg/L for DCE. The USEPA established MCL value for PCE and TCE is 5 µg/L, and the value for *cis* DCE is 70 µg/L. This makes it extremely difficult to effectively remediate immiscible-liquid contaminated sites and meet specific cleanup goals. Therefore, it is very important to study the effectiveness of various enhanced-solubilization agents for the removal of multi-component immiscible liquids from saturated porous media systems to better understand the factors controlling the removal of immiscible liquids and improve pump-and-treat remediation efforts. The columns were established with a NAPL saturation of 10-20%, consisting of an equal 1:1:1 mole mixture of tetrachloroethene (PCE), trichloroethene (TCE), and *cis*-1,2-dichloroethene (DCE). The range of desired NAPL saturation (S_n) was chosen to be consistent with those values utilized in previous studies similar in scope and to represent realistic higher saturations observed and reported at NAPL-contaminated field sites (McCray and Brusseau, 1998; Boving and Brusseau, 2000; Brusseau et al., 2002; Tick et al., 2003; Brooks et al., 2004; Childs et al., 2006;

Tick and Rincon, 2009; McCray et al., 2011; Harvell, 2012). PCE, TCE, and DCE were selected due to their prevalence at contamination sites, in particular TCE and PCE. PCE and TCE are both used as degreasing agents and, therefore, both of these compounds have a high potential to exist at many contamination sites such as military and airfield installations.

Previous Research and Literature Review

Chemically-Enhanced Flushing Technologies

Chemically-enhanced flushing is commonly used to remediate in-situ groundwater contamination. Chemical agents are used to enhance the solubility and mobility of nonaqueous phase liquid contaminants in the groundwater system. Enhanced-solubilization agents have the effect of increasing what is termed the “apparent” solubility of the contaminant above maximum aqueous solubility within the solution. The “apparent” solubility of the contaminant is the maximum concentration which results due to the additional contaminant mass that can dissolve into the “aqueous” enhanced-solubilization flushing solution compared to the aqueous solubility limit (in water alone). In order to determine which flushing (enhanced solubilization) agents are most effective, experiments must be designed and conducted to quantify the ideal scenario to treat a contamination sites polluted with complex multicomponent NAPL mixtures. Four flushing agents were used and evaluated in these series of experiments including: 5 wt.% hydroxypropyl- β -cyclodextrin (HPCD), 5 wt.% methyl- β -cyclodextrin (MCD), a 5 wt.% surfactant, sodium dodecyl sulfate (SDS), and a 50 wt.% solution of ethanol (EtOH).

A large amount of research has been done to analyze the effectiveness of flushing agents on a single immiscible-liquid, specifically TCE (Boving and Brusseau, 2000; Brusseau et al., 2007, Brusseau, 1992; Nambi and Powers, 2000; Tick and Rincon, 2009; Imhoff et al., 1995). The majority of research has been to test the response of TCE to flushing agents in a

homogeneous system. The results of [Boving and Brusseau \(2000\)](#) showed that flushing agents greatly increase the apparent (enhanced) solubility of TCE and dramatically increased the removal of single-component TCE compared to that of water flushing conditions.

[Nambi and Powers et al. \(2000\)](#) studied the effect of aqueous dissolution of TCE in a heterogeneous system. In this study, a 2D flow cell, packed with a heterogeneous medium, was saturated, and the effluent was collected and tested for TCE concentration. This study indicated that aqueous dissolution was well below the equilibrium solubility, and water-flushing was ineffective as a primary flushing agent.

[Imhoff et al. \(1998\)](#) also studied the aqueous dissolution of TCE under water-flushing conditions. In this experiment, columns packed with media of various heterogeneities were saturated with TCE and flushed with water to test the dissolution rates of TCE as a function of heterogeneity. The results of this study showed that heterogeneity and medium have a significant effect on the aqueous dissolution of an immiscible liquid and the efficiency of contaminant removal from the system.

[Tick and Rincon \(2009\)](#) studied the effects of various flushing agents on residual TCE in a homogeneous system. These experiments tested the dissolution and mass-flux of TCE in a saturated column when flushed with one of four flushing agents. This study showed that flushing agents, such as cyclodextrins, surfactants, and co-solvents greatly increase the rate of dissolution of TCE by increasing the apparent solubility (the solubility with respect to aqueous solubility). In addition, [Tick and Rincon \(2009\)](#) found that contaminant mass flux behavior significantly varied for each specific enhanced-solubilization agent. These findings suggest that multiple mass removal criteria should be used when selecting a particular enhanced-solubilization agent to maximize contaminant removal efficiency.

Carroll and Brusseau (2009) tested the effect of HPCD (hydroxypropyl- β -cyclodextrin) on the dissolution of a multi-component system consisting of toluene, ethylbenzene, and butylbenzene, in a heterogeneous system. This experiment showed that flushing agents greatly increase the apparent solubility of these immiscible liquids, and that the mass-flux of the contaminants behaves ideally according to Raoult's Law.

A two-dimensional flow cell study by Harvell (2012) showed that SDS removed a three component DNAPL (PCE, TCE, and DCE) mixture approximately ten times faster than HPCD. However, HPCD outperformed SDS for all contaminant components when compared on a contaminant-mass to reagent-mass ratio basis and moles-contaminant to moles of reagent removed ratio basis for an emplaced rectangular DNAPL source zone. The findings from this study indicate that the selection of a particular flushing agent should be evaluated carefully prior to remediation, as the mass flux and removal behavior of each component may vary significantly, depending on the flushing agent employed as well as the proximity to the contaminant source zone itself.

Enhanced-Solubilization Agents

Surfactants. A surfactant is a "surface active agent" that significantly reduces the surface tension of water, or, when used in low concentrations, the interfacial tension between two fluid phases. Single surfactant molecules, 'monomers', have both hydrophilic and hydrophobic moieties. A variety of these surfactant molecules are termed 'amphiphilic' as they are comprised of both hydrophobic and hydrophilic groups. The hydrophobic tail is water insoluble, while the hydrophilic head is water soluble. Surfactants adsorb at the liquid-gas or aqueous-NAPL interface to achieve thermodynamic stability. This in turn causes a reduction in the surface tension of water. Similarly, they reduce the interfacial tension between water (or aqueous phase

flushing solution) and NAPL by adsorbing at the liquid-liquid interface. Under high enough concentrations, surfactants reach or exceed the critical micelle concentration, or CMC. Under these concentrations, surfactants aggregate into micelle complexes. In water, micelles form with the hydrophobic tails at the core, which can encapsulate a contaminant, or provide a place for the contaminant to partition. An outer shell is formed by the hydrophilic heads, and it maintains favorable contact with water. While these spherical surfactant micelles might have the ability to increase the solubilization of a pure-phase NAPL component, the remediation may be affected by possible sorption of the surfactant in the subsurface and/or contamination zone, or precipitation in that area (Jafvert and Heath, 1991; Brusseau, 1993; Palmer and Fish, 1992). Subsurface reactions are very sensitive to conditions such as groundwater ionic strength, pH, and temperature (Edwards et al., 1991; Harwell, 1991; Jafvert and Heath, 1991; Sabatini et al., 1996a, 1996b; Boving, 2002).

Solubilization of a contaminant increases when the organic material partitions into the micelle's interior, thereby increasing NAPL dissolution, desorption, and apparent solubility. This is known as micellar solubilization. The degree of solubility can depend on numerous factors, such as ionic strength, aggregation number, surfactant structure, solute size, chemistry, micelle geometry (Edwards et al., 1991; Harwell, 1991; Jafvert and Heath, 1991; Sabatini et al., 1996a, 1996b; Boving and Brusseau, 2000). Studies have also shown that surfactants can enhance NAPL removal by way of mobilization. Surfactants reduce the surface tension of water, which can induce NAPL displacement and mobilization from the surrounding contaminant matrix. This is achieved by overcoming the capillary forces holding the NAPL in place (Abdul and Gibbson, 1991).

In 1985, the USEPA and the American Petroleum Institute (API) became the first to apply surfactant flushing to the subsurface. The USEPA conducted studies with batch experiments to test the removal of polychlorinated biphenyls (PCBs). Field experiments demonstrated removal success between 42-81% using enhanced solubilization and mobilization of NAPL source zones by a surfactant (Knox et al., 1999; Childs et al., 2004; McCray et al., 2011). The American Petroleum Institute conducted the original experiments in 1985 in which one-, two-, and three-dimensional laboratory experiments were performed using two surfactants to enhance the removal of gasoline from sediment. The mass removal for these experiments varied between 60 and 80% (API, 1985).

Cyclodextrins. Cyclodextrins (i.e. hydroxypropyl- β -cyclodextrin, HPCD, and methyl- β -cyclodextrin, MCD) are polycyclic oligosaccharide molecules, also termed “complexing sugars” that have toroidal or lampshade-shaped structure. These molecules possess a hydrophobic, non-polar interior which can receive (complex) a single (sometimes more) contaminant molecule (i.e. PCE, TCE, or DCE). The exterior shell is hydrophilic allowing the molecule to have a high aqueous solubility that can be extracted easily from the groundwater or subsurface. However, the specific contaminant properties will control the enhanced solubility and the enhancement factor for the particular cyclodextrin molecule. Because cyclodextrins are essentially innocuous sugar (glucose) molecules and do not pose any toxicity concerns there are regulatory advantages when injecting into the subsurface as remediation agents. As previously mentioned, they are considered to be non-toxic to humans so there are generally no concerns for health-related problems due to injection into the subsurface. Also, lab studies have shown that cyclodextrins likely do not harm microbial communities (Wang et al., 1997). Cyclodextrins do not readily adsorb onto subsurface solids, experience no appreciable partitioning to the NAPL phase, and rarely

precipitate out of solution (Brusseau et al., 1994; McCray and Brusseau, 1998). Because of this, the cyclodextrin molecules are easy to extricate from the subsurface, and likely have no effect on the aquifer permeability when concentrations remain relatively low (i.e. < 20-wt%). Further benefits of cyclodextrins include insensitivity to pH and ionic strength and they do not reduce or impact the interfacial tension the water-NAPL interface. This prevents mobilization of the contaminant (Wang et al., 1993; Bizzagotti et al., 1997; McCray and Brusseau, 1998).

Co-solvents. Co-solvents are water-miscible or partially water-miscible organic compounds that can increase organic contaminant solubility by changing the polarity of the water (or introduced flushing solution) around the immiscible liquid contaminant source. Co-solvents, such as methanol (MtOH), ethanol (EtOH), and isopropyl alcohol (IPA), were first studied for the remediation of organic contaminants in the mid-1980's (Rao et al., 1985; Nkedi-Kizza et al., 1985). These studies focused more on organic contaminant sorption processes in mixed solvents. Later studies focused on the dissolution, mobilization and the enhanced removal of organic contaminants (Boyd and Farley, 1992; Peters and Luthy, 1993; Augustijn et al., 1994; Wood and Enfield, 1995; Wood and Enfield, 2005; Roy et al., 1995; Imhoff et al., 1995; Rao et al., 1997). Co-solvents can be expected to enhance removal of NAPL by solubilization and mobilization processes. Co-solvents enhance solubilization of organic contaminant by surrounding the NAPL molecules approximately in proportion to its volume in the solution. This action reduces the polarity of the aqueous phase and therefore increases the solubility of the hydrophobic organic contaminant. This theory of cosolvency was first developed in pharmaceutical applications and research (Yalkowsky et al., 1976; Yalkowsky et al., 1981). Co-solvents may also reduce interfacial tension between the aqueous phase and NAPL by partitioning into the NAPL and induce swelling. This swelling can make it easier to mobilize

NAPL droplets during remediation using pump-and-treat (Brandes and Farley, 1993; Imhoff et al., 1995). However, partitioning of co-solvents is rapid and vertical mobilization of NAPL (i.e. DNAPL) is a concern. Some researchers have experimented with alcohols that do not partition significantly into NAPLs. Methanol, for example, does not significantly partition into NAPLs and thus will not enhance migration due to swelling. One advantage of the partitioning of co-solvents is that it can reduce the density of DNAPLs compared to the aqueous phase, thereby decreasing the chances of further downward migration (Imhoff et al., 1995).

Mass Flux Reduction and Contaminant Mass Removal

As NAPL migrates in the subsurface it can distribute as zones of residual saturation or pools where it will gradually dissolve into the aqueous phase. NAPL distributed as ‘residual saturation’ is defined by a relatively small fraction of NAPL occupied within the pore spaces, trapped (i.e. immobile) under capillary forces, whereby typical groundwater gradients as well as induced gradients cannot displace the NAPL phase. Pooled NAPL distributions are typically characterized as highly saturated NAPL zones where the pore space may be completely occupied by the NAPL phase. DNAPL pools tend to accumulate on top of low permeability lenses or layers within the subsurface (i.e. clay and silt). As the NAPL source zone dissolves into the groundwater it will create a contaminant plume that can be extensive and lead to the contamination of groundwater or drinking water supply wells down-gradient or within the spreading of the dissolved phase contaminants. Because of the low solubility limits, a small amount of NAPL can create a large contamination plume (i.e. TCE aqueous solubility limit: ~1,200 mg/L; TCE MCL = 5 µg/L). The dissolved plume concentration of the contaminant is used as a standard for site assessment, and is commonly used for determining remediation goals

and developing remediation strategies. While the plume concentration is a useful standard, each contamination site will vary with respect to field conditions and plume concentration. This makes using plume concentrations as a benchmark for flushing efficiency and contaminant removal very difficult and sometimes impractical. Remediating a dissolved plume does not ensure that the source will be effectively removed from the system. For example, one remediation site had 85% of the source zone removed. However, the remaining 15% continued to produce a contaminant plume equal to the initial concentration (Soga et al., 2004). In addition, a recent review study has shown that even under ideal conditions, typically only a fraction of the most accessible contaminant mass can be effectively removed (i.e. 40-70%) (McCray et al., 2011). Because of this, remediation success and evaluation should be based on a number of factors including mass flux reduction analyses, contaminant elution behavior, and the rate of NAPL removal over time from the remediation site.

The mass flux of a contaminant (also known as mass discharge, mass-flow rate, and source strength) is normally defined as the rate at which a dissolved contaminant mass moves across a control plane ($M/L^2/T$). Using mass flux and its relationship to the process of mass removal and source zone properties, and its impact on risk, is a concept that has been established for a relatively long time (e.g., Fried et al., 1979; Pfannkuch, 1984). Recent studies have used mass flux analyses to determine whether or not the source zone is likely to pose a long-term threat to the groundwater system during active remediation (flushing) and after remediation has ceased (i.e., contaminant concentrations stabilize). Furthermore, the impact of subsurface heterogeneity and non-uniform immiscible liquid distribution on mass removal behavior and associated aqueous phase concentrations (mass flux) can be examined through laboratory, modeling and field studies. For ideal systems (homogeneous porous media and uniform NAPL

distributions) the effect of the enhanced-solubilization agent on contaminant removal can be evaluated through the specific relationship between mass flux reduction and mass removal (Suchomel and Pennell, 2006; Tick and Rincon, 2009). Specifically, these time-continuous mass flux analyses incorporate a “complete” characterization of the relationship between mass flux reduction and mass removal, from the initial stages of mass removal to a given end point. This approach provides more robust characterization of mass-flux behavior as a function of mass removal. The benefit of these analyses allow for the examination of the impact of source-zone architecture at many scales from column experiments to large scale Superfund sites (Fure et al., 2006; Brusseau et al., 2007).

Mass flux measures the mass of a contaminant passing across a control plane (DiFilippo et al., 2010; Tick and Rincon, 2009). Ideally, the contaminant will be at its maximum concentration. This indicates that the contaminant is dissolving efficiently, at the highest rate possible, and that the maximum possible mass is being transferred. As the source becomes depleted, the mass flux reduces. Efficient mass removal is characterized by low mass flux reduction (high mass flux maintained) until the source zone is depleted. Nonideal mass flux reduction demonstrates inefficient flushing conditions whereby the contaminant mass flux is reduced quickly while a significant portion of the mass still remains in the system. Under these conditions such time and cost-intensive remediation strategies will be ineffective and mass discharge will continue to contribute to plume persistence indefinitely (infeasible remediation time scales).

The rate of mass flux reduction (MFR) behavior is determined by plotting the mass flux reduction versus fractional mass removal. Using this analysis, MFR can be characterized as either ideal or nonideal (Carroll et al., 2009; DiFilippo et al., 2010; Tick and Rincon, 2009). The

mass flux rate in each stage may be different or similar for each specific flushing agent depending on the interaction between the contaminant and flushing agent, distribution of contaminant, and flow dynamics of the system. MFR is described in the following equation:

$$MFR = 1 - \frac{J_f}{J_i} = 1 - \frac{Q_f C_f}{Q_i C_i} \quad (1)$$

Where J is the mass flux (M/T), C is the concentration (M/L³), Q is the volumetric flow rate (L³/T), and the subscripts i and f represent *initial* and *final*. This expression can be simplified to the equation shown below, as long as the volumetric flow rate Q remains constant:

$$MFR = 1 - \frac{C_f}{C_i} \quad (2)$$

These analyses were conducted to evaluate the mass flux behavior from a three-component DNAPL source uniformly distributed within a homogeneous porous medium (i.e. saturated conditions) under dynamic flow conditions (one-dimensional column experiments). There have been numerous studies conducted to test the relationships between MFR and mass removal (Enfield et al., 2002; Rao and Jawitz, 2003; Brooks et al., 2004; Lemke et al., 2004; Parker and Park, 2004; Soga et al., 2004; Falta et al., 2005; Jawitz et al., 2005; NRC, 2005; Fure et al., 2006; Lemke and Abriola, 2006; Brusseau et al., 2007, 2008; Basu et al., 2008; DiFilippo and Brusseau, 2008; Marble et al., 2008; Carroll and Brusseau, 2009; Tick and Rincon, 2009). Many of these studies described mass flux behavior as either ideal or non-ideal, depending on the heterogeneity of the porous medium, and in some cases the aquifer, and/or by the immiscible liquid that was distributed throughout the test system. Contaminant mass flux that results from immiscible liquid dissolution can be significantly limited in a heterogeneous system due to the

non-uniform NAPL distribution that affects the dissolution process (Tick and Rincon, 2009). This is typically described as nonideal (inefficient mass removal), shown in figure 2.1. Mass flux is greatly reduced under nonideal conditions requiring long remediation times to deplete most of the mass in the system. Conversely, immiscible liquid dissolution whereby a contaminant maximum mass flux is maintained throughout the majority of the mass removal process is typically described as ideal MFR (efficient mass removal) (Figure 2.1). Ideal MFR is usually observed in relatively homogeneous porous media systems whereby NAPL mass is distributed uniformly and is hydraulically accessible to the flow regime. Therefore, ideal mass flux behavior can be characterized by maximum mass flux during the majority of the mass removal process so that almost all the contaminant mass is depleted before significant mass flux reduction occurs.

The relationship between mass removal and mass flux reduction can be described in a simple mass removal function (DiFilippo and Brusseau, 2008; Tick and Rincon, 2009). In this method, mass flux is treated as a direct function of the change in contaminant mass, as shown:

$$MFR = 1 - \frac{J_f}{J_i} = \left(1 - \frac{M_f}{M_i} \right)^{1/n} \quad (3)$$

where n is a fitting parameter, and M is a source zone mass (M) (Figure 2.2). Parameter n specifies the mass flux reduction/mass removal relationship with incorporated the specific removal dynamics associated with a specific flushing agent itself, flow field dynamics, and mass transfer processes. Values of $n > 1$ represent more nonideal conditions whereby the MFR rapidly increases before any significant fraction of the contaminant mass is removed from the system (i.e. inefficient mass removal). Values of $n < 1$ represent conditions in which maximum mass flux is maintained during flushing until nearly all of the contaminant mass has been depleted (i.e. efficient mass removal) (Figure 2.2). Investigations of source-zone depletion with resultant mass

flux behavior have been evaluated by other researchers using similar mass removal approaches (Rao et al., 2002; Zhu and Sykes, 2004; Falta et al., 2005; Jawitz et al., 2005; Brusseau et al., 2008; DiFilippo and Brusseau, 2008, Carroll and Brusseau, 2009; Tick and Rincon, 2009).

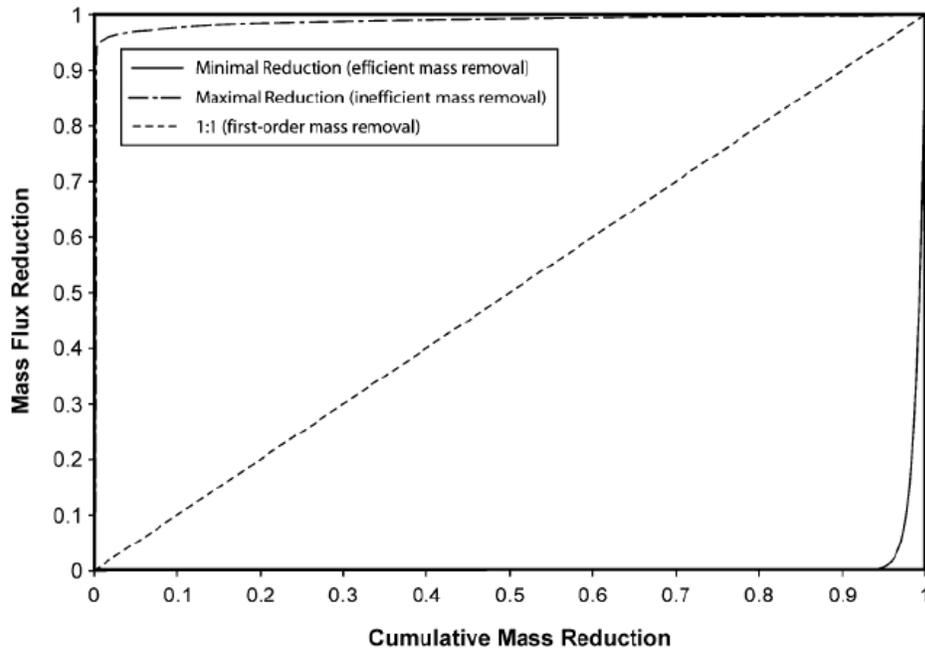


Figure 2.1. Mass-flux reduction relationships from the dissolution of immiscible liquids in porous media. Theoretical relationship for mass flux reduction (from DiFilippo and Brusseau, 2008; Tick and Rincon, 2009).

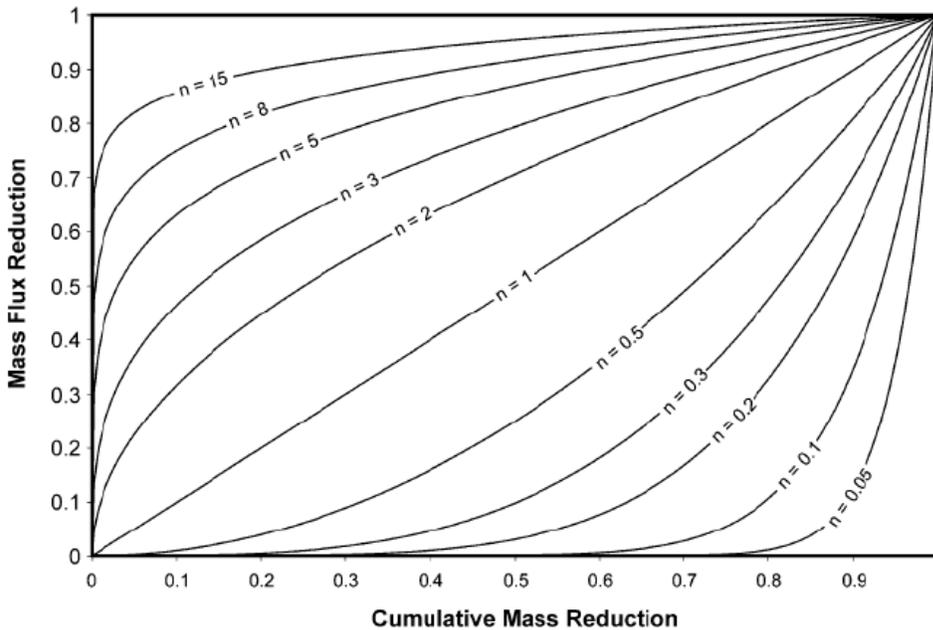


Figure 2.2. Mass-flux reduction relationships from the dissolution of immiscible liquids in porous media. Mass-flux relationships calculated from a simple mass removal function.

Multicomponent NAPL Dissolution Behavior

Equilibrium Dissolution Behavior - Raoult's Law Analysis

The quantification of equilibrium solubilization of chemical mixtures was developed from thermodynamic studies (Burriss and MacIntyre, 1985). When organic-liquid mixtures are comprised of compounds with similar size and functional groups they are considered ideal (NAPL-phase activity coefficient is equal to unity). Raoult's Law is used to describe ideal equilibrium dissolution. Raoult's Law was used to help predict equilibrium concentrations in the aqueous phase in contact with immiscible-liquid mixtures (Banerjee, 1984; Burriss and MacIntyre, 1985; McCray and Brusseau, 1998, 1999; McCray and Dugan, 2002; McColl et al., 2008; Carroll et al., 2008; Carroll and Brusseau, 2009; Burke, 2012). Raoult's Law states that the solubility of a compound is equal to its molar fraction in the solution times its pure-phase

solubility (Moeller et al., 1980). As noted in Feenstra et al. (1991), the effective solubility (S_{Ei}) [mg L^{-1}] of each component of a mixture can be expressed mathematically as:

$$S_{Ei} = X_i^N S_i \gamma_i^N \quad (4)$$

Where, X_i^N is the NAPL-phase molar fraction of component i in a mixture [-], S_i is the pure-phase solubility limit of component i [mg L^{-1}], and γ_i^N is the NAPL-phase activity coefficient [-]. For ideal NAPL mixtures γ_i^N is assumed to be equal to unity. The molar fraction is the percentage of each component (i) within the mixture based on its molecular weight instead of directly on the component mass as follows:

$$X_i = \frac{m_i}{m_T} \quad (5)$$

Where, m_i is the number of mole of component i in the mixture [moles] and m_T is total sum of moles [moles] for the mixture. The sum of all the component (i) effective solubility values (S_{Ei}) in an equilibrated mixture is equal to the total solubility of the mixture, and the sum of all the molar fractions (X_i) is equal to 1. The density and vapor pressure of a mixture, like solubility, may be calculated using molar fractions.

Enhanced Solubilization of Organic-Liquid Mixtures

The enhanced agent (ESA) solution's enhancement of a single-component organic-liquid constituent can be defined as (e.g., Ji and Brusseau, 1998):

$$E_i^O = \frac{S_E^O}{S_A^O} \quad (6)$$

Where, E_i^O is the solubility enhancement factor for the single-component organic liquid in the presence of the ESA, S_A^O is the single component's (i) solubility limit [mg L^{-1}], and S_E^O is the

pure component's (*i*) enhanced (apparent) solubility [mg L^{-1}]. For cyclodextrin solutions, the enhanced equilibrium solubility is a function of the cyclodextrin concentration expressed as:

$$S_E^O = S_A^O(1 + K_{CW}C_{CD}) = S_A^O E_i^O \quad (7)$$

Where, C_{CD} is the aqueous concentration of cyclodextrin [mg L^{-1}], and K_{CW} is the partition coefficient of the solute (*i*) between cyclodextrin and water [L mg^{-1}]. Alternatively, the enhancement factor (E_i^O) can be expressed as a function of the cyclodextrin concentration and the solute's partition coefficient between cyclodextrin and water as:

$$E_i^O = 1 + K_{CW}C_{CD} \quad (8)$$

For ideal dissolution, the value of E_i in a multi-component NAPL system is the same as that measured for a single-component NAPL system E_i^O ($E_i = E_i^O$) since activity NAPL phase activity coefficients are unity. The cyclodextrin (i.e. HCPD, MCD) enhanced solubility Raoult's Law expression can be further expressed by substituting Eq. (4) into the multicomponent version of Eq. (6) or (7) for an ideal organic-liquid mixture as (Ji and Brusseau, 1998; McCray and Brusseau, 1999):

$$S_E^O = S_A^O X_i^N E_i^O \quad (9)$$

Similar to that for cyclodextrin, enhanced apparent solubilization due to the presence of surfactant solution can be described as (Ji and Brusseau, 1998):

$$S_E^O = S_A^O [1 + K_M(C - CMC)] = S_A^O E_i^O \quad (10)$$

Where, K_M is the partition coefficient of solute (*i*) between the surfactant micelle and water [L mg^{-1}], CMC is the critical micelle concentration [mg L^{-1}], and C is the concentration of the surfactant [mg L^{-1}] (when $C > \text{CMC}$). For ideal dissolution, the value of E_i in a multi-component NAPL system is the same as that measured for a single-component NAPL system E_i^O and therefore reduces to a form identical to equation (9).

The solubility of an organic contaminant in the presence of a co-solvent can be expressed as a function of the volume fraction of co-solvent (f_c) in solution and σ represents the cosolvency power of the co-solvent in terms of the slope of the solubilization profile (i.e. log solubility vs. f_c) as:

$$\log S_E^O = \log S_A^O + \sigma f_c \quad (11)$$

Therefore, the enhancement factor (E_i^O) of an organic contaminant molecule in the presence of a co-solvent can be rearranged as follows:

$$E_i^O = 10^{\sigma f_c} \quad (12)$$

The enhanced solubilization due to a co-solvent (i.e. EtOH) is also similar to previous derivations and can be described as (Ji and Brusseau, 1998):

$$S_E^O = S_A^O (10^{\sigma f_c}) = S_A^O E_i^O \quad (13)$$

Similar to the previous description, the enhanced solubility Raoult's Law expression can be expressed by substituting Eq. (4) into the multicomponent version of Eq. (6) or (13) for an ideal organic-liquid mixture to form the general expression as Eq. (9).

The remediation of NAPL source zones is critical to meet the cleanup criteria of soil and groundwater pollution (commonly existing as aqueous phase contamination). Remediation of these source zones can be quite costly; therefore, one promising remediation technique based on what is termed “enhanced solubilization” or “enhanced flushing” has gained increasing attention over the past decade. Enhanced solubilization remediation techniques use enhanced-solubilization agents (ESAs) to more effectively remove NAPL from the subsurface (i.e. groundwater) by increasing the rate of dissolution from these persistent contaminant sources.

Sites contaminated by NAPL are often comprised of multiple compounds, further complicating remediation efforts and enhanced-flushing strategies due to such factors as

nonideal dissolution processes (Rostad et al., 1985; Borden and Kao, 1992; Chen et al., 1994; Lesage and Brown, 1994; Whelan et al., 1994; Adeel et al., 1996; Mukherji et al., 1997; McCray and Dugan, 2002; Burris et al., 2006; McColl et al., 2008; Carroll et al., 2008; Carroll et al., 2009; Burke, 2012). NAPLs can exist as single component liquids, or as a complex mixture of multiple organic liquids. These liquids are slowly released by partitioning to soil pore-vapor or pore-water from the source zones into the vadose and saturated zones (groundwater). Quantification of NAPL in the subsurface is challenging because of inter-media transfer within the soils (i.e. capillary trapping, diffusion, adsorption), poorly characterized subsurface heterogeneity, and unknown location, distribution, and migration of the NAPL. Additionally, complex organic mixtures can have chemical and physical properties (i.e. compositional-dependent factors such as varying mole-fractions and solubilities) that make quantification difficult (USDOE, 2007).

**CHAPTER 3: ENHANCED SOLUBILIZATION AND REMOVAL OF A MULTI-
COMPONENT DENSE IMMISCIBLE LIQUID FROM HOMOGENEOUS POROUS
MEDIA**

Materials

Pertinent physical and chemical properties of the porous medium, target contaminants (NAPLs), and column experimental conditions can be found in [Tables 3.1; 3.2, and 3.3](#). Stainless steel columns (2.2 cm I.D., 7 cm length, Alltech Co.) were used in all experiments. The columns were fitted with 1-inch opti-flow endfittings and designed to have minimum void volume in the endplates. Column experiments were conducted using homogeneous 20/30-mesh quartz Accusand® (Unimin Corp., Le Sueur, MN, USA) as the representative porous medium. The porosity of this medium was 0.32 and was determined gravimetrically and also consistent with values determined by conservative tracer tests. The bulk density is $1.78 \text{ g}\cdot\text{cm}^{-3}$, with an intrinsic permeability of $1.38 \times 10^{-10} \text{ cm}^2$.

Property	Value
*Uniformity coefficient d_{60}/d_{10}	1.184 ± 0.039
*Mean grain size d_{50} [mm]	0.724 ± 0.031
Porosity	0.32
*Bulk density [$\text{g}\cdot\text{cm}^{-3}$]	1.78
*Organic carbon content [%]	0.03
*k intrinsic permeability [cm^2]	1.38E-10
*K hydraulic conductivity [$\text{m}\cdot\text{s}^{-1}$]	1.29E-03

* from [Brusseau et al. \(2002\)](#)

Table 3.1. Properties of porous medium (20/30-mesh Accusand®) for column experiments.

Analytical grade trichloroethene (TCE: >99.5% purity) was purchased from Sigma-Aldrich Chemical Company and both *cis*-1,2-dichloroethene (DCE:>99.8% purity) and

tetrachloroethene (PCE; 99% purity) were purchased by Acros Organics. A 1:1:1 PCE/TCE/DCE (0.33/0.33/0.33 mole fraction) mole mixture DNAPL was created to be used as the multicomponent contaminant source. Methyl- β -cyclodextrin (MCD; >99% purity) was also purchased from Sigma-Aldrich Chemical. Hydroxypropyl- β -cyclodextrin (HPCD; 90% purity) was supplied by Cerestar USA (now Cargill Incorporated, Indiana). HPLC grade ethanol (EtOH; 99.5%), dodecyl sulfate, sodium salt (SDS) 85% purity, and calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) were purchased from Fisher Scientific. Ethanol and SDS were selected based on their relatively widespread use as solubilization agents and relative high solubilization power. MCD and HPCD were used based on their availability at a commercial scale and recent interest as flushing agents.

To best represent a mixed DNAPL waste system, a mixture of chlorinated compounds was used for the series of column flushing experiments ([Table 3.2](#)). A dense nonaqueous phase liquid (DNAPL) contaminant mixture was chosen for several reasons. First, the presence of DNAPL contamination is ubiquitous at many hazardous waste sites across the U.S., including Department of Defense (DoD) and Department of Energy (DoE) waste sites. Secondly, DNAPL presents unique challenges for remediation due to their ability to migrate downward with a higher potential to escape remediation control. Finally, in terms of DNAPL contamination, PCE, TCE, and DCE, specifically represent the most common chemicals present at such waste sites across the U.S. For such contamination sites (i.e. with DNAPL present), flushing-based remediation technologies relying on enhanced-solubilization mechanisms (as opposed to enhanced-mobilization) are preferred so as to minimize concerns of downward movement and loss of remediation control. Properties for the flushing agents used are presented in [Table 3.3](#).

Target Contaminant (NAPL)	*Molecular Weight (g·mol ⁻¹)	#Solubility (mg·L ⁻¹)	*Density (g·cm ⁻³)
<i>cis</i> -1,2-Dichloroethene (DCE)	96.94	3,500	1.28
Trichloroethene (TCE)	131.39	1,200	1.46
Tetrachloroethene (PCE)	165.83	170	1.64

Note: * Values from literature (Tick and Rincon, 2009)

Values determined from literature and from experimental analysis.

Table 3.2. Relevant chemical properties of the target contaminants (NAPLs).

For the enhanced-flushing experiments, a uniform immiscible liquid distribution was created employing a mixing technique to minimize mass flux and elution behavior artifacts due to bypass flow, immiscible liquid fingering, and wall effects (Tick and Rincon, 2009). First, a 20/30-mesh dry sand was homogeneously mixed with a measured amount of electrolyte solution (0.01 N CaCl₂·2H₂O) to establish a 10% water saturation. The electrolyte solution was used as a synthetic groundwater for all experiments. Pure-phase PCE, TCE, and DCE in equal mole fractions were then mixed into the moist sand to achieve a uniform immiscible liquid distribution targeted at 10–20% saturation (S_n). To account for volatilization losses during packing, a predetermined amount of PCE, TCE, and DCE were mixed thoroughly into the moist sand directly prior to incrementally packing the column. Once packing was complete and the column endfittings secured, the column was slowly saturated from the bottom with PCE/TCE/DCE saturated synthetic groundwater aqueous solution using a single-piston pump (Lab Alliance, Series I) for 48 hr at a rate of 0.03 cm³·min⁻¹ (Darcy velocity, $q=0.008$ cm·min⁻¹). This step ensured that dissolution of TCE did not occur in the column before the commencement of the enhanced-dissolution experiment. The column was successively weighed over the 48-hr saturation period until the weight stabilized ensuring complete saturation of the porous-medium filled column. For each flushing experiment, the appropriate enhanced-solubilization agent was

pumped through the column at a flow rate of $0.59 \text{ cm}^3 \cdot \text{min}^{-1}$ ($q=0.15 \text{ cm} \cdot \text{min}^{-1}$; $v_p=29 \text{ cm} \cdot \text{hr}^{-1}$) (Figure 3.1). For all experiments, effluent samples were collected with a glass syringe and either analyzed immediately by being injected into glass headspace vials and then analyzed using a gas chromatograph (Shimadzu GC-17A) equipped with an AOC-5000 autosampler (Leap Technologies) and a flame ionization detector (FID).

Samples were collected using a gas-tight glass syringe and 0.5 - 5 mL (i.e. based on dilutions) were transferred immediately into 20-mL glass (borosilicate) headspace vials and total volume in the vial was adjusted to 5 mL (depending on desired dilution factor); vials were then immediately then crimped with an aluminum cap and airtight septa prior to GC analysis. Depending on the sample (early flush vs. late flush flushing stages), dilution with synthetic groundwater solution was necessary because the contaminant concentrations due to the enhanced flushing agent would otherwise potentially oversaturate the GC column and maximize the voltage response from the detector. Because the contaminant concentrations changed throughout the experiments, sample dilutions were adjusted accordingly throughout the flushing process. Upon analysis, each headspace sample vial was agitated at $80 \text{ }^\circ\text{C}$ for 10 minutes to effectively transfer the aqueous phase contaminant into the headspace. The headspace was subsampled and transferred to the injection port on the GC (automated) and the response (voltage-signal vs. retention time) from the FID was recorded and converted to concentrations using standard curves. Samples not analyzed immediately were stored at 4°C until analyzed on a gas chromatograph (Shimadzu GC-17A) using the same methods as described previously. The quantifiable detection limit was $0.1 \text{ mg} \cdot \text{L}^{-1}$ for the organic compounds (PCE, TCE, cis-1,2-DCE).

Properties	5% HPCD	5% MCD	5% SDS	50% EtOH	Water
Column Pore Volume (cm ³) ^a	8.5	8.5	8.5	8.5	8.5
Darcy Velocity (cm·min ⁻¹)	0.15	0.15	0.15	0.15	0.15
Density of solution (g·cm ⁻³)	1.01	1.01	1.01	0.91	1
Molecular weight of reagent (g·mole ⁻¹)	1,365	1,303	288	46	18
Interfacial tension ^b (σ _{TCE-agent} ; dyn·cm ⁻¹)	18.8±0.6	10.2±0.2	4.4±0.5	3.3±0.1	34.5 ^c
Initial NAPL Saturation (S _N) ^d	9.7	15.8	19.6	21.8	5.0

Note: ^a Calculated by gravimetric method.

^b Interfacial tension for TCE-agent (from [Boving and Brusseau, 2000](#)).

^c Interfacial tension for TCE in contact with water (from [Mercer and Cohen, 1990](#)).

^d Calculated by mass removed as determined by method of moments and by solvent extraction.

Table 3.3. Experimental conditions for various column flushing experiments and relevant chemical properties of flushing agents.

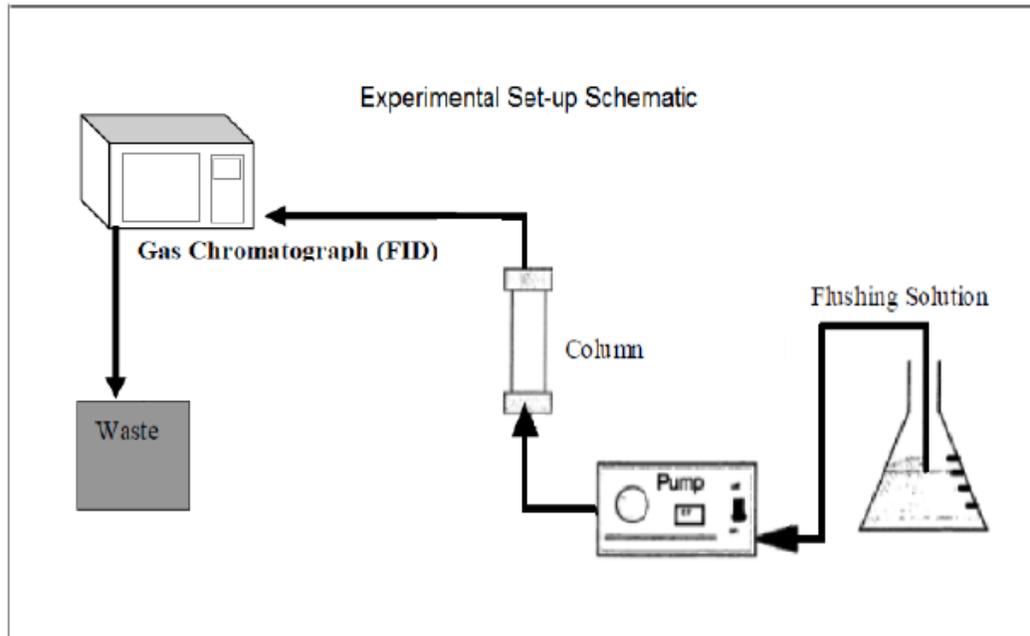


Figure 3.1. Schematic of experimental set-up for enhanced flushing experiments.

Experimental Procedures

Conservative Tracer Tests

Before beginning the enhanced-flushing experiments, pentafluorobenzoic acid (PFBA) conservative tracer tests were conducted to determine the bulk density of the column, as well as its pore volume. These tests were also used to verify that the dominant mechanism of transport in the column was advection. For each PFBA test, the column was incrementally packed with dry porous medium to achieve uniform bulk density. The column was then saturated from the bottom up using a calcium chloride (0.01 N $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) electrolyte solution (synthetic groundwater) with a single-piston pump (Lab Alliance, Series I) for 48 hr at a rate $0.03 \text{ cm}^3 \cdot \text{min}^{-1}$. During saturation, the column was weighed successively until the weight was stabilized, ensuring that saturation was complete. The pore volume of the column was calculated by weighing the mass of the water once the column was saturated. The column pore-volume was gravimetrically determined to be 8.5 cm^3 . Once the column was saturated, a PFBA solution ($250 \text{ mg} \cdot \text{L}^{-1}$) was pumped through the column at a flow rate of $0.58 \text{ cm}^3 \cdot \text{min}^{-1}$ (linear $v_p = 29 \text{ cm} \cdot \text{hr}^{-1}$) and was analyzed every minute using a UV-Vis spectrophotometer (Shimadzu UV-1700) at a wavelength of 262 nm. The resulting breakthrough curves ([Appendix I](#)) were modeled using CFITIM model ([Van Genuchten, 1981](#)), a nonlinear least squares program, to determine Peclet number (Pe), swept pore volume, and porosity. The model results confirmed that porous media packing method consistently produced transport conditions that were dominantly advective controlled as indicated by the resulting Peclet numbers (EXP1-Pe=82; EXP2-Pe=111). In addition, the model results were consistent with gravimetric measurement-determined porosity values for each column-packed system measured prior to each PFBA experiment.

Enhanced-Solubilization Flushing Experiments

After the PFBA conservative tracer test confirmed the primary mode of transport was advection dominant, a series of columns were prepared for the enhanced flushing (Figure 3.1). For the enhanced-flushing experiments, a uniform immiscible liquid distribution was created employing the mixing technique described previously. This technique was implemented to minimize mass flux and elution behavior artifacts due to bypass flow, immiscible liquid fingering, and wall effects (Tick and Rincon, 2009). For each flushing experiment, the appropriate enhanced-solubilization agent was pumped through the column at a flow rate of $0.59 \text{ cm}^3 \cdot \text{min}^{-1}$ ($q=0.15 \text{ cm} \cdot \text{min}^{-1}$; $v_p=29 \text{ cm} \cdot \text{hr}^{-1}$). This flow rate was based on rates consistent with other published values for similar enhanced flushing experiments, and representative of conditions with induced hydraulic gradients consistent with that of remediation scenarios (Imhoff et al. 1996; Imhoff et al. 1998; Boving and Brusseau, 2002; Tick and Rincon, 2009).

Each flushing (enhanced-solubilization) agent (HPCD, MCD, and SDS) was prepared at a concentration of 5 wt.%, with the exception of EtOH, which was prepared at 50 wt.% because concentrations less than that do not demonstrate substantial mass-removal capability. For each enhanced flushing agent experiment, column effluent was collected using a glass syringe to limit volatilization during the sampling process. A pre-determined sample volume was then delivered to a 20-mL headspace vial and diluted (if necessary) to maintain a total of 5 mL within the headspace vial. The vial was then immediately enclosed and sealed using VOC-septa and magnetic crimp tops. Samples were then analyzed immediately using a gas chromatograph (Shimadzu GC-17A) instrumented with an AOC-5000 autosampler (Leap Technologies) and a flame ionization detector (FID). Samples not analyzed immediately were stored at 4°C until analyzed on a gas chromatograph using the same methods as described previously. The

quantifiable detection limit was $0.1 \text{ mg}\cdot\text{L}^{-1}$. During each experiment, effluent curves were obtained for the multi-component mixtures over time until the detection limit was reached for each component, or significant tailing was present so as to make continued flushing of the column unfeasible.

Results and Discussion

Elution and Dissolution

The contaminants exhibited similar elution behavior in the enhanced flushing experiments. In general, the experiments showed several stages of elution behavior: (1) rapid rise of concentrations of each contaminant, (2) steady-state dissolution, (3) transient-state dissolution (decline in concentrations), and finally (4) tailing until experiment ended. (Figures 3.1-3.6) While the behavior is similar in the contaminants, the removal rate displayed in each stage is unique to each individual flushing agent. The graphs of the elution behavior show the normalized concentration plotted against the number of pore volumes required to remove the contaminants. Normalized concentration is found by dividing the effluent concentration by the aqueous solubility of the compound. [Table 3.3](#) shows the conditions and properties for the flushing agents for each specific column experiment.

Water Flushing

[Figure 3.2 \(a, b\)](#) shows the total effluent elution curve for the Water Flush. DCE, the highest-solubility component, attained the greatest concentration the soonest of the three ($\sim 1,160 \text{ mg/L}$) and then rapidly declined until the majority of mass was removed. TCE was slightly delayed relative to DCE (27 PVs) in reaching its peak concentration (average $\sim 545 \text{ mg/L}$), consistent with the order of solubility for all three components, until tailing behavior was observed after about 100 pore volumes (PVs) of flushing. PCE, the lowest-solubility component,

exhibited the most pronounced delay in peak concentration (~160 mg/L) after about 100 PVs of flushing, at which point concentration slowly declined until extensive tailing behavior occurred after 300 PVs. As DCE concentrations declined, both TCE and PCE increased due to the relative increase in component mole fractions. Furthermore, as TCE became depleted, PCE continued to increase based on the relative mole fraction increase. After approximately 300 PVs of flushing, nearly all constituent mass (DCE, TCE, and PCE) was removed from the system.

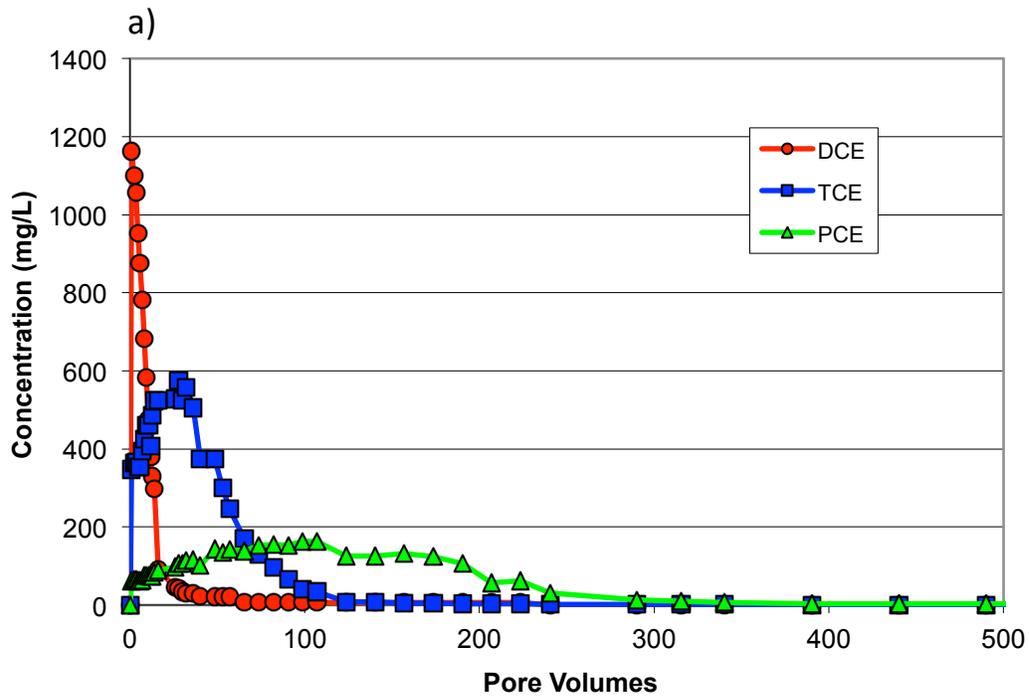
Tables 3.4, 3.5, 3.6, and 3.7 summarize the results of average peak concentration during flushing and calculated enhancement factors (E) and the initial versus predicted elution concentrations for each component (DCE, TCE, and PCE). The standard form of E was used to determine the effectiveness of the flushing experiment in comparison to Water Flushing conditions (as comparative baseline) for these analyses. Under this definition, E is calculated by the maximum peak concentration for the specific component during the enhanced flushing experiment divided by the resulting peak concentration during the Water Flush for the respective contaminant component of interest as:

$$E = \frac{C_{EF}^{\max}}{C_{WF}^{\max}} \quad (14)$$

Where, C_{EF}^{\max} [ML⁻³] is the maximum peak concentration [ML⁻³] of the contaminant constituent observed during enhanced flushing, and C_{WF}^{\max} is the maximum peak concentration [ML⁻³] of the contaminant constituent during the Water Flush (Table 3.4).

The initial concentration for DCE was ~1,070 mg/L, which was close to the predicted initial concentration of 1,000 mg/L based on calculated mole fractions after complete removal. An initial TCE concentration of approximately 360 mg/L was observed which predicted very well by Raoult's Law (~360 mg/L). Initial concentration for PCE was about 65 mg/L which was predicted reasonably well by Raoult's Law (~50 mg/L) assuming initial mole fractions present in

the system. Overall, these results show that, under Water Flushing conditions, the multicomponent dissolution process was relatively ideal. Enhancement factors (E) for the Water Flush are normalized by itself, and therefore, equal to one for all contaminant components. Thus, as expected, there was no relative enhancement for Water Flushing conditions.



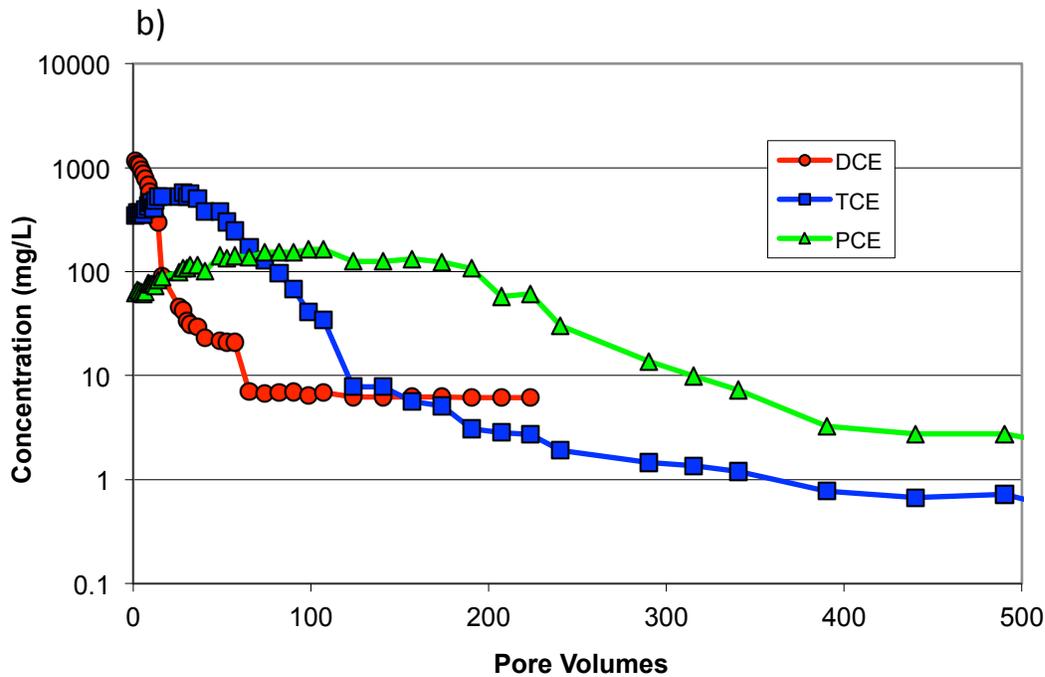
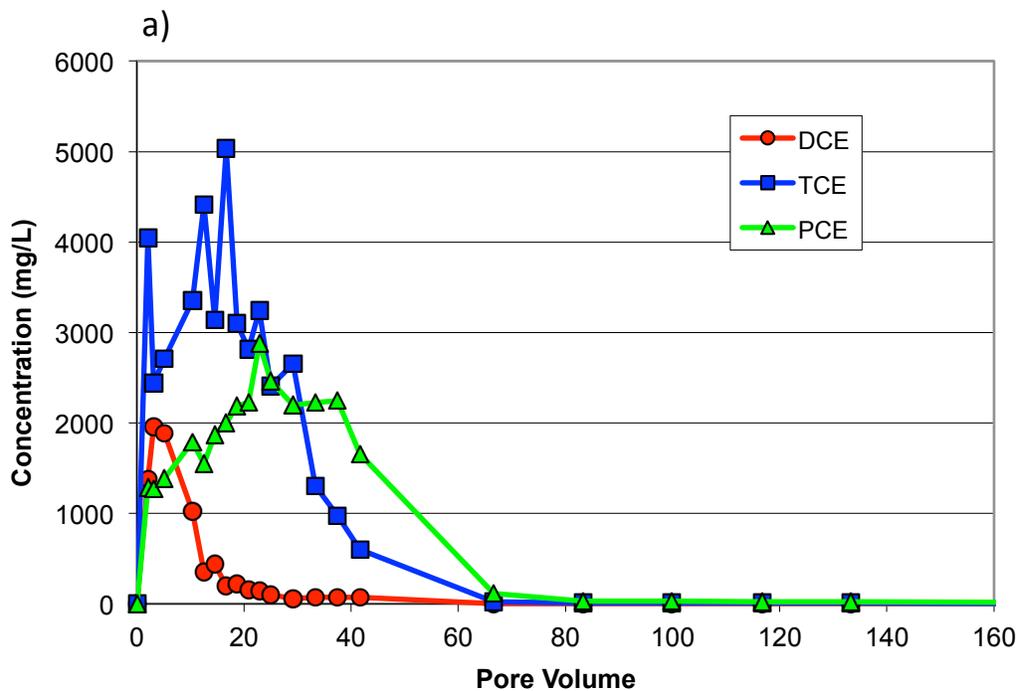


Figure 3.2. DCE/TCE/PCE elution curves during the Water Flush, a) arithmetic scale; b) logarithmic scale.

MCD Flushing

One of the most efficient flushes was the MCD flush, as shown in figure 3.3 (a, b). During this flush, DCE reached detection limit in 66 PV. The initial DCE concentration was observed to be about 1,700 mg/L, which was slightly elevated compared to that of the water flushing conditions (~1,100 mg/L). The maximum (average peak) observed DCE concentration was approximately 1,900 mg/L (at 3 PV) which corresponded to an enhancement (E) of about 1.6. The average initial eluted concentration of TCE was approximately 3,000 mg/L compared to 360 mg/L for the Water Flush. The maximum (average peak) observed TCE concentration was approximately 4,200 mg/L (2-22 PV) corresponding to an enhancement of 7.7 compared to Water Flushing conditions. TCE reached detection limit after about 80 PV of MCD flushing. The average initial concentration of PCE during MCD flushing was about 1,300 mg/L, a significant

increase over the initial concentrations eluted during the Water Flush. The maximum (average peak) observed PCE concentration was approximately 2,400 mg/L (at 23-30 PV) which corresponded to an enhancement factor (E) equal to 15. The reason for TCE and PCE reaching detection limit simultaneously was likely due to the fast removal of DCE, allowing the two less soluble components (TCE and PCE) to dissolve at similar rates. MCD proved to be one of the most effective flushing agents, causing all the contaminants to reach detection limit in relatively few PVs of flushing. Based on the average initial concentrations, mole fraction, and respective E factors, DCE, TCE, and PCE exhibited relatively ideal behavior as predicted by Raoult's Law (Tables 3.5, 3.6, and 3.7).



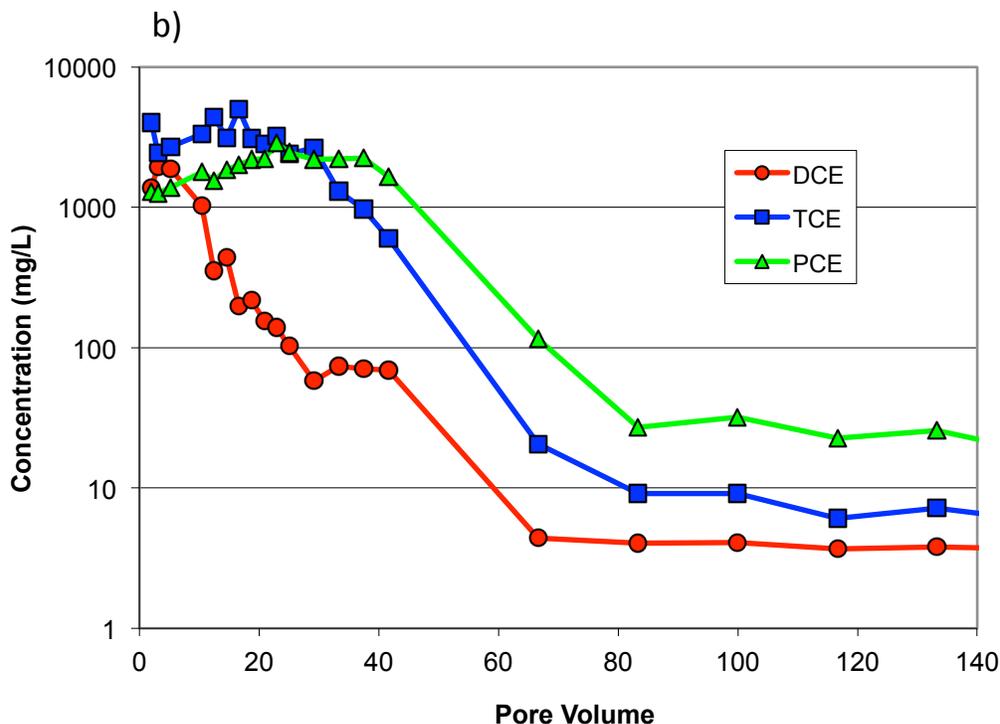
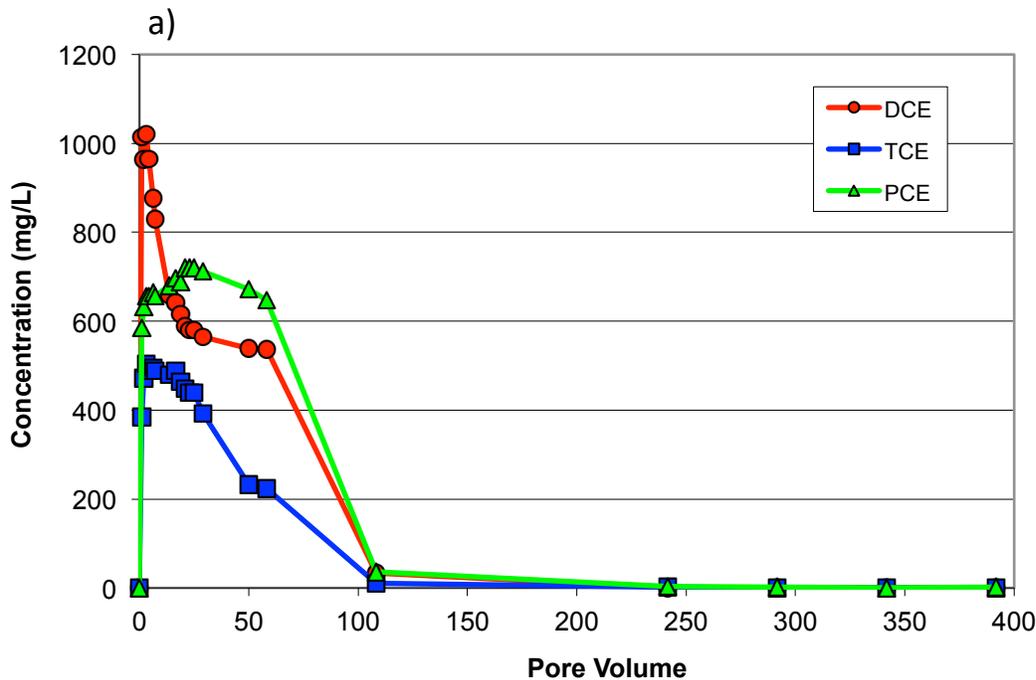


Figure 3.3. DCE/TCE/PCE elution curves during the MCD Flush, a) arithmetic scale; b) logarithmic scale.

HPCD Flushing

Figure 3.4 (a, b) shows the elution curves for DCE, TCE, and PCE during HPCD flushing. HPCD proved to be the least effective flushing agent showing insignificant enhancement for the target contaminants (DCE, TCE, and PCE). None of the contaminants had reached detection limit after 240 PV, further demonstrating the ineffective removal under the HPCD flushing experiments. The average initial DCE concentration was observed to be about 1,000 mg/L, which was essentially the same compared to that of the water was flushing conditions (~1,070 mg/L). The maximum (average peak) observed DCE concentration was approximately 1,000 mg/L (at 1-3 PV) showing no enhancement from the peak Water Flushing concentration. The average initial eluted concentration of TCE was approximately 430 mg/L (2-

1-2 PV) compared to 360 mg/L for the Water Flush, demonstrating minimal effective enhancement during initial flushing. The maximum (average peak) observed TCE concentration was approximately 500 mg/L (at 2-16 PV) corresponding to no enhancement. As shown, DCE nor TCE showed no appreciable enhancement in solubility as a result of HPCD flushing. However, PCE showed a slight enhancement during HPCD flushing. The average initial observed concentration of PCE was 600 mg/L which was elevated compared to the Water Flushing concentrations (~65 mg/L). The maximum (average peak) observed PCE concentration was approximately 710 mg/L (at 21 PV) which corresponded to an enhancement factor (E) equal to 4.4. Based on the average initial concentrations, mole fraction, and respective E factors, DCE, TCE, and PCE exhibited relatively ideal behavior as predicted by Raoult's Law (Tables 3.5, 3.6, and 3.7) but least effective in enhanced removal for the target contaminants.



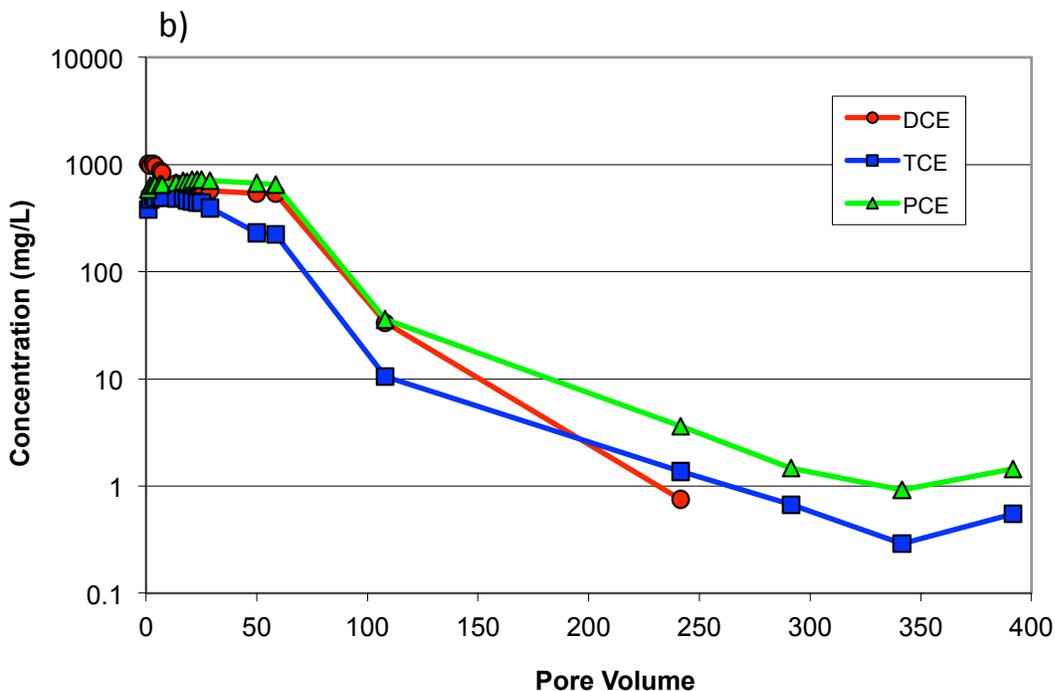
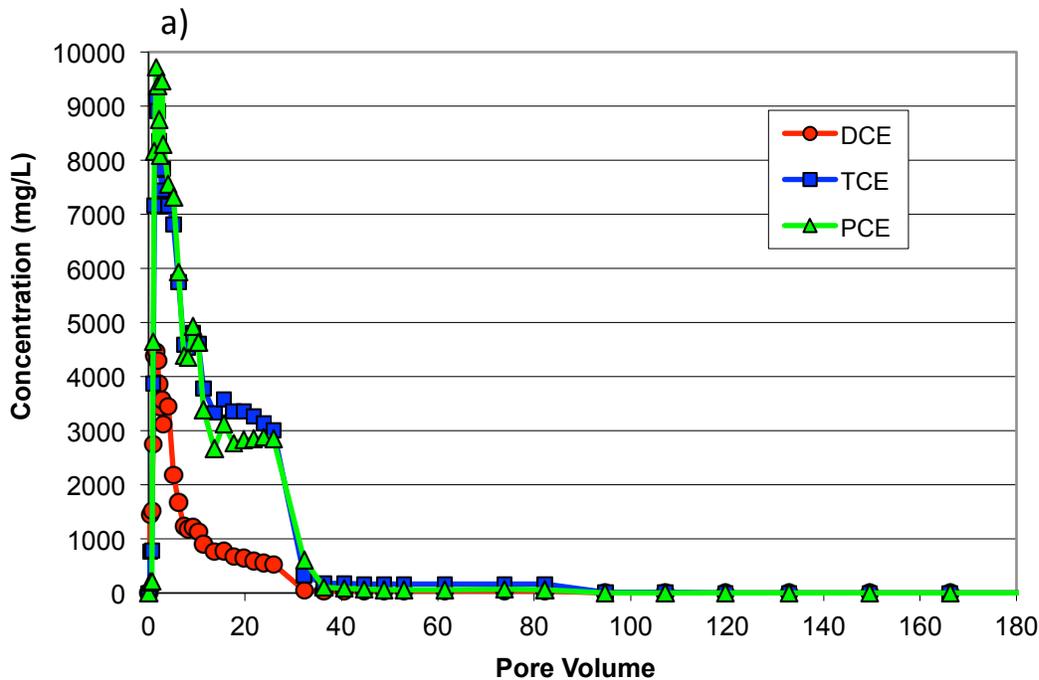


Figure 3.4. DCE/TCE/PCE elution curves during the HPCD Flush, a) arithmetic scale; b) logarithmic scale.

SDS Flushing

SDS showed a drastic enhancement for the target contaminant (DCE, TCE, and PCE) concentrations, proving to be most effective at removing most of the contaminant mass in the least amount of pore volumes (Figure 3.5). However, the three contaminants exhibited significant tailing towards the later stages of flushing. Overall, however, SDS proved to be one of the most powerful agents for removing contaminant mass from the system. The initial DCE concentration was observed to be about 1,500 mg/L, which was elevated compared to that of the water flushing conditions (~1,100 mg/L). The maximum (average peak) observed DCE concentration was approximately 4,400 mg/L (at 1-2 PV) which corresponded to an enhancement (*E*) of about 3.8. The average initial concentration of TCE during SDS flushing was about 770 mg/L resulting in an increase over the initial concentrations eluted (~360 mg/L)

during the Water Flush. The maximum (average peak) observed TCE concentration was approximately 9,000 mg/L (at 1.5 PV) which corresponded to an enhancement factor (E) equal to 16.5. The average initial eluted concentration of PCE was approximately 210 mg/L compared to 65 mg/L for the Water Flush. The maximum (average peak) observed PCE concentration was approximately 9,500 mg/L (at 1.5 PV) corresponding to an enhancement of 60 compared to Water Flushing conditions. PCE reached the detection limit after about 120 PV of SDS flushing. Based on the average initial concentrations, mole fraction, and respective E factors, DCE, TCE, and PCE exhibited relatively ideal behavior as predicted by Raoult's Law (Tables 3.5, 3.6, and 3.7).



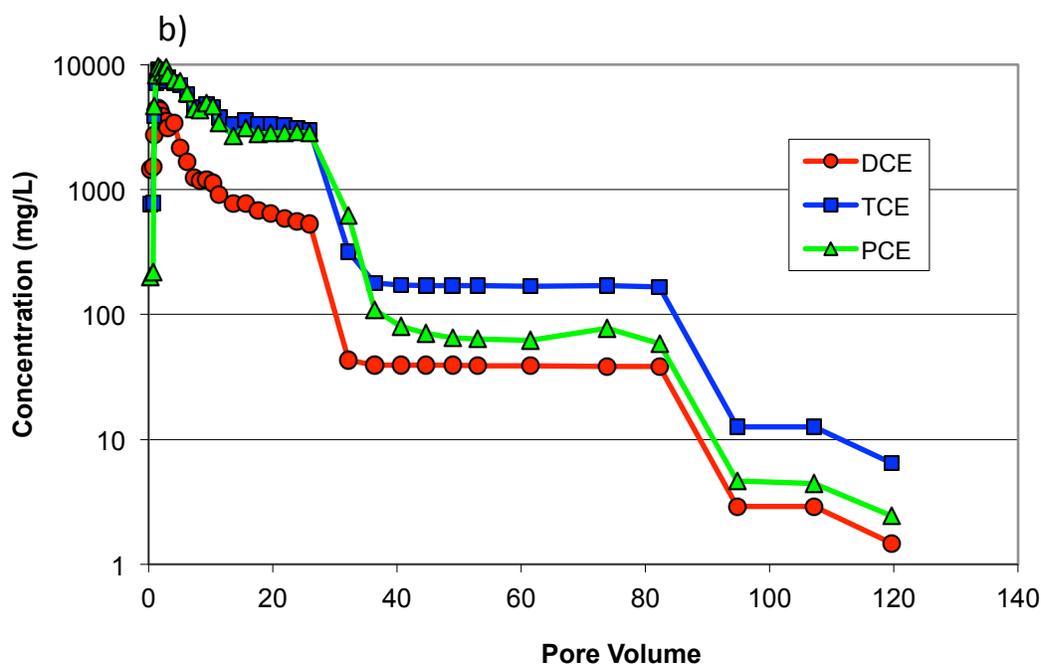


Figure 3.5. DCE/TCE/PCE elution curves during the SDS Flush, a) arithmetic scale; b) logarithmic scale.

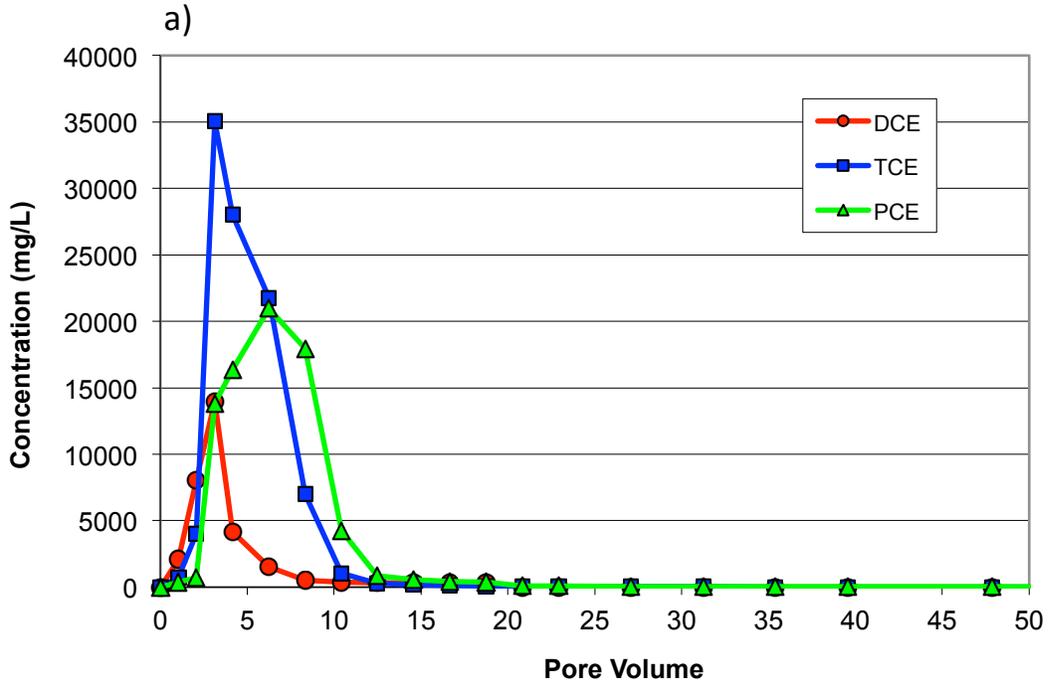
EtOH Flushing

Ethanol (EtOH) caused a large increase in apparent solubility for all three target contaminant compounds (DCE, TCE, and PCE). It showed the highest enhancement factors of all the flushing agents. All three target contaminants peaked quickly, and then showed tailing until reaching detection limit. It should be noted that the EtOH concentration was 50 wt.% due to the fact that substantial fractions of co-solvent are required to produce effective enhanced solubilization of such target contaminants (Boving and Brusseau, 2000; Tick and Rincon, 2009). The average initial eluted concentration for DCE was about 2,000 mg/L, elevated compared to that of the Water Flush (~1,100 mg/L). The maximum (average peak) observed DCE concentration during the EtOH flush was about 14,000 mg/L (at 3 PV) which corresponded to an enhancement (E) of about 12. The average initial concentration of TCE during EtOH flushing

was 740 mg/L, approximately a 2-fold increase over the initial concentrations eluted (~360 mg/L) during the Water Flush. The maximum (average peak) observed TCE concentration was approximately 32,000 mg/L (at 3 PV) which corresponded to an enhancement factor (E) equal to about 60 ($E=58.7$). The average initial eluted concentration of PCE was approximately 375 mg/L compared to 65 mg/L for the Water Flush. The maximum (average peak) observed PCE concentration was approximately 19,500 mg/L (at 6 PV) corresponding to an enhancement of 122 compared to Water Flushing conditions. Based on the average initial concentrations, mole fraction, and respective E factors, the EtOH flush resulted in the greatest deviation from initial predicted enhanced concentrations (DCE, TCE, and PCE) as calculated from Raoult's Law analysis (Tables 3.5, 3.6, and 3.7). Similar to all of the enhanced flushing agents tested, the EtOH flush resulted in relatively ideal initial elution (enhanced dissolution) for the three target contaminant compounds (DCE, TCE, and PCE).

It should be noted that during the ethanol (EtOH) flush ([Figure 3.6](#)) small amounts of pure-phase immiscible liquid were collected, indicating that the ethanol did cause some minor mobilization of the immiscible liquid. At the end of each enhanced flushing experiment (i.e. MCD, HPCD, SDS, and EtOH), a solvent extraction was conducted on the column sediments to determine any remaining immiscible liquid from the systems. In each case, trace amounts of immiscible liquid, usually PCE were noted, indicating that the least soluble chemical had not been completely removed by the flushing agents. This is likely due to the lower solubility limits of PCE, which is an order of magnitude less soluble than TCE and DCE. Because tailing behavior was observed in all experiments, it is safe to assume that tailing will continue until the remaining mass was removed. However, this research was not focused on analyzing specific

tailing behavior during immiscible liquid dissolution but rather on first-order and initial dissolution processes and overall mass removal effectiveness during enhanced-solubilization.



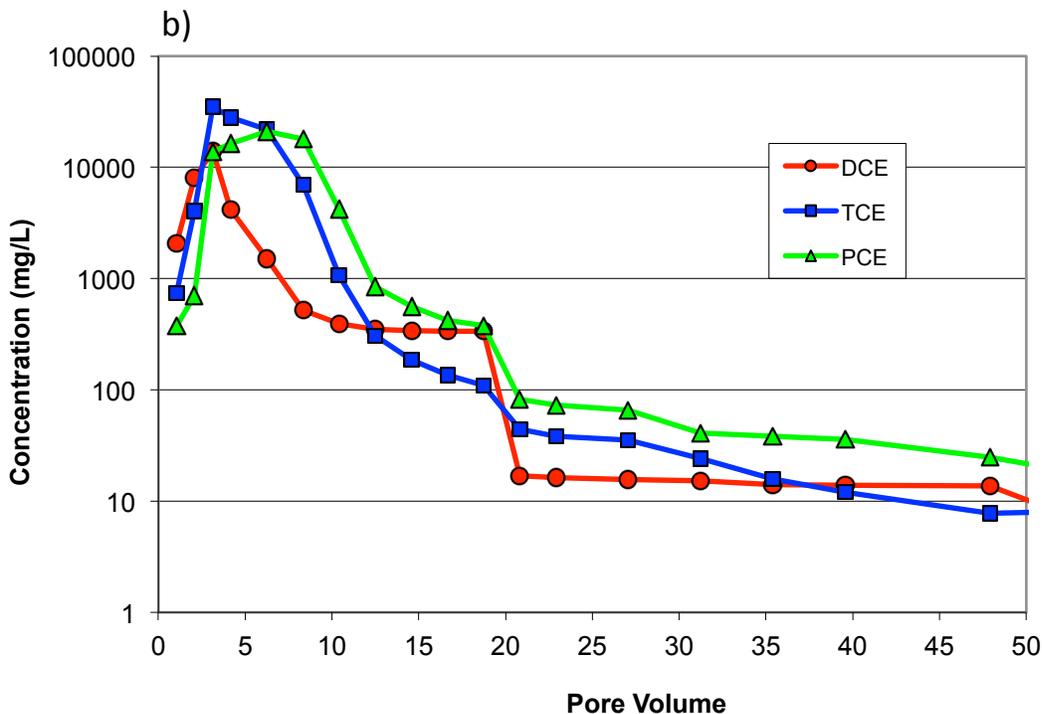


Figure 3.6. DCE/TCE/PCE elution curves during the EtOH Flush, a) arithmetic scale; b) logarithmic scale.

Raoult's Law Analysis – Ideal vs. Nonideal Initial Dissolution Processes

Tables 3.5, 3.6, and 3.7 summarize the results of initial versus predicted elution concentrations for each component (DCE, TCE, and PCE) to assess if Raoult's Law could be used to predict initial elution concentration from the columns. This analysis was used to determine if dissolution processes were ideal or nonideal during Water flushing (i.e. pump-and-treat) and enhanced flushing conditions. Additionally, this analysis was used to elucidate the specific flushing agents likely to induce greater nonideal dissolution behavior and further complicate extrapolation of resulting concentrations in the field based on ideal dissolution theory (Raoult's Law). Knowing if the system will behave under ideal dissolution conditions and knowing how a particular enhanced-solubilization agent will influence these processes can be tremendously useful for predicting expected concentration from multicomponent NAPL source

zones and aid in remediation design and implementation. In contrast to the standard approach for determining enhancement factor (E) (i.e. comparison of resulting peak concentrations), this analysis relies on a modified form of E to determine the effectiveness of initial flushing conditions in comparison to initial Water Flushing (as a comparative baseline). For this analysis, enhancement factor, E , is calculated by the initial average concentration (1-2 PV) for the specific contaminant component during the enhanced flushing experiment divided by the resulting initial average concentration (1-2 PV) during the Water Flush for the respective contaminant component of interest as:

$$E = \frac{C_{EF}^{initial}}{C_{WF}^{initial}} \quad (14)$$

Where, $C_{EF}^{initial}$ [ML⁻³] is the initial average concentration [ML⁻³] of the contaminant constituent observed during enhanced flushing, and $C_{WF}^{initial}$ is the initial average concentration [ML⁻³] of the contaminant constituent during the Water Flush (Table 3.5).

Flush	Avg. Peak Concentration (mg·L ⁻¹)			Enhancement Factor (E)		
	DCE	TCE	PCE	DCE	TCE	PCE
-						
Water	1,160	545	160	1	1	1
MCD	1,900	4,200	2,400	1.6	7.7	15.0
HPCD	1,000	500	710	0.9	0.9	4.4
SDS	4,400	9,000	9,500	3.8	16.5	59.4
EtOH	14,000	32,000	19,500	12.1	58.7	122

Table 3.4. Average peak concentrations during each flushing experiment and corresponding enhancement factors (E) based on peak concentrations.

Flush	Avg. Initial Concentration (mg·L ⁻¹)			Enhancement Factor (<i>E</i>)		
	DCE	TCE	PCE	DCE	TCE	PCE
-						
Water	1,070	360	65	1	1	1
MCD	1,740	3,000	1,315	1.6	8.3	20.2
HPCD	1,000	430	600	0.9	1.2	9.2
SDS	1,490	770	210	1.4	2.1	3.2
EtOH	2,080	740	375	1.9	2.1	5.7

Table 3.5. Average initial concentrations during each flushing experiment and corresponding enhancement factors (*E*) based on average initial concentrations.

Predicted Initial Elution Concentration

The prediction of contaminant component concentration during an entire enhanced-flushing experiment remains challenging if not impossible due to the complex nature of constantly changing mole fraction, NAPL saturation, and NAPL distribution during the time of flushing. For this reason, the prediction of initial target contaminant component elution concentration (i.e. initial dissolution processes) were evaluated since it is assumed the initial mole fraction is known (i.e. predetermined, 0.3:0.3:0.3 mole fraction of DCE, TCE, and PCE). Since only initial dissolution processes were evaluated, the average initial concentration enhancement factors (Table 3.5) could be utilized to predict resulting initial enhanced concentrations through Raoult's Law analysis as:

$$S_E^O = S_A^O X_i^N E_i^O \quad (15)$$

Where S_E^O is the enhanced aqueous concentration of the contaminant component i , S_A^O is the pure-phase aqueous solubility limit of contaminant component i , X_i^N is the NAPL-phase mole fraction for contaminant component i , and E_i^O is the initial phase (concentration) enhancement factor (*E*) for the respective contaminant component i (Table 3.5).

Tables 3.6 and 3.7 show the results of the initial enhanced dissolution (elution) predictions using the form of Raoult's Law (eq. 15). In general, the results demonstrate that

enhanced dissolution processes were dominantly controlled under ideal dissolution due to the fact the Raoult's Law predicted the observed initial concentrations for each enhanced-flushing experiment reasonably well (Table 3.7). In fact, deviations of the predicted from the observed values, for the most part, showed less than 6% error, with most of the predicted values slightly less than that observed (as indicated by the negative sign) (Table 3.7). In addition, these results show that no single flushing agent (MCD, HPCD, SDS, or EtOH) exerted unique, different, or significantly more nonideal enhanced dissolution control on resulting initial phase contaminant concentrations. In fact, the high solubility components (i.e. DCE and TCE) showed consistently ideal initial elution (dissolution) conditions for all enhanced flushing agent flushing experiments. However, for all enhanced flushing experiments (MCD, HPCD, SDS, or EtOH), the lowest solubility component (PCE) showed the most significant deviation from ideal dissolution conditions with percent errors consistently between about 21-23 % for observed and predicted initial concentration values (by Raoult's Law). Although PCE (lowest solubility components) showed the most nonideal initial enhanced dissolution behavior, observed versus predicted error values of 20-30% are still considered relatively ideal (Schwarzenbach et al., 1993). This does indicate, however, that lower solubility components may be subject to more nonideal dissolution processes. This behavior for extremely low solubility components was also observed in field-scale enhanced-solubilization remediation demonstrations for sites contaminated with NAPL (McCray and Brusseau, 1998; 1999). This may suggest that for sites contaminated with multicomponent NAPL, with high toxicity and extremely low solubility priority pollutants, that conventional prediction techniques using Raoult's Law may be subject to a high degree of error and uncertainty and may therefore require more characterization, monitoring, and more detailed assessment.

Flush Type	^s Initial Mole Fraction (x_i)			Initial Concentration ($\text{mg}\cdot\text{L}^{-1}$)			Pred. Initial Conc. Raoult's Law: $C_A=x_i\cdot C_S\cdot E$ ($\text{mg}\cdot\text{L}^{-1}$)		
	DCE	TCE	PCE	DCE	TCE	PCE	DCE	TCE	PCE
-									
Water	0.3	0.3	0.3	1,070	360	65	1,050	360	51
MCD	0.3	0.3	0.3	1,740	3,000	1,315	1,680	2,990	1,030
HPCD	0.3	0.3	0.3	1,000	430	600	945	432	470
SDS	0.3	0.3	0.3	1,490	770	210	1,470	756	163
EtOH	0.3	0.3	0.3	2,080	740	375	1,995	756	290

^sMole fractions based on prepared NAPL mixtures.

Table 3.6. Initial mole fraction and initial concentration for each flushing experiment based on enhancement factors determined by average initial concentrations.

Flush	^s % Error (Experimental vs. Predicted)		
	DCE	TCE	PCE
-			
Water	-1.9	0.0	-21.5
MCD	-3.4	-0.3	-21.7
HPCD	-5.5	+0.5	-21.7
SDS	-1.3	-1.8	-22.4
EtOH	-4.1	+2.2	-22.7

^s Based on prepared NAPL mixture equal mole fractions (0.3:0.3:0.3).

Table 3.7. Raoult's law predicted initial concentrations and error between experiment concentration and Raoult's Law-predicted concentration based on enhancement factors determined by average initial concentrations.

Mass Flux Reduction/Mass Removal Behavior

Water Flushing

Overall, mass flux reduction (MFR) for all three components (DCE, TCE, and PCE) was nonideal during the Water flushing conditions. DCE (highest solubility component) showed the most pronounced nonideal behavior in which mass flux reduction occurred almost immediately even while a significant portion of the mass remained in the system. The MFR/Mass-removal (MFR/MR) relationship followed that of 1:1 first order mass removal trend and persisted as such

until all nearly all of the mass was removed (Figures 2.1, 2.2). The TCE and PCE MFR/MR behavior was nearly identical and significantly more ideal than the high solubility component (DCE) in which mass flux reduction occurred only after about 40-50% of the respective component mass was removed (Figures 2.1, 2.2). The initial greater removal of the higher solubility component may have reduced the mole fraction enough so that the lower solubility components could achieve a maximum mass flux (minimal mass flux reduction) as the depletion of mass occurred due to their relative increases in mole fraction (Figure 3.7).

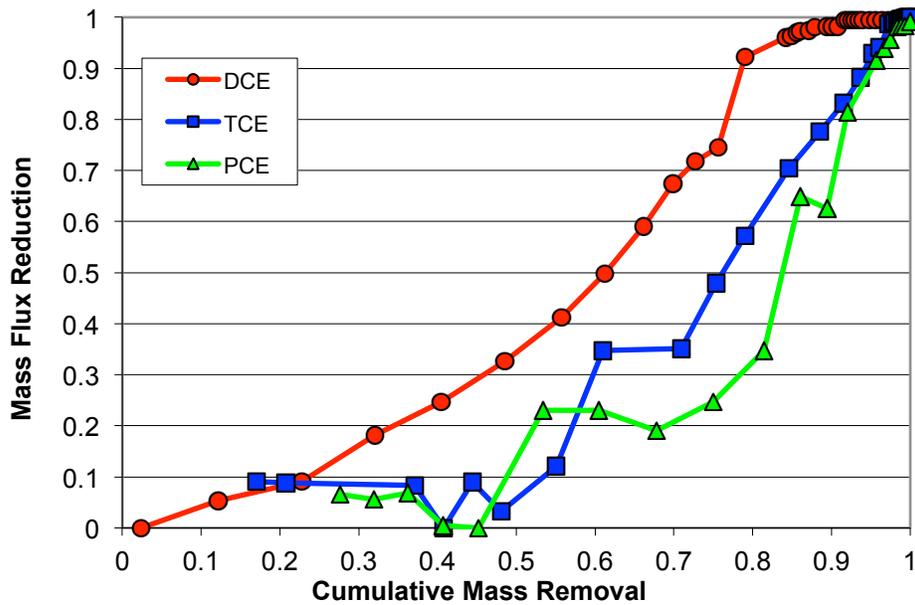


Figure 3.7. Mass flux reduction versus cumulative mass removed for DCE, TCE, and PCE during the Water Flush.

MCD Flushing

During the MCD flush, DCE (highest solubility component) exhibited significantly more ideal MFR/MR behavior than that observed for the Water Flush. Mass flux reduction occurred after about 30% of the DCE mass was removed and continued at a constant rate until most of the mass was removed (Figures 2.1, 2.2). However, in general, the TCE and PCE followed a similar trend in MFR/MR relationship whereby mass flux reduction occurred only after about 40-50% of the respective component mass was removed and mass flux reduction continued at a relatively rapid rate until nearly all of the mass was removed (Figure 3.8).

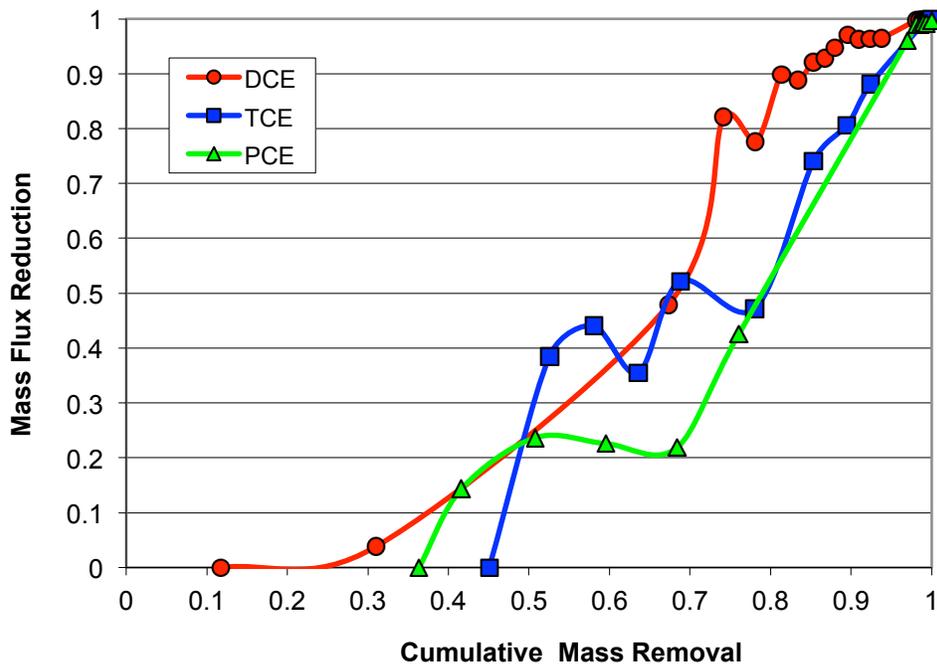


Figure 3.8. Mass flux reduction versus cumulative mass removed for DCE, TCE, and PCE during the MCD Flush.

HPCD Flushing

During the HPCD flush (Figure 3.9), DCE exhibited substantially greater nonideal MFR/MR behavior compared to TCE and PCE (Figures 2.1, 2.2). The MFR increased almost immediately even while majority of mass remained in the system. A quasi-steady state mass flux reduction occurred after about 20% of the mass was removed and then increased rapidly after 70% of the mass was removed until nearly 100% removal was achieved. TCE and PCE exhibited nonideal MFR/MR behavior but not as extreme as the DCE. Of these two compounds, TCE exhibited more nonideal behavior whereby MFR occurred after about 30% of the mass was removed and followed a constant MFR rate until nearly all of the mass was removed. PCE (lowest solubility component) was most ideal whereby MFR occurred between 40-60% of the mass had been removed maintaining a constant MFR rate until most of the mass was removed (Figure 3.9).

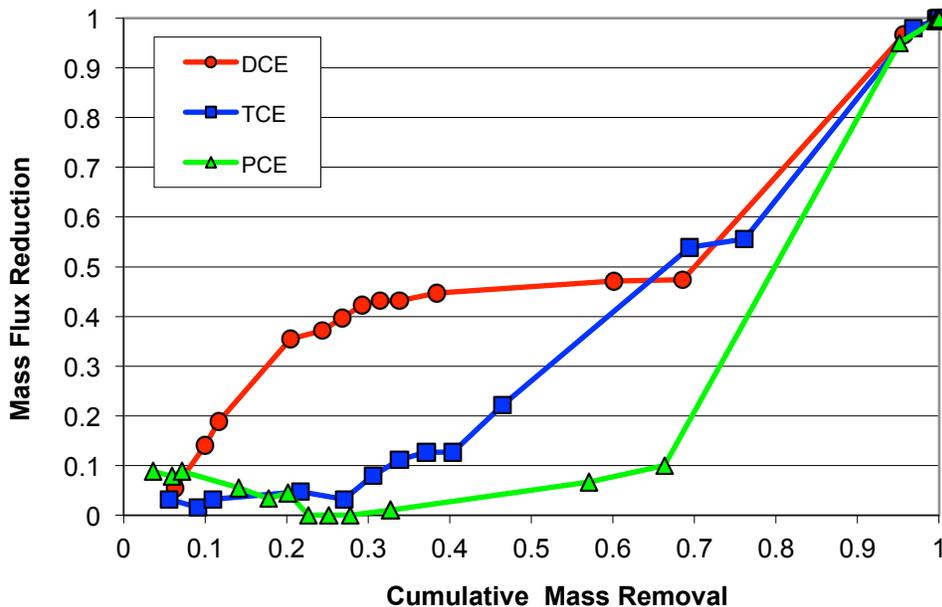


Figure 3.9. Mass flux reduction versus cumulative mass removed for DCE, TCE, and PCE during the HPCD Flush.

SDS Flushing

The target contaminants (DCE, TCE, and PCE) all exhibited relatively significant nonideal MFR/MR behavior during the SDS flush (Figure 3.10). MFR increased almost immediately upon flushing even while the majority of mass remained in the system for each component. The MFR/MR relationship for all three contaminant components was slightly more nonideal ($n=1$ to 2) than the 1:1 first order mass removal trend (Figures 2.1 and 2.2). The MFR rate was nearly constant until nearly all the mass was removed for each component. Unlike the MFR/MR behavior produced from any of the other enhanced-solubilization agents (i.e. MCD, HPCD, and EtOH), MFR/MR behavior was almost identical for all three contaminant components and overall showed some of the most inefficient mass removal effects based on mass flux reduction (MFR) analysis. While SDS proved to be a very effective at removing mass and solubilizing the contaminants, it exhibited the least efficient MFR of all the flushing agents. All three target contaminants (DCE, TCE, and PCE) showed almost immediate mass flux reduction prior to any notable mass removal from the system.

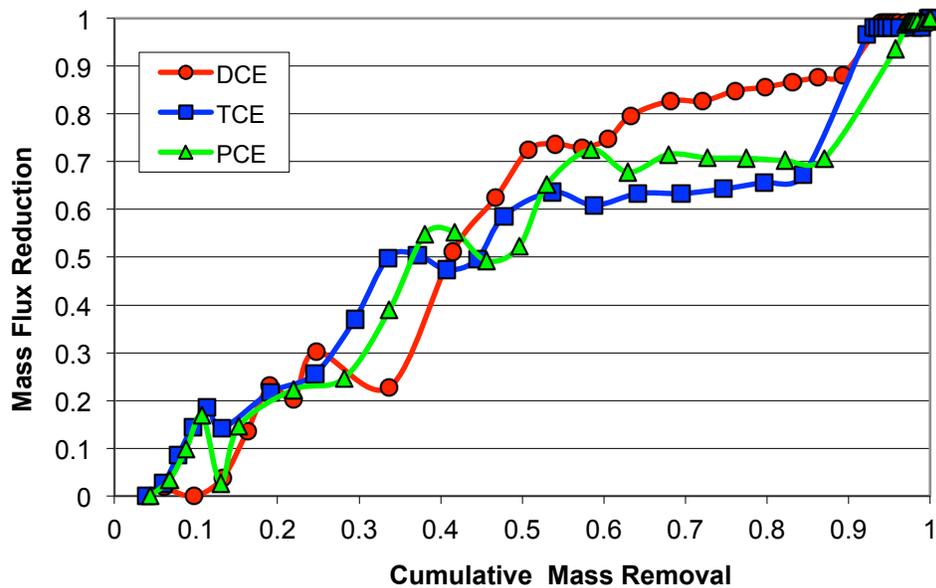


Figure 3.10. Mass flux reduction versus cumulative mass removed for DCE, TCE, and PCE during the SDS Flush.

EtOH Flushing

During EtOH flush (Figure 3.11) all three target contaminants (DCE, TCE, and PCE) displayed significantly more ideal MFR/MR behavior than the SDS and the Water Flush. TCE showed the most nonideal MFR/MR behavior initially whereby mass flux reduction occurred after only about 15% of the mass was removed (Figures 2.1 and 2.2). However, a quasi-steady state MFR rate was maintained and then rapidly increased after about 70% of the mass had been removed and remained constant until nearly all of the mass was removed. The later stage of TCE MFR/MR behavior was consistent with more efficient mass removal behavior. DCE and PCE exhibited more ideal (efficient) MFR/MR behavior initially compared to TCE in which mass flux reduction occurred after approximately 50% of the mass had been removed (i.e. DCE and PCE). Under these conditions a maximum mass flux was maintained for the first 50% of mass removal for DCE and PCE. However, PCE showed more ideal MFR/MR behavior during later stages of

removal whereby minimal mass flux reduction (MFR) occurred until about 80% of the mass was removed and then a rapid rate of MFR remained until nearly all of the mass was removed from the system. Although the DCE MFR/MR behavior was initially similar to PCE, the later stages of removal was significantly more nonideal (inefficient) with a constant rate of MFR occurring after 50% of the mass was removed until nearly all of the mass was removed (Figures 2.1 and 2.2). During the EtOH flush, TCE exhibited the most nonideal (inefficient mass removal) MFR-MR behavior initially, however, DCE showed the most nonideal MFR/MR behavior over the later stages of mass removal (Figure 3.11).

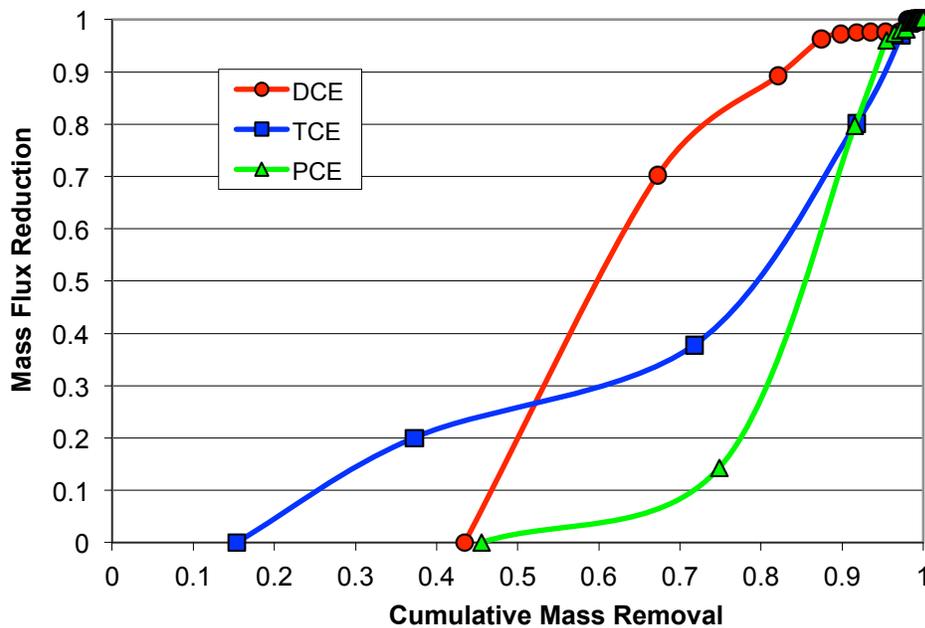


Figure 3.11. Mass flux reduction versus cumulative mass removed for DCE, TCE, and PCE during the EtOH Flush.

Mass Removal Efficiency

Contaminant Mass to Reagent Mass Recovery

Another way to evaluate the effectiveness of the flushing agents is to calculate the mass removal of the contaminants per unit mass of the flushing agent. This is important for the evaluation of overall cost of the remediation activity, reagent, and the total amount of flushing solution that will be needed to effectively remediate a site. The normalized mass ratio (mass of DCE, TCE, and PCE removed at each pore volume interval divided by the total mass) was divided by the cumulative mass of agent flushed through the flow cell at each pore volume. The mass-contaminant to mass-reagent removal efficiency results of the flushing experiments are shown in Figures 3.12b, 3.13b, 3.14b, 3.15b, and 3.16b. Alternatively, a comparative analysis of flushing reagent efficiency (mass-to-mass) was conducted whereby the maximum efficiency for each flushing agent (efficiency peak) was compared to the maximum efficiency for the water flush (efficiency peak). Effectively, this analysis provides a simple approach to evaluate how much more effective a particular enhanced-flushing agent was compared to that of water flushing (i.e. conventional pump-and-treat scenario) (Table 3.8). Similar analyses were conducted when comparing efficiency based on a mole of contaminant to mole of reagent method (described in subsequent section)

Flush Type	Efficiency –Effluent Port					
	DCE	× improved	TCE	× improved	PCE	× improved
-	0.008	-	0.002	-	0.0005	-
Water	0.008	-	0.002	-	0.0005	-
MCD	0.152	19	0.066	33	0.043	86
HPCD	0.038	5	0.038	19	0.027	54
SDS	0.192	24	0.111	56	0.128	255
EtOH	0.038	5	0.027	14	0.021	42

Table 3.8. Improved effectiveness of enhanced flushing over Water flushing for “mass contaminant to mass-reagent removal” efficiency approach.

Contaminant Moles to Reagent Moles Recovery.

The results of the flushing experiments were also compared based on the moles of DCE, TCE, and PCE removed per moles of chemical reagent used. These analyses were conducted by calculating the cumulative moles of DCE, TCE, and PCE removed (using moment analysis) per cumulative moles of flushing agent removed for each pore volume. These analyses provide a quantitative relationship between the number of molecules of contaminant that are removed based on each molecule of the flushing agent used (removed). This is important for the evaluation of overall cost of the remediation activity, reagent, and the total amount of flushing solution that will be needed to effectively remediate a site. The moles-contaminant to moles-reagent removal efficiency results of the flushing experiments are shown in Figures 3.12c, 3.13c, 3.14c, 3.15c, and 3.16c. As described in the previous section, a comparative analysis of flushing reagent efficiency (mole-to-mole) was conducted whereby the maximum efficiency for each flushing agent (efficiency peak) was compared to the maximum efficiency for the water flush (efficiency peak). Effectively, this analysis provides a simple approach to evaluate how much more effective a particular enhanced-flushing agent was compared to that of water flushing (i.e. conventional pump-and-treat scenario) (Table 3.9).

Flush Type	Efficiency –Effluent Port					
	DCE	× improved	TCE	× improved	PCE	× improved
-	1.66E-4	-	2.45E-7	-	1.39E-5	-
Water	0.362	2.2E+3	0.630	2.6E+6	0.303	2.2E+4
MCD	0.238	1.4E+3	0.096	3.9E+5	0.111	8.0 E+3
SDS	0.189	1.1E+3	0.276	1.1E+6	0.235	1.7E+4
EtOH	0.009	5.4E+1	0.012	4.9E+4	0.007	5.0E+2

Table 3.9. Improved effectiveness of enhanced flushing over Water flushing for “mole contaminant to mole-reagent removal” efficiency approach.

Mass Removal Effectiveness

Water Flush

Normalized Contaminant Mass Recovery

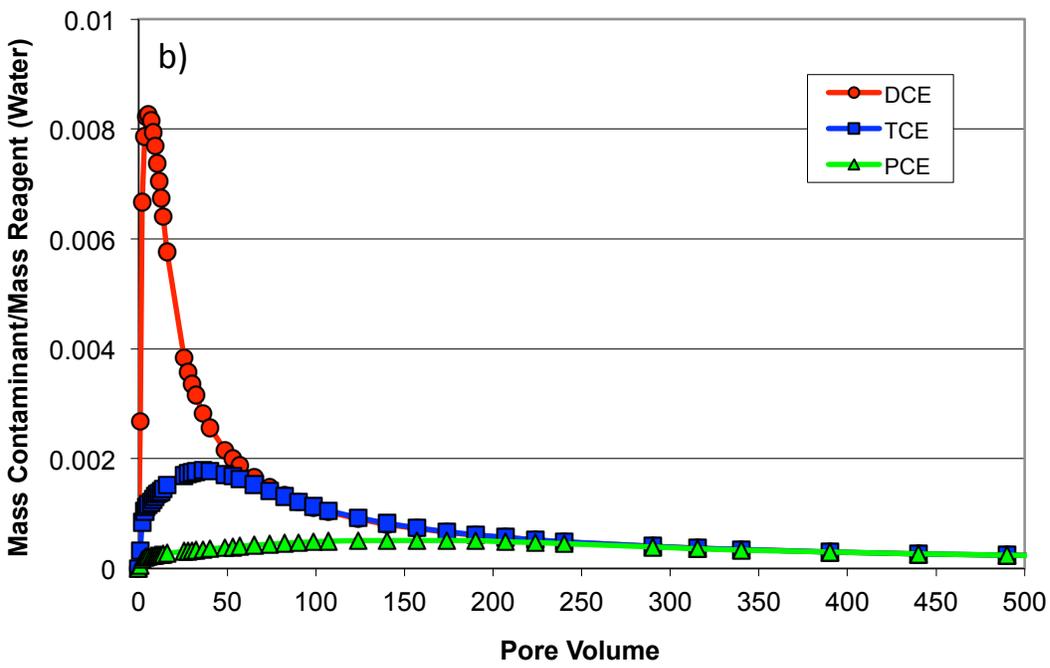
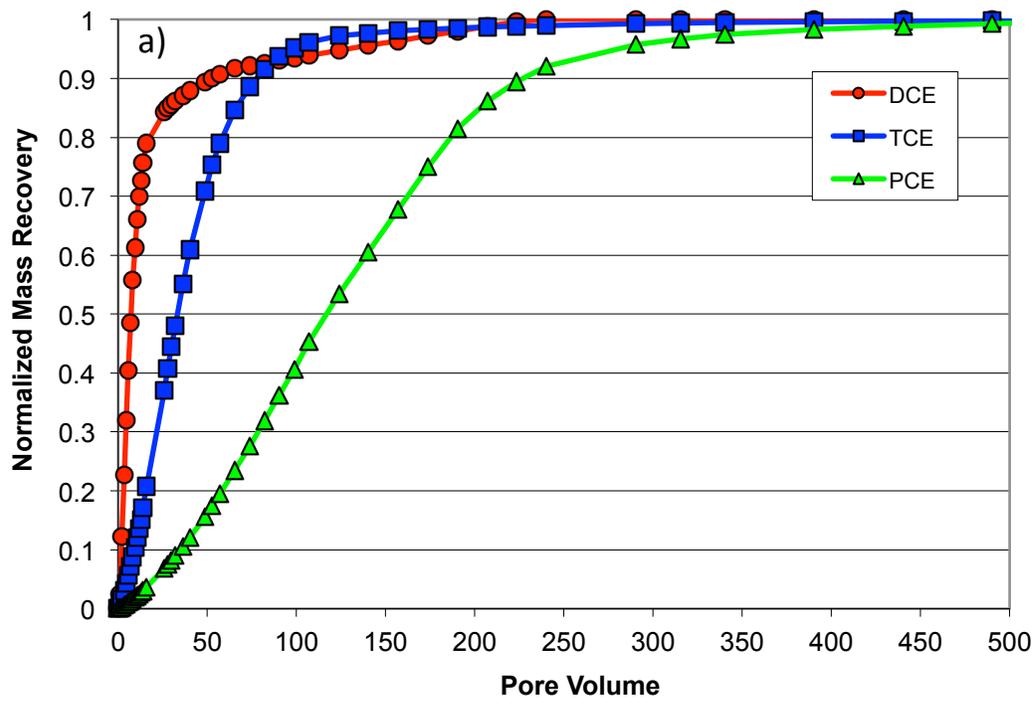
As expected, the water flush was the least effective flush in terms of contaminant mass removal, especially with PCE, which had the lowest solubility of the three compounds (Figure 3.12a). All three contaminants exhibited tailing until 500 pore volumes, at which the experiment was terminated.

Mass-Contaminant to Mass-Reagent Recovered

All enhanced flushes were compared the water flush (Figure 3.12b) to evaluate the effectiveness of the mass of the flushing agent compared to the mass of the recovered contaminants. In this flush, PCE and TCE were both more efficient in mass removal compared to mass of water. DCE exhibited the least efficient behaviour. The water flush was the least effective method for removing contaminants. However, the behavior of this experiment did show trends that were continued in the subsequent experimental flushes. In general, PCE and TCE behaved much more efficiently, while DCE behaved less efficiently than the others.

Mole-Contaminant to Mole-Reagent Recovered

The water flush, as anticipated was the least effective as a flushing agent when using the ratio of moles of contaminant to moles of reagent recovered. Interestingly, DCE proved to have the most efficient contaminant removal, followed by the others (Figure 3.12c). It quickly peaked, then was removed. The mole contaminant-to-mole of reagent ratio for DCE, TCE, and PCE during the water flush was $1.66\text{E-}4$, $2.45\text{E-}7$, and $1.39\text{E-}5$, respectively.



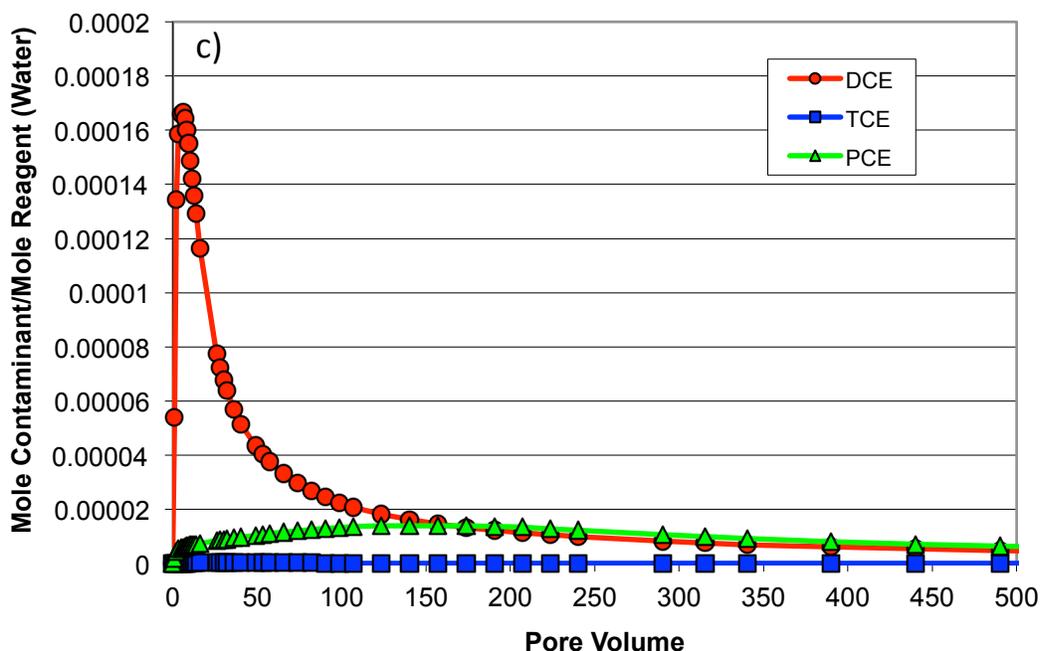


Figure 3.12. Mass removal effectiveness for DCE, TCE, and PCE during the Water Flush, a) normalized mass recovery; b) mass of contaminant to mass of reagent removed; c) mole of contaminant to mole of reagent removed.

MCD Flush

Normalized Contaminant Mass Recovery

MCD (Figure 3.13a) exhibited much more effective mass recovery, and the difference in removal times for the different target compounds was much faster. Complete mass removal for DCE was reached at 125 pore volumes, while TCE and PCE reached complete mass removal at 175 pore volumes.

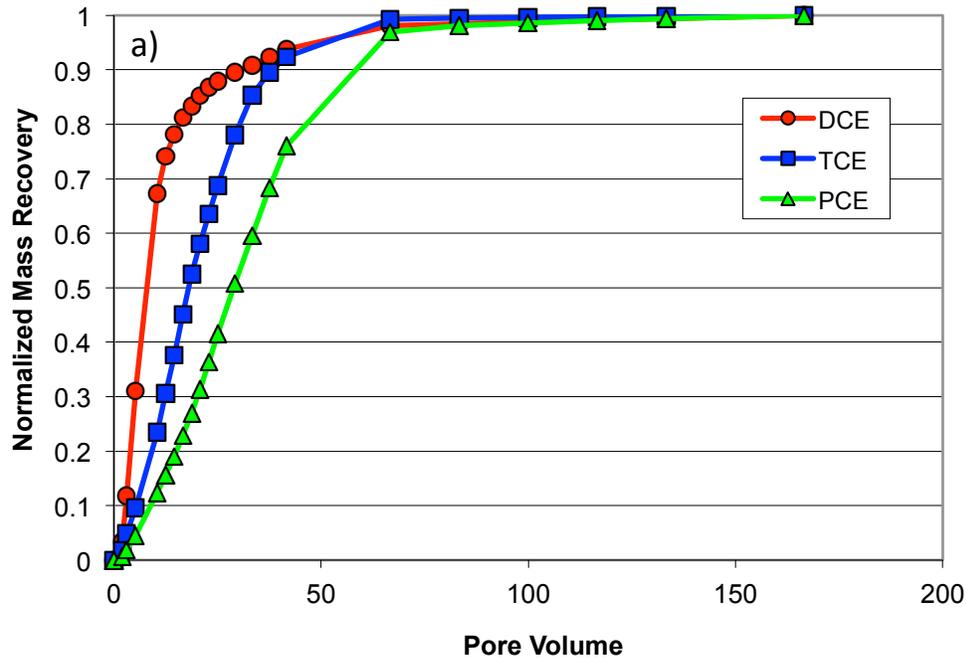
Mass-Contaminant to Mass-Reagent Recovered

Figure 3.13b describes the mass contaminants to mass reagent analysis for the MCD flush. Similar to the water flush, DCE behaved the least efficiently, requiring as greater amount of flushing agent to remove the contaminant, while PCE and TCE behaved more efficiently. Furthermore, DCE exhibited the least improvement in flushing efficiency; it was removed 19

times faster than during the water flush. TCE and PCE were removed 33 and 86 times faster, respectively, than during the water flush.

Mole-Contaminant to Mole-Reagent Recovered

MCD (Figure 3.13c) performed well in this analysis. During this experiment, TCE showed the greatest improvement in efficiency, as it improved by a factor of $2.6E+6$, compared to DCE ($2.2E+3$) and PCE ($2.2E+4$)



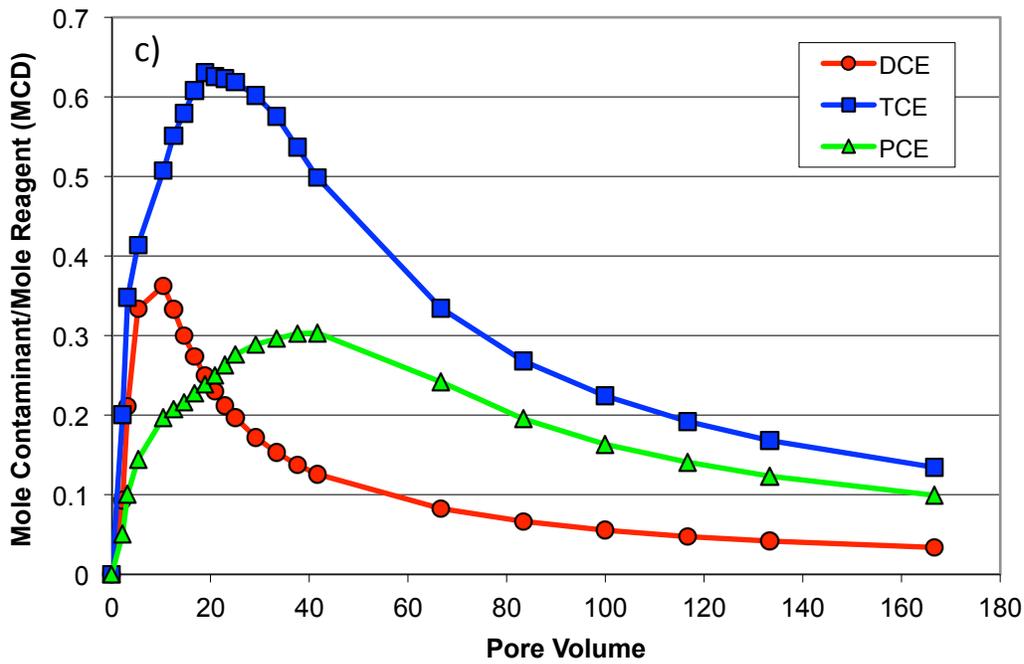
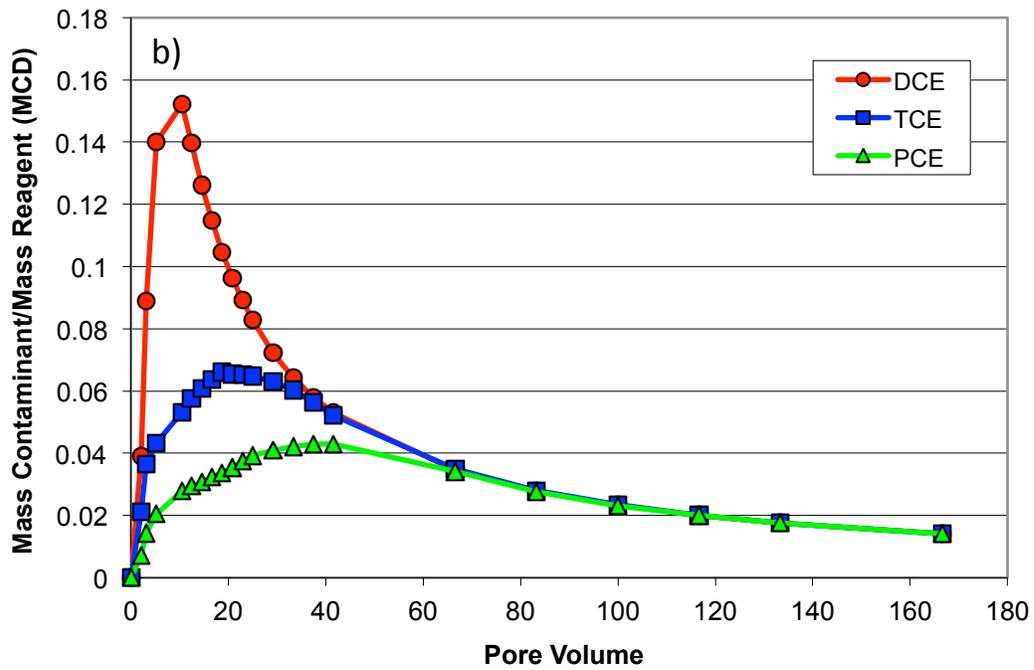


Figure 3.13. Mass removal effectiveness for DCE, TCE, and PCE during the MCD Flush, a) normalized mass recovery; b) mass of contaminant to mass of reagent removed; c) mole of contaminant to mole of reagent removed.

HPCD Flush

Normalized Contaminant Mass Recovery

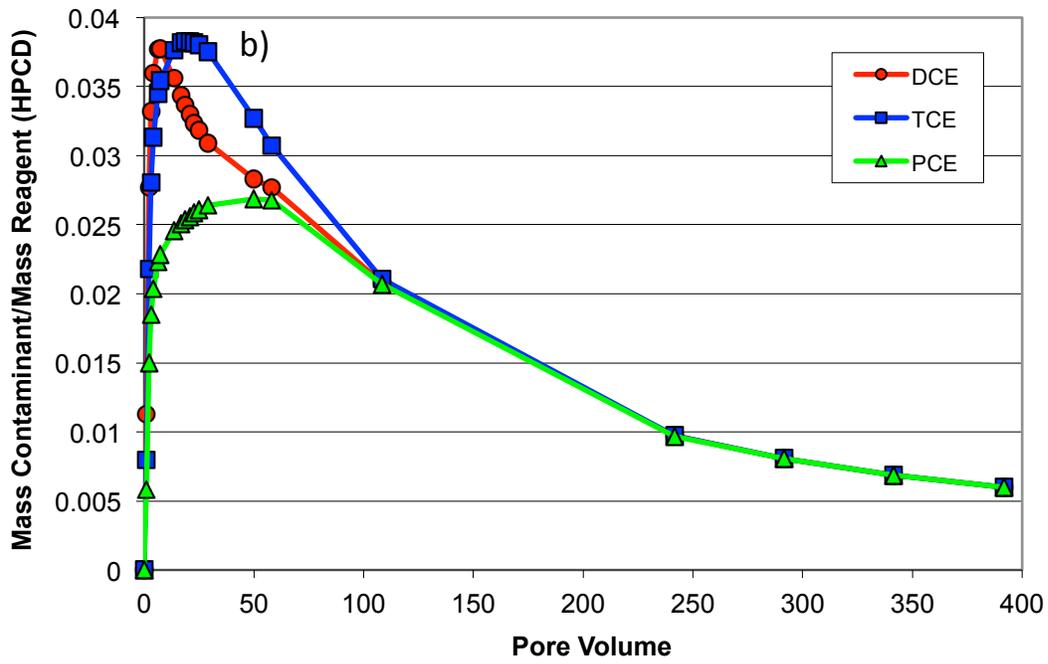
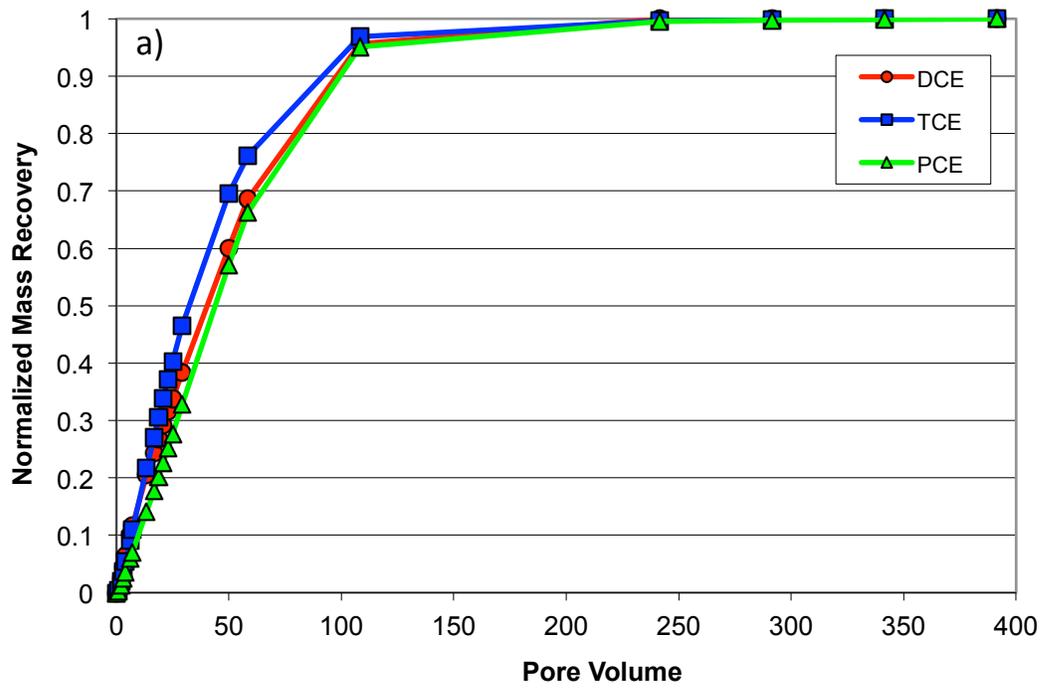
During the HPCD flush (Figure 3.14a), TCE and DCE exhibited behavior that was similar to the water flush, both reaching full mass removal. PCE, though exhibited a much more accelerated rate of mass removal, keeping pace with TCE and DCE. All contaminants reached complete mass removal just before 400 pore volumes.

Mass-Contaminant to Mass-Reagent Recovered

HPCD (Figure 3.14b) exhibited somewhat more efficient mass removal than water. Following the observed trends, DCE was the least efficiently removed contaminant, and removal improved by a factor of five for this experiment, while TCE removal was improved by 19 times, and PCE was improved by 54 times.

Mole-Contaminant to Mole-Reagent Recovered

HPCD (Figure 3.14c) proved to be effective at removing the contaminants. DCE exhibited an improvement factor of $1.4E+3$, TCE improved by $3.9E+5$, and PCE improved by a factor of $8.0E+3$. While more effective than water, HPCD did not show marked improvement over some of the other flushing agents included in the experiments.



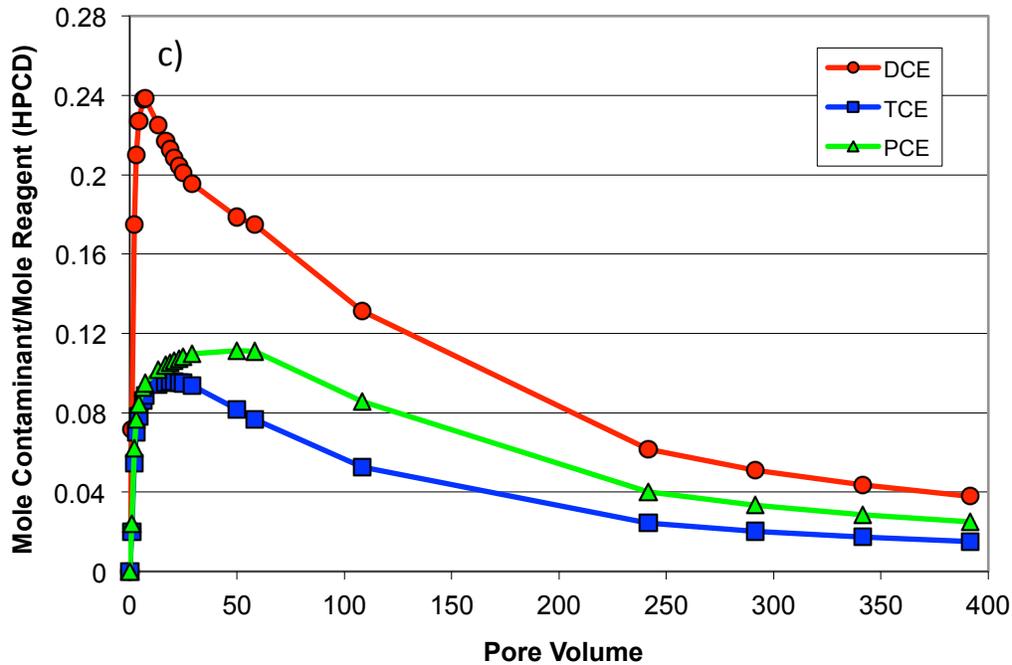


Figure 3.14. Mass removal effectiveness for DCE, TCE, and PCE during the HPCD Flush, a) normalized mass recovery; b) mass of contaminant to mass of reagent removed; c) mole of contaminant to mole of reagent removed.

SDS Flush

Normalized Contaminant Mass Recovery

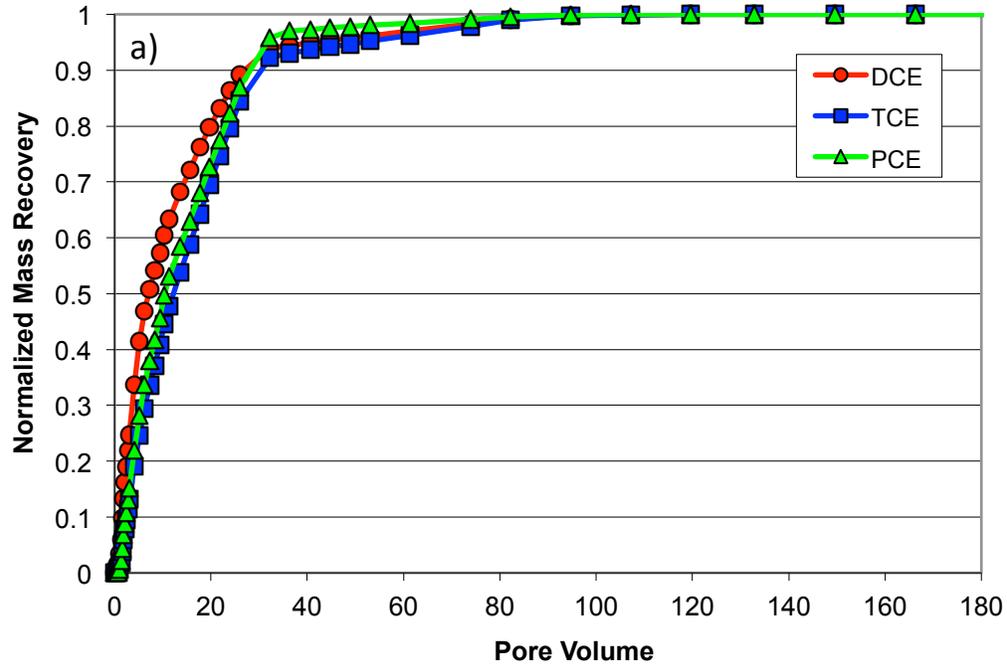
SDS (Figure 3.15a) proved to be one of the more effective flushing agents, with DCE reaching complete mass removal at 80 pore volumes, and TCE and PCE reaching complete mass removal at 170 pore volumes.

Mass-Contaminant to Mass-Reagent Recovered

The SDS experiment proved to be the most efficient flush in terms of contaminant to reagent mass (Figure 3.15b). DCE was improved by 24 times over the water flush. TCE improved by a factor of 56, and PCE improved 255 times. This shows that SDS is a very powerful tool for enhancing the mass recovery of certain contaminants.

Mole-Contaminant to Mole-Reagent Recovered

SDS showed good efficiency in the mole-to-mole test compared to water, but did not outperform any of the other flushing agents (Figure 3.15c). DCE improved by a factor of $1.1E+3$, TCE improved by $1.1E+6$ times, and PCE improved by $1.7E+4$ times. TCE exhibited the most efficiency with this analysis, followed by PCE and DCE.



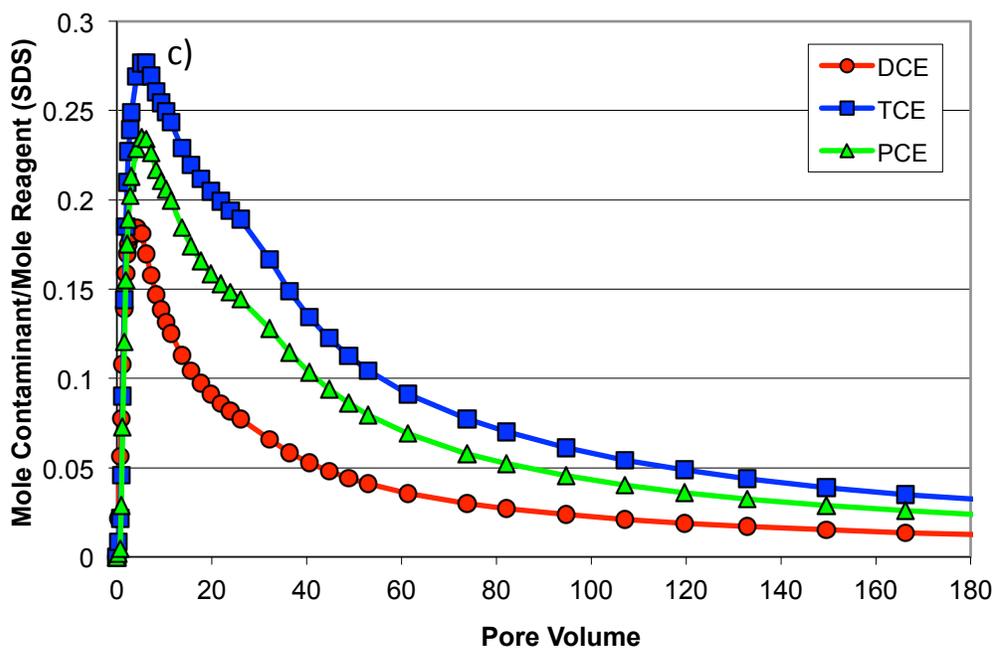
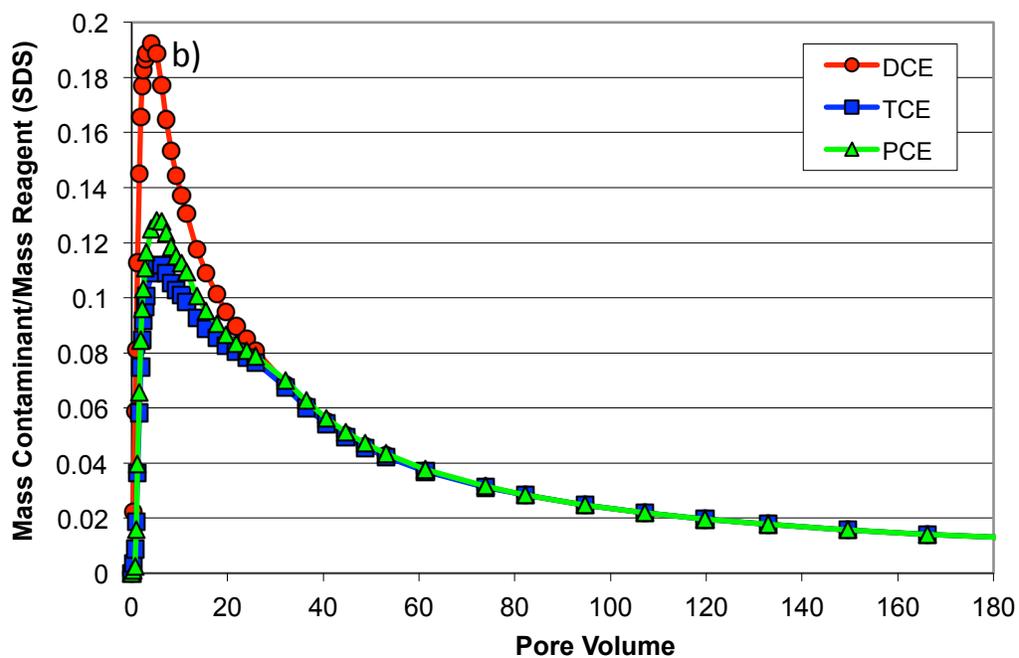


Figure 3.15. Mass removal effectiveness for DCE, TCE, and PCE during the SDS Flush, a) normalized mass recovery; b) mass of contaminant to mass of reagent removed; c) mole of contaminant to mole of reagent removed.

EtOH Flush

Normalized Contaminant Mass Recovery

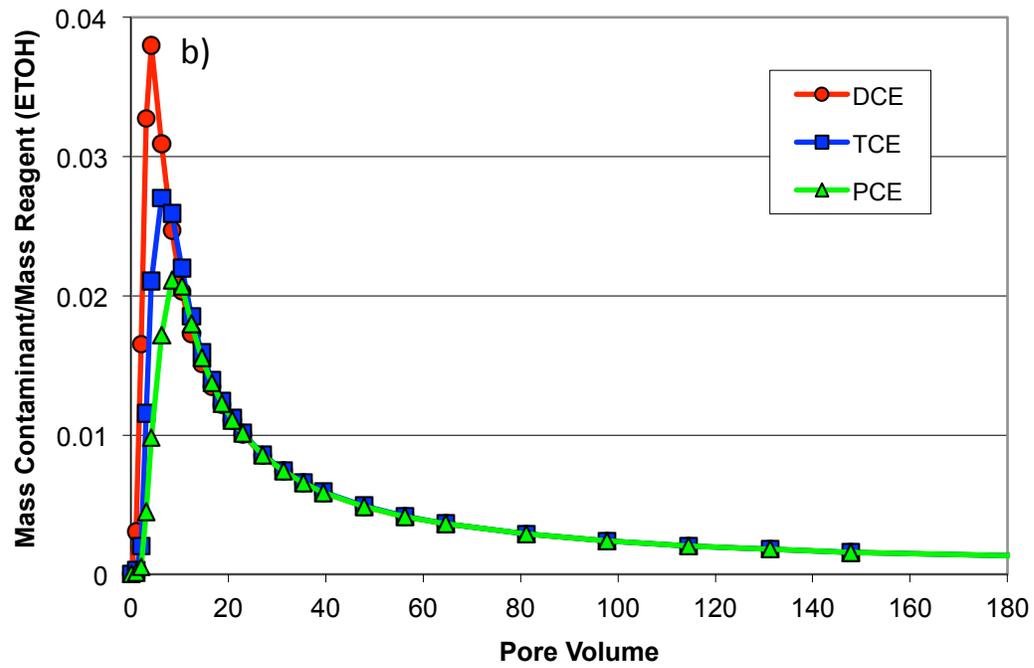
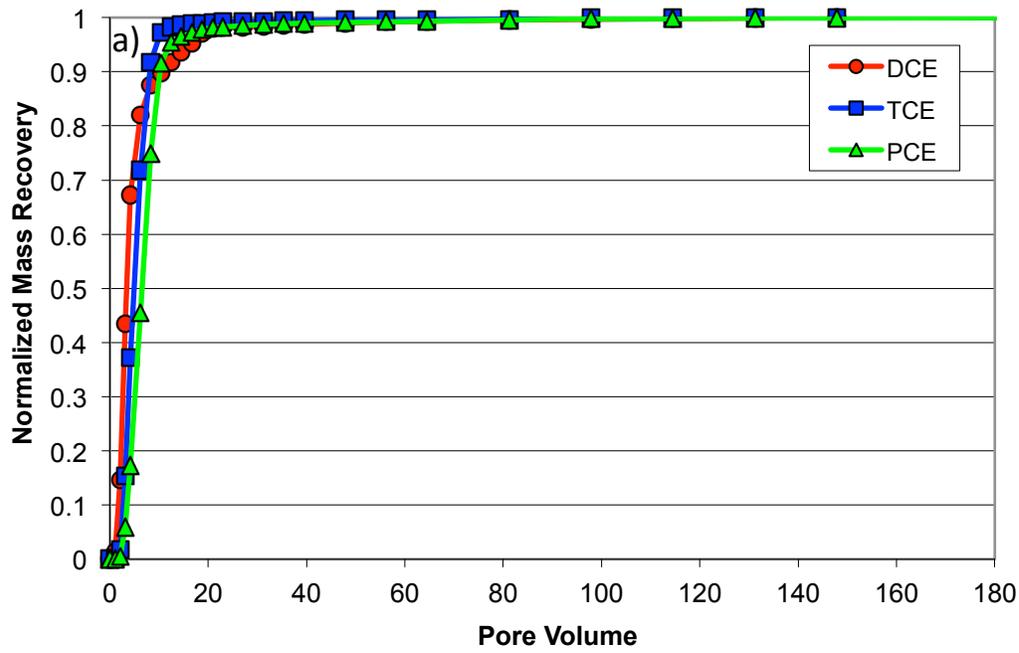
EtOH (Figure 3.16a) showed some of the fastest mass removal behavior of all the experiments. DCE was fully removed at about 40 pore volumes. TCE and PCE were completely removed at 150 pore volumes. During this experiment, the three contaminants exhibited a rapid spike in contaminant mass removal, followed by a brief period of tailing, as the pure phase contaminant dissolved and was removed.

Mass-Contaminant to Mass-Reagent Recovered

During the Ethanol flush, the contaminants exhibited the least efficient removal. DCE removal only improved by a factor of 5 over the water flush, and TCE and PCE only improved by factors of 14 and 42, respectively (Figure 3.16b). This is due to Ethanol being used in a 50 wt.% solution. Therefore, while Ethanol was very effective at quickly removing the contaminants in terms of pore volumes, it is the least efficient in terms of the ratio of contaminant mass recovered to mass of flushing agent.

Mole-Contaminant to Mole-Reagent Recovered

Ethanol (Figure 3.16c) exhibited the worst efficiency compared to the other flushing agents, although still better than the water flush. Again, this is due to the Ethanol being mixed as a 50 wt.% solution opposed to a 5 wt.% solution like the other flushing agents. DCE removal performance was improved by a factor of $5.4E+1$. TCE and PCE were improved by factors of $4.9E+4$ and $5.0E+2$, respectively.



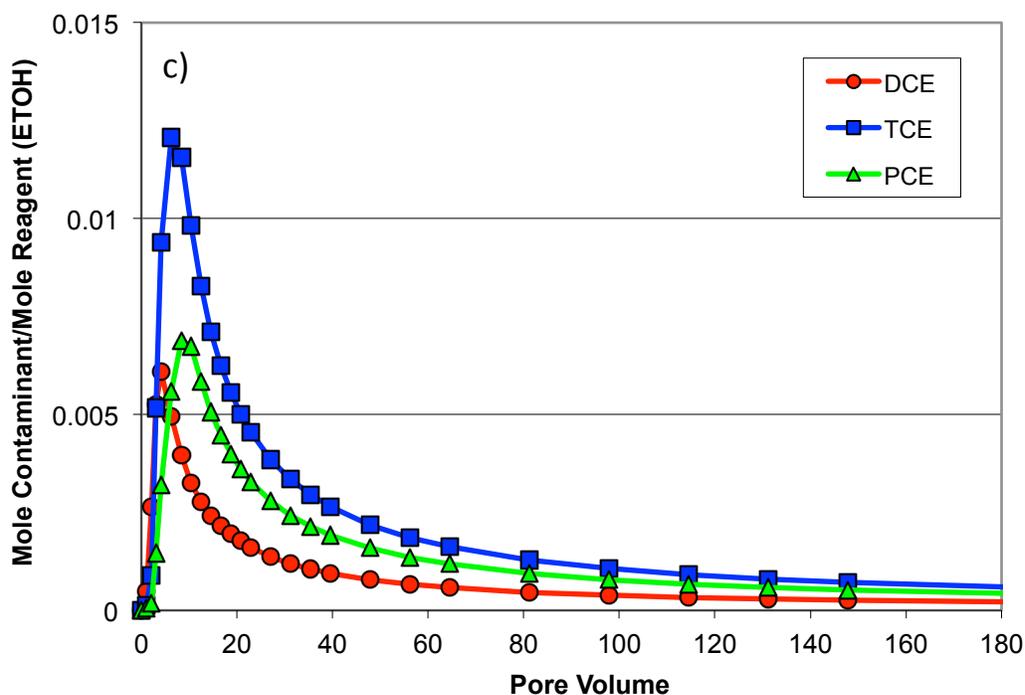


Figure 3.16. Mass removal effectiveness for DCE, TCE, and PCE during the EtOH Flush, a) normalized mass recovery; b) mass of contaminant to mass of reagent removed; c) mole of contaminant to mole of reagent removed.

Contaminant Mass to Reagent Mass Recovery

Summarization of the mass removal effectiveness/efficiency results can be observed in Figures 3.12 -3.16 and in Tables 3.8 and 3.9. Contaminant removal effectiveness, in terms of normalized mass recovery analysis, show that EtOH had the most effective mass removal capability, removing over 95% of the total mass (for all components, DCE, TCE, and PCE) in the least amount of flushing duration (i.e. ~ 10-12 pore volumes). However, it should be noted that EtOH was used in the highest concentration (50 wt%) compared to all other agents which used only 5 wt% concentrations. Since EtOH has the highest solubilization power, this result is not surprising especially accounting for the higher concentrations used. SDS, the second greatest solubilization power agent, performed best among the enhanced-solubilization agents which used

5 wt% mixture concentrations. The SDS removed over 95% of the total mass (for all components, DCE, TCE, and PCE) in about 35 pore volumes (PVs) of flushing. MCD was slightly less effective than SDS (in terms of normalized mass recovery), removing over 95% of the total mass (for all components, DCE, TCE, and PCE) in about 66 PVs of flushing. HPCD was least effective under this analysis, removing 95% of the total mass (for all components, DCE, TCE, and PCE) in about 110 PVs of flushing. HPCD had about the same effectiveness as the Water flush did for removing DCE and TCE from the system. However, HPCD was more effective than Water Flushing for the lowest solubility component (PCE) removing 95% of the mass in about 110 PVs compared to about 300 PVs for the Water Flush. This may suggest that although HPCD might not be as effective for higher solubility contaminant compounds that HPCD may be useful for removal of priority pollutants with extremely low solubilities.

Contaminant Moles to Reagent Moles Recover

Contaminant removal, in terms of the ratio of mass of contaminant removed to mass of reagent used per volume of flushing, shows that SDS was most effective (efficient) at contaminant removal (Table 3.8). SDS also showed the largest relative effectiveness (enhancement) for the lowest solubility component PCE compared to all other enhanced-solubilization agents. MCD was second most effective enhanced-solubilization agent for contaminant removal when evaluated in terms of mass-contaminant to mass of reagent used per volume of flushing (Table 3.8). Although not as great as SDS, MCD also showed a relative greater effectiveness (enhancement) for the lowest solubility component PCE compared to HPCD and EtOH. HPCD was the third most effective enhanced-solubilization agent under this analysis evaluation and also showed the greatest relative enhancement for the lowest solubility

component PCE (Table 3.8). EtOH was the least effective enhanced-solubilization flushing agent when evaluated under this analysis metric due to the high concentrations (50 wt%) that had to be used to induce any significant solubilization enhancement and contaminant removal (Table 3.8).

Contaminant removal, in terms of the ratio of moles of contaminant removed to moles of reagent used per volume of flushing, shows that MCD was most effective (efficient) at contaminant removal (Table 3.9). MCD, also showed the largest relative effectiveness (enhancement) for the intermediate solubility component TCE compared to all other enhanced-solubilization agents. SDS and HPCD were the second most effective enhanced-solubilization agents for contaminant removal when evaluated in terms of moles-contaminant to moles of reagent used per volume of flushing, however, SDS performed slightly better overall (all contaminant components) (Table 3.9). Although not as great as MCD, SDS and HPCD also showed relative greater effectiveness (enhancement) for the intermediate solubility component TCE compared to the other components (DCE and PCE). EtOH was the least effective enhanced-solubilization flushing agent when evaluated under this analysis metric due to the high concentrations or mole concentrations (50 wt%) that had to be used to induce any significant solubilization enhancement and contaminant removal (Table 3.9). Similar to the other agents, EtOH showed relative greater effectiveness (enhancement) for the intermediate solubility component TCE compared to the other components (DCE and PCE).

MCD may have outperformed HPCD, a similar glucose compound due to the presence of the methyl groups which solvate readily in water, thus allowing more of the NAPL constituent to be solubilized and removed more efficiently. However, more studies are needed to determine the fundamental mechanisms responsible (i.e. molecular structure, apolar cavity dimensions,

complexation association strengths) for the observed removal differences between the two sugars. Currently, there is a lack of published information for MCD as a flushing agent.

CHAPTER 4: CONCLUSIONS

Extensive soil and groundwater contamination can result due to the presence of nonaqueous phase liquids (NAPLs) that leak or spill or are dumped into the subsurface. Such NAPLs can act as long-term contaminant sources to the groundwater. Furthermore, the constituents making up many of these NAPL sources are of major concern due to their typically high persistence and associated high toxicities in the environment. These chemicals often pose significant threat to human health as they are released from various sources such as industrial and agricultural facilities or sites. As the demand for potable water increases, the urgency to protect and remediate contaminated groundwater sources and implement source-zone treatment/removal has been and continues to be a major focus of groundwater researchers, practitioners, and regulatory agencies. Enhanced flushing technologies, via enhanced-solubilization agents, have shown great potential to improve mass removal performance over basic pump-and-treat methods. However, many of the chemical agents are fairly new to enhanced flushing applications, so there is still ambiguity surrounding their effectiveness at removing contaminants from the subsurface, especially for complicated NAPL contaminant mixtures. The experiments conducted as part of the thesis research was done to test the effectiveness of various enhanced-solubilization agents on the dissolution of multicomponent NAPL and removal of their mass from groundwater.

Raoult's Law was used to successfully predict the initial concentrations resulting during enhanced flushing conditions. The results generally indicated that the target contaminants were

controlled initially under ideal dissolution conditions for each of the respective enhanced flushing experiment, indicating that enhanced-solubilization agents themselves did not significantly alter resulting dissolution processes and that initial concentrations could be predicted. As expected through equilibrium dissolution theory (Raoult's Law), the higher solubility contaminant concentrations increased sooner than the lower solubility contaminants. Generally, deviations from the predicted initial concentrations were less than 6%. These experiments also showed that no single flushing agent exhibited any kind of significant nonideal or drastically different behavior from each other (in terms of Raoult's Law behavior). Furthermore, the high-solubility contaminants exhibited ideal initial dissolution in all flushes. For all enhanced-flushing experiments (HPCD, MCD, SDS, EtOH), the low-solubility contaminant (PCE) showed the greatest deviation (21%-23%) from ideal dissolution behavior for observed and predicted initial concentrations. However, this deviation is relatively minimal and, therefore, dissolution processes (i.e. initial) were still considered to be relatively ideal.

The flushing agents that were the target of this study included two complexing sugars hydroxypropyl- β -cyclodextrin and methyl- β -cyclodextrin (5wt% solution); a surfactant (5 wt.%), sodium dodecyl sulfate (SDS), and a co-solvent solution, ethanol (EtOH) (50 wt.%). In terms of normalized mass recovery, EtOH outperformed the others, followed by SDS, MCD, and finally HPCD. This is to be expected, since EtOH was used in a 50 wt.% solution as opposed to a 5 wt.% solution. HPCD performed least efficiently, consistent to that of water flushing, although it was more efficient than water when removing PCE, the low-solubility contaminant. Mass removal in terms of mass-contaminant to mass-reagent, however, indicated that SDS displayed the most efficient removal. SDS was also displayed the largest relative effectiveness (enhancement) in removing PCE. MCD was the next most efficient solubilization-agent in terms

of mass removal, and also the second most effective agent in removing PCE, compared to HPCD and EtOH. HPCD was the third most effective solubilization agent in this test, but was least effective in removing PCE. Due to its high concentration, EtOH proved to be the least effective agent when evaluated under this analysis metric (i.e. mass-contaminant removed to mass-reagent used). When analyzed in terms of moles contaminant removed to moles of reagent used, MCD outperformed all other enhanced-solubilization agents, and also showed the greatest efficiency in removing the intermediate solubility contaminant, TCE. HPCD and SDS were the second most effective flushing agents under this analysis and were also more efficient at removing TCE (intermediate solubility contaminant). Although efficiencies were nearly identical for HPCD and SDS, SDS did slightly outperform HPCD in terms of removal efficiency for all of the contaminants based on this evaluation approach (mole-contaminant removed to mole of reagent used). EtOH was the least effective flushing agent due to its high concentration (mole concentration). Similar to all of the enhanced-solubilization agents tested under this evaluation metric, TCE was the most efficiently-removed contaminant compared to DCE and PCE.

These observations are valuable when evaluating remediation scenarios involving DNAPLS, in particular DCE, TCE, and PCE. Factors such as cost of remediation, environmental impact, proximity of residential wells, and other variables found at many remediation sites, can have an impact in designing an appropriate remediation plan. HPCD and MCD, glucose derivatives, have a relatively low impact (toxicity) on the environment and, therefore, may be more appropriate for sites in close proximity to environmentally sensitive regions or residential/public supply wells where negligible toxicity concerns for human health exist. EtOH, however, might be a more appropriate agent in a remediation scenario whereby the reagent is not a concern on the natural biodegraders (microbes) and or residential/public water supply wells are

far from the source. EtOH may also be useful for sources that require quick remediation due to imminent danger posed by the toxicity of the contaminants and risk to groundwater contamination. HPCD and MCD are also more expensive than EtOH, and that can also play a factor when determining the appropriate flushing agent.

This study contributes valuable insight for understanding how various enhanced flushing agents (enhanced solubilization) effect mass removal effectiveness and remediation performance for more complicated NAPL mixtures present in a groundwater environment. These more complex contaminant mixture scenarios are common quite common at many sites throughout the world and furthering the research of treatment strategies is important for the overall health and welfare of many communities and environments. Enhanced flushing techniques improve the efficacy of the remediation process demonstrating significant mass removal subsurface environments contaminated by NAPL sources and effectively reducing mass discharge to groundwater and aquifers that may be sources for drinking water. In general, these findings show that careful evaluation of a particular flushing agent is necessary for safe and effective removal of specific NAPL contaminants when more complex mixtures threaten the quality of the groundwater and pose risks to potential drinking water supplies. Different flushing agents have different characteristics and behaviors for different contaminant compounds within NAPL mixtures that make the careful selection of a specific reagent vital for any kind of enhanced flushing remediation plan. In a real world environment, whereby a high degree of subsurface heterogeneity typically exists, differences from these ideal experiments with physically homogeneous porous media systems and uniform NAPL distributions would be expected. The presence of bedrock, clays, and naturally structured soils/strata would be expected to dramatically affect NAPL distribution processes, NAPL architecture, and NAPL accessibility.

These factors will increase nonideal NAPL dissolution behavior as result of NAPL bypass flow, NAPL pooling, and NAPL inaccessibility further controlling the effectiveness of enhanced-solubilization flushing techniques for soil and groundwater remediation.

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APPENDIX I: TRACER TESTS

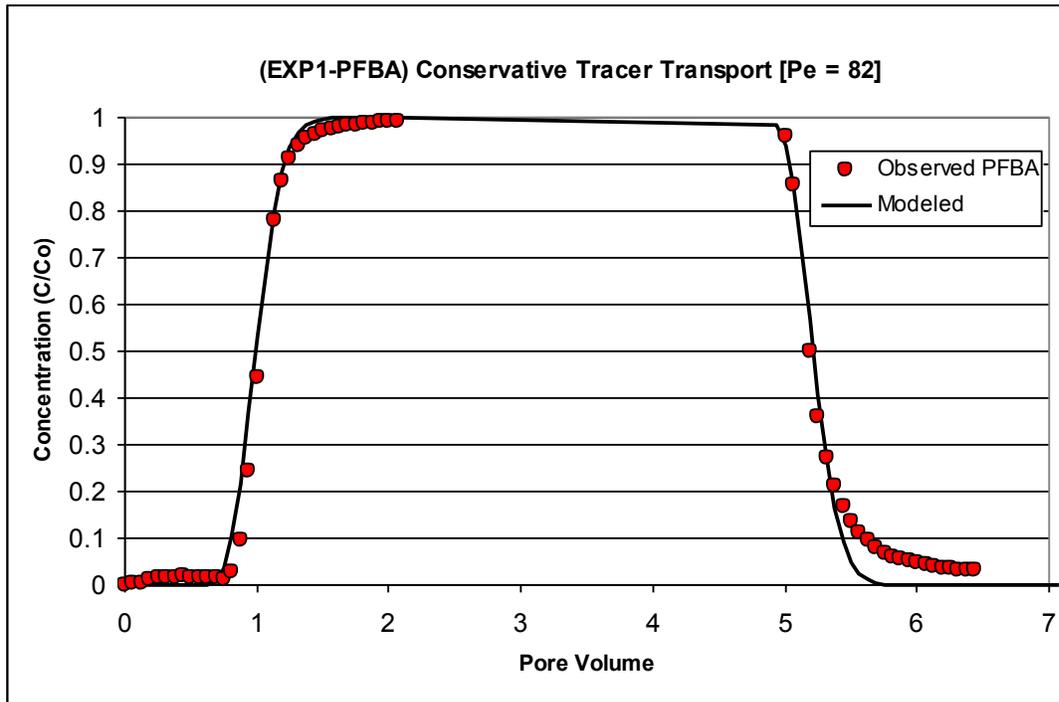


Figure A1. CFITIM Results for Conservative Tracer Breakthrough [EXP1-PFBA].

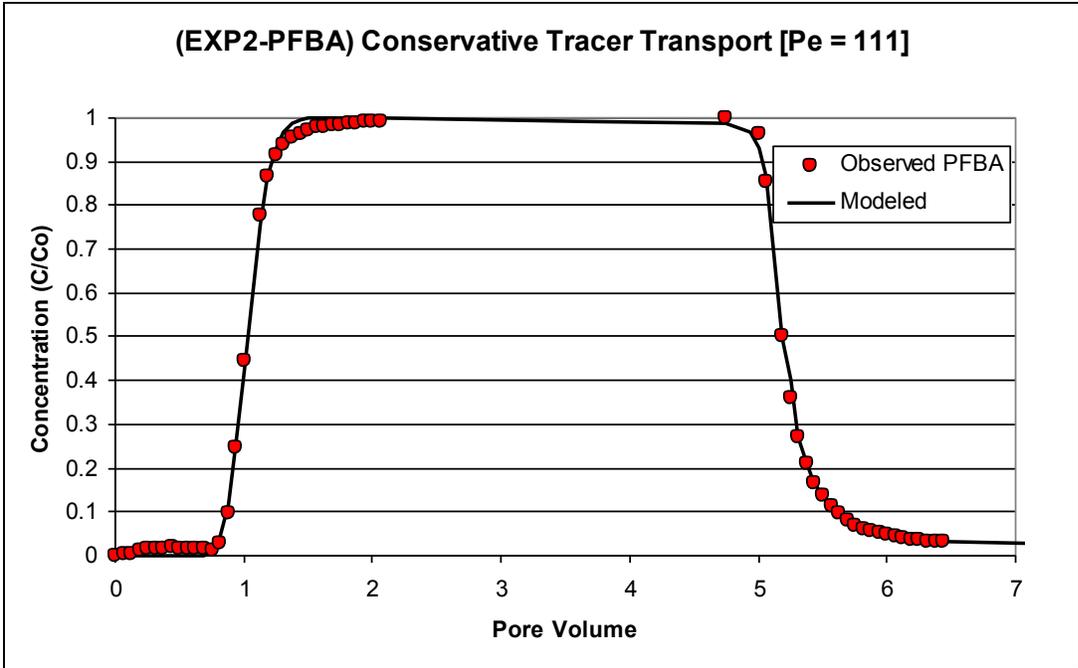


Figure A2. CFITIM Results for Conservative Tracer Breakthrough [EXP2-PFBA].

Conservative Tracer Tests (PFBA)	*Pelet # [Pe]
EXP1-PFBA	82
EXP2-PFBA	111

*Values determined by CFITIM; Van Genuchten, 1981.

Table A1. Peclet number results from conservative tracer tests with the porous-medium filled columns. Values demonstrate that transport was dominated by advection for the experiments in this research.