USING MULTILEVEL SAMPLERS TO ASSESS ETHANOL FLUSHING AND ENHANCED BIOREMEDIATION AT FORMER SAGES DRYCLEANERS

BY

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVIATIONS

PCE	perchloroethylene, tetrachloroethene, or perc
TCE	trichloroethylene or trichloroethene
DCE	dichloroethene
VC	vinyl chloride
DNAPL	dense non-aqueous phase liquid
NAPL	non-aqueous phase liquid
VOC	volatile organic chemical
bgs	below ground surface
MLS	multi-level sampling well
RW	recovery or extraction well
IW	injection well
PITT	partitioning interwell tracer test
BTC	breakthrough curve
ISB	in situ bioremediation
SERB	solvent extraction residual biotreatment
MCL	maximum contaminant limit
RBCA	risk-based corrective action
CDF	cumulative distribution function
FNR	fractional NAPL removal
ENR	estimated NAPL removal
FFR	fractional flux reduction
IFT	interfacial tension

Abstract of Thesis Presented to the Graduate School
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As a result of dry cleaning operations, there are hundreds of sites where the subsurface aquifer has been contaminated by perchloroethylene (PCE), the dry cleaning agent. One of the more challenging problems facing environmental scientists and engineers today is locating PCE source areas and cleaning up these sites to reduce the risk of contaminated groundwater reaching water supplies. The high specific gravity, low solubility, and recalcitrance make PCE highly persistent in the environment. Without some remedial action, many of these sites would serve as a source of dissolved groundwater contamination for decades. The Sages former drycleaning site in Jacksonville, FL, was the test ground for a pilot scale in-situ alcohol flushing test in 1998. The sandy aquifer was contaminated with PCE, found as a separate phase in discrete layers in the subsurface.

A network of multilevel sampling wells (MLS) was installed in the source area to collect liquid samples before, during and for six years after the pilot test. The depth level sampling of MLS allows three dimensional spatial analyses. Multilevel samples were able to determine the initial and post-remedial PCE architecture at the site. This information will help the site manager

target residual PCE for future corrective action. Site characterization determined that hydraulic conductivity decreased with depth. Thus, ethanol flushing encountered the difficulty getting high concentrations to the deep, low flow zones. Furthermore, once remedial fluids penetrated the lower depths, they were difficult to recover in the pumping rate and time frame of this test.

The remedial performance was evaluated through comparison of pre and post-remedial groundwater samples and partitioning tracer tests. The ethanol flushing test was effective at removing significant levels of subsurface PCE and favorably reduced the contaminant flux at most MLS locations.

One of the benefits of using ethanol as the remedial fluid was the fostering of microbial reductive dechlorination of residual PCE. Ethanol served as an electron donor in biodegradation. From long term transect monitoring, the mass discharge of the source zone and downgradient control plane were determined. Once higher levels of unrecovered ethanol were carried away by natural gradient flow, microbial activity spiked up until four years after the 1998 event. Then, dechlorination declined rapidly as all the ethanol was exhausted by microbes or removed by groundwater flow. While residual PCE dissolution was microbially enhanced, significant PCE remained in the source zone at the end of this study. Therefore, another combined effort took place at the conclusion of this study in 2004 with a second full scale ethanol flushing.

The combination of enhanced solubililization and residual source biotreatment was effective at removing significant PCE mass, reducing PCE flux, and fostering bioremediation in the source zone and plume. This combined technology will serve to decrease source strength and longevity for sites meeting the proper criteria. Clean up and site closure will occur much faster than natural gradient dissolution and plume control via a pump-and-treat system.

CHAPTER 1
INTRODUCTION AND BACKGROUND

1.1 Project Introduction

The Sages former drycleaning site in Jacksonville, FL was the test ground for a pilot scale in-situ alcohol flushing test in 1998. The groundwater at the site was contaminated with the drycleaning chemical perchloroethene, (PCE), also called tetrachloroethylene and perc. PCE was found in discrete layers in the sandy aquifer. Four previous studies have been published about the Sages site. The first two papers studied the NAPL removal effectiveness of the 1998 alcohol flushing test [*Sillan*, 1999; *Jawitz et al*., 2000]. Next, the bioremediation of residual PCE stimulated by the unrecovered ethanol was studied by the US EPA in the three years after the pilot test [*Mravik et al*., 2003; *Sewell et al*., 2006].

This thesis presents the analysis of data from multilevel sampling wells installed in the PCE source zone and up to ten meters downgradient. These wells consist of bundles of smaller stainless steel tubes each installed to a different depth, allowing the collection of discrete vertical liquid samples normally diluted in standard well screen intervals. In the remedial zone, the spatial distribution of initial groundwater concentrations of PCE, partitioning interwell tracer tests, ethanol flushing, and post-remedial groundwater concentrations of PCE and ethanol were obtained by sampling the multilevel well depths. After the ethanol flushing test, long term monitoring commenced in the source zone and the additional downgradient multilevel wells. Semi-annual sampling was conducted to monitor contaminant concentrations and to estimate contaminant mass discharges out of the site over the six-year period from 1998-2004.

Much of the data presented in this thesis was collected in the period prior to this author's contributions. Field sampling continued in 2003 and 2004 while the author analyzed the results

of all the previous data. The termination of this study occurred when the second phase of remediation, a full scale ethanol flushing, was initiated in July 2004.

1.2 Motivation for the Project

The Sages site is currently abandoned but was operational from 1968-1973 and from 1979-1989. The suspected source of PCE, a dense non-aqueous phase liquid (DNAPL), was a floor drain at the site [*Levine-Fricke Recon (LFR)*, 1997; *Sillan*, 1999; *Jawitz et al*., 2000]. The high specific gravity of PCE caused it to flow downward by gravity drainage, through the highly sandy media. The subsurface region containing PCE was subject to groundwater flow, generating a dissolved contaminant plume flowing downgradient. The area containing free phase PCE is referred to as the source zone, consisting of PCE pools collecting on lenses of finer grained materials and residual PCE entrapped by the capillary forces in the subsurface media. The source zone was approximately 7.3 m long by 2.7 m wide and existed from 7.9 to 9.6 m below the ground surface (bgs) [*LFR*, 1997; *Sillan*, 1999; *Jawitz et al*., 2000]. Although hydraulic conductivity estimates are high in the mostly sandy media, the hydraulic gradient is very small such that local groundwater velocity is very slow. The low solubility of PCE combined with the low groundwater velocity would generate a contaminated groundwater plume for decades or centuries if depletion of entrapped and pooled DNAPL was strictly by natural gradient dissolution [*Kueper et al*., 1993; *Lemke et al*., 2004].

In 1998, the Florida Department of Environmental Protection (FDEP), Levine Fricke, Inc. (LFR), and the University of Florida conducted a pilot-scale ethanol flushing test to evaluate the enhanced removal of PCE at Sages field site. A mixture of 95% food grade ethanol and 5% water was injected into the subsurface and recovered through a hydraulically controlled remedial

flow field. The project also served as a pilot test of solvent extraction residual biotreatment (SERB) technology [*Mravik et al*., 2003; *Sewell et al*., 2006].

Recently, scientists and engineers have defined a need for data and analyses of DNAPL source zone depletion technologies and the resultant changes in site mass flux and mass discharge [*USEPA*, 2003; *Stroo et al*., 2003; *NRC*, 2005]. The research presented in this thesis evaluates the multilevel well samples taken during the pilot remediation and the six-year period after the flushing until 2004. The primary goals of this work are to define the DNAPL architecture in the source zone before and after the flushing test, to assess the remedial performance in terms of NAPL removal and flux reduction, and to evaluate the groundwater plume response in terms of the mass discharge changes over time after the remedial test.

1.3 Multilevel Sampling

The use of multi-level sampling (MLS) wells for groundwater study delivers a vertical resolution of the subsurface fluids that traditional wells dilute or integrate over their screened interval. Bundled MLS piezometers consists of a cluster of small stainless or Teflon tubes inserted into the ground at designed intervals to pump small groundwater samples at each respective depth [*Pickens et al*., 1978; *Lerner and Teutsch*, 1995]. There is a sand filter on the in-ground end of each tube to prevent clogging. MLS wells have been used at contaminated sites for various groundwater monitoring purposes including natural dissolution, plume development, and remedial assessment [*Lerner and Teutsch*, 1995; *Sillan et al*., 1997; *Broholm et al*., 1999; *Jawitz et al*., 2000; *Rivett et al*., 2001; *Gauilbeault et al*., 2005; *Rivett and Feenstra*, 2005; *Zhang et al*., 2006]. Additionally, MLS have been employed to elucidate the spatial distribution of NAPL from partitioning tracer tests at several field sites [*Rao et al*., 2000].

At the Sages site, bundled MLS wells were employed to add a vertical component to remediation and monitoring studies for three dimensional analyses. A month prior to the August 1998 ethanol flood, MLS 1-7 were installed in the source zone, each coupled to a respective RW. During sampling, each MLS well tube was pumped and purged to 40 mL before the sample was collected. The samples were analyzed by gas chromotagraphy for alcohol tracers, ethanol, and volatile organic chemicals (VOCs). The map below in Figure 1-1, displays the locations of the MLS wells at the Sages site in Florida State Plane Coordinate System units.

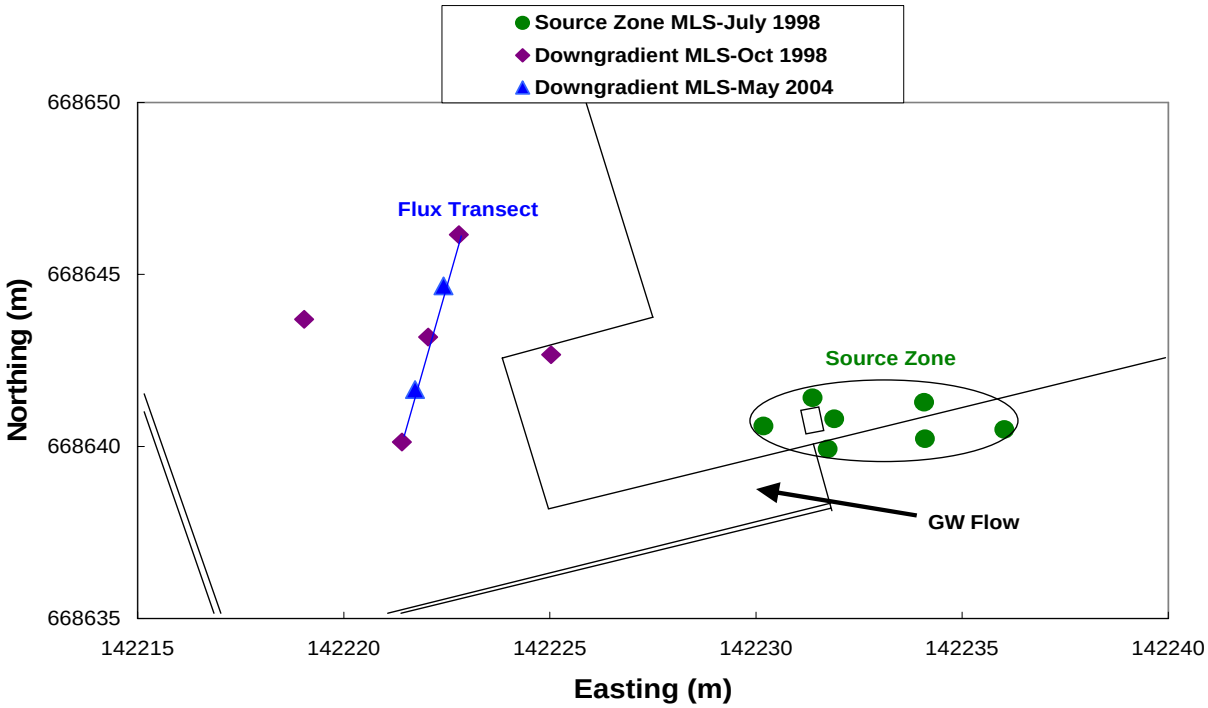

Figure 1-1. Map view of Sages site multilevel sampling wells (units are Florida State Plane Coordinate System). The gray area is the suspected source zone.

For the tracer tests and the ethanol flood, only the seven source zone multilevel wells (MLS 1-7) were in place to collect samples. After the flushing test, five additional multilevel wells (MLS 8-12) were installed downgradient of the source area to monitor the contaminant

plume, including a transect of wells perpendicular to the natural gradient flow (MLS 9-11). Finally in 2004, two additional MLS wells (13 & 14) were installed in the downgradient transect, between the central and outer wells.

1.4 The DNAPL Problem

As a result of many industrial, military, and commercial practices, there are thousands of sites of subsurface contamination by the chemicals used at these places. One of the more challenging problems facing environmental engineers and scientist today is finding and cleaning up these sites to reduce the risk of contaminated groundwater reaching water supplies. DNAPLs often exist as a separate liquid phase in groundwater. Due to their high specific gravity (>1.2), they flow downward by gravity drainage when spilled or released into soil and groundwater [*McKay and Cherry*, 1989; *Broholm et al*., 1999]. They tend to collect on less permeable layers spreading out until meeting courser media to continue downward flow in fingers rather than a uniform front [*Illangasekare et al*., 1995].

To assess a DNAPL contaminated site, the architecture of the source must be identified [*Sale and McWhorter*, 2001; *Rao et al*., 2002]. This refers to the geometry of the source in terms of shapes, sizes, and interconnections of the spatial distribution and DNAPL content in the subsurface. Generally, a DNAPL site is described as a source zone and a dissolved plume [*Rao et al*., 2002; *NRC*, 2005]. The region of the site with separate phase DNAPL is termed the source zone. This is further separated into the areas of entrapped residual saturation, or ganglia, and pools of accumulated DNAPL on confining units [*McKay and Cherry*, 1989; *Kueper et al*., 1993; *NRC*, 2005]. Pooling can lead to diffusion into the aquitard [*Parker et al*., 2004]. Entrapped residual DNAPL is held in pore spaces by capillary forces or as films coating the media [*Bradford et al*., 2003].

As groundwater flows through a source zone, small amounts of DNAPL are dissolved and carried away in a plume of contaminated water. Advection and dispersion forces tend to dilute and spread this plume as it moves away from the source area. However, the low solubility of most DNAPLs makes them highly persistent and the DNAPL acts as a reservoir for sustaining dissolved plumes. Thus, media heterogeneities, sorption to subsurface media, and diffusion into low permeable layers makes DNAPL source zones highly complex and unique at each site.

Another difficulty of DNAPL cleanup efforts is finding the source of groundwater contamination. Although sufficient technologies exist to delineate a source zone, some sites will require extensive sampling due to the spatial distribution of free phase DNAPL in the subsurface [*EPA*, 2003]. Since deposits can be highly localized, multiple methods should be used to locate the source of dissolved contamination. Therefore, it is important to perform accurate, detailed site characterization including hydrogeology, source delineation, and biogeochemistry to best assess site risk and to develop to the proper treatment regimen for the specific site [*NRC*, 2005].

Unfortunately, due to their low solubility and recalcitrance many of the sites contaminated with these compounds will persist for decades or centuries. Although conventional pump-and-treat measures can contain the dissolved plume and slightly enhance DNAPL dissolution, there would be great cost to implement and maintain this type of treatment for the long timescales required [*McKay and Cherry*, 1989; *NRC*, 2005]. Thus, innovative methods to remove DNAPLs have been devised and tested over the past two decades, including enhancements of aqueous solubility, mobility, volatility, and biodegradation. Many of these new technologies are highly successful at removing DNAPL mass from the subsurface. However, due to the complex entrapment architecture of field sites, complete removal of free phase and residual DNAPL has been thus far not possible [*Soga et al*., 2004]. Consequently, remediation at

very few sites has been unable to remove sufficient mass to restore the entire site to drinking water standards [*NRC*, 2005]. Although most DNAPL sites currently have pump-and-treat systems in place to contain contaminant plumes, only a small fraction of sites have attempted aggressive source remediation [*NRC*, 2005].

1.5 Natural Dissolution of DNAPLs

Understanding the dissolution of nonpolar compounds in groundwater is vital to predict the persistence of a DNAPL source zone. The saturated equilibrium concentration (C_{iw}^{sat}) of chemical (i) in water is related to its activity coefficient (γ_{iw}^{sat}) by Eq.1-1 [*Schwarzenbach et al*., 2002].

$$C_{iw}^{sat} = \frac{1}{\overline{V}_w \cdot \gamma_{iw}^{sat}} \tag{1-1}$$

The chemical solubility is inversely proportional to the product of the activity coefficient of the chemical of interest and the molar volume of water ($\overline{V}_w$) which is constant. Most of the nonpolar organic compounds like PCE have high activity coefficients and so they are highly insoluble [*MacKay et al*., 1991].

Natural gradient dissolution of PCE and other DNAPLs has been studied extensively over the past 3 decades. Many laboratory physical models and computer models have attempted to describe DNAPL dissolution [*MacKay et al*., 1985; *MacKay et al*., 1991; *Unger et al*., 1998; *Sahloul et al*., 2002; *Bradford et al*., 2003; *Parker and Park*, 2004]. However, field conditions are considerably more heterogeneous than lab or model conditions, making the process extremely complex.

Researchers at the University of Waterloo have conducted recent field studies of controlled releases of multicomponent DNAPLs into the Borden aquifer to better understand

deposition morphology and dissolution behavior in natural media [*Broholm et al*., 1999; *Frind et al*., 1999; *Rivett et al*., 2001; *Broholm et al*., 2005; *Rivett and Feenstra*, 2005]. Rivett and Feenstra [2005] monitored the dissolution and plume development of an emplaced multicomponent DNAPL source in a natural sandy aquifer. Both source mass and source strength were monitored over a three year period by soil coring and a downgradient multilevel sampling well transect. Dissolution fingering and groundwater flow bypass resulted in 77% of the source mass remaining after 3 years and they predicted source longevity of 25 years. Pooling and entrapment in low permeable media fostered lower hydraulic conductivity zones, leading to groundwater flow bypassing. The study predicted that as pores are cleaned out by dissolution, additional bypassing will follow these new DNAPL free paths [*Rivett and Feenstra*, 2005].

This process is called aging. Over time, many groundwater flow paths are cleaned out by dissolution. The flow paths still containing higher residual or pooled DNAPL will divert groundwater flow around these zones, making them diffusion limited [*NRC*, 2005]. The aging process may reduce plume concentration but may also increase source longevity since groundwater preferentially flows through cleaner, higher conductivity paths. As Sages began operation as a drycleaning facility in 1968, the single component PCE spills may have occurred many years ago. The low groundwater velocity has limited the natural dissolution of subsurface PCE. However, many flow paths may have been cleaned out by dissolution over time, making Sages an aged DNAPL site.

Because PCE is very slowly solubilized by groundwater flow, scientists and engineers have been researching means to enhance the dissolution process. One of these methods is in situ alcohol flushing.

1.6 Cosolvency and Alcohol Flushing

It has been demonstrated that adding a cosolvent to an oil-water system will increase the aqueous solubility of the oil [*Nkedi-Kizza et al*., 1987; *Banerjee and Yalkowsky*, 1988]. An alcohol will decrease the polarity of the water, allowing the nonpolar organic compound to dissolve more readily [*Augustijn et al*., 1997]. The relationship of the cosolvent in the aqueous phase to the solubility of the hydrophobic compound was described by Rao et al. [1990].

$$\log S_{imix} = \log S_{iw} + \beta_i \cdot \sigma_i \cdot f_c \qquad (1\text{-}2)$$

The log of the solubility of component *i* in the cosolvent-water mixture (S_{imix}) is equal to the sum of the log of the aqueous solubility of *i* (S_{iw}) and the product of the water-cosolvent interaction (β_i), the cosolvency power of the solvent for *i* (σ_i), and the volume fraction of cosolvent (f_c). For most completely miscible organic solvents (CMOS), β = 1.0.

The cosolvency power (σ_i) is defined by Eq.1-3, where S_{ic} is the solubility of *i* in pure cosolvent [*Rao et al*., 1990].

$$\sigma_i = \log\left(\frac{S_{ic}}{S_{iw}}\right) \qquad (1\text{-}3)$$

This is the most important parameter in cosolvency theory. There is a well validated linear relationship between the interfacial free energy of the cosolvent and the molecular surface area of the hydrophobic organic compound [*Banerjee and Yalkowsky*, 1988]. Thus, the solubility of solute *i* increases with decreasing solvent polarity.

Due to costs and duration for conventional pump-and-treat systems for plume control at DNAPL sites, enhanced dissolution techniques are desirable. One of these methods is cosolvent flushing, in particular using alcohols as the solubility enhancement agent. This has been called a variety of terms like cosolvent flooding, enhanced pump-and-treatment, enhanced dissolution,

but for this paper it will be referred to as in-situ alcohol flushing or ethanol flooding. Alcohol flushing has been demonstrated to be an effective method for enhancing the removal of DNAPLs from sand in laboratory tests and from the subsurface in sandy aquifers [*Augustijn et al*., 1994; *Imhoff et al*., 1995; *Augustijn et al*., 1997; *Rao et al*., 1997; *Sillan et al*., 1998; *Jawitz at al*., 2000; *Falta et al*., 2000; *Brooks et al*., 2003].

There is always a risk of mobilization when using alcohols as the cosolvent for in-situ flushing [*Lunn and Kueper*, 1999; *Padgett and Hayden*, 1999]. Ethanol was chosen by LFR [1998] from ternary phase diagrams because it exponentially increases PCE solubility but provides a lower risk of PCE mobilization [*Falta*, 1998]. Shorter chain alcohols tend not to lower the interfacial tension (IFT) associated with entrapped DNAPL, reducing the binding capillary forces. Thus, the risk of IFT reduction and downward mobilization of DNAPL during flushing is reduced when employing ethanol as the solubilization enhancing agent [*Lunn and Kueper*, 1999].

1.7 Site Characterization

The hydrogeology of the Sages site was characterized by soil cores, pumping tests, water table levels, and an electromagnetic borehole flowmeter test. The results will be summarized here but extensive studies at the site have been performed and published [*LFR*, 1997, 1998a, 1998b; *Sillan*, 1999; *Jawitz et al*., 2000; *Mravik et al*., 2003]. The water table is approximately 3 m bgs, and the natural hydraulic gradient is 0.0025. The media was characterized to be fine to very fine sand down to 9 m bgs. In the lower zone, from 9 m to 10.7 m, very fine to silty sand was observed down to the discontinuous clay layer at 10.7 m bgs. Hydraulic conductivities were estimated at 6 m/day in the upper region and 3 m/day in the lower. Combined with the low

hydraulic gradient, groundwater velocity is very slow, from 0.0075 to 0.015 m/day (see Eq. 1-12).

The standard methods for source zone characterization include soil coring, direct push methods, geophysical methods, downhole methods, and tracer tests [*NRC,* 2005]. An effective method of estimating the mass of DNAPLs in a source zone is the partitioning interwell tracer test (PITT) [*Jin et al.,* 1995*; Annable at al.,* 1998]. At the Sages site, the PCE source zone was characterized through soil coring, cone penetrometer tests, and partitioning interwell tracer tests.

In the site evaluation process, it was deemed that Sages was not a good candidate for natural attenuation of chlorinated solvents [*LFR*, 1997]. Based on the criteria put forth by Weidemeier et al. [1996], the biodegradation potential of the groundwater at Sages was considered inadequate for natural attenuation. The LFR survey concluded that reductive dechlorination was not favored by aerobic conditions, low levels of dechlorination daughter products, and lack of sulfate reduction and methane production [*Sewell et al*., 2006]. Thus, a coupled site restoration method was developed to aggressively remove source PCE mass, while facilitating subsurface microbial processes. The US EPA continued to monitor the site following the 1998 ethanol flood for three years at monitoring wells throughout the site. Its assessment is available in Mravik et al. [2003], and Sewell et al. [2006].

1.8 Partitioning Tracer Tests

The development and implementation of a subsurface chromatographic means to determine DNAPL mass and volume is highly advantageous. The partitioning interwell tracer test (PITT) method is well established and described in both laboratory tests [*Jin et al.,* 1995; *Cho and Annable*, 2005] and field tests [*Annable et al*., 1998; *Jawitz et al*., 1998; *Dwarakanath et al*., 1999; *Setarge et al*., 1999, *Rao et al*., 2000; *Brooks et al*., 2002]. Around or across a

suspected source zone, a hydraulic flow field is established using injection wells (IWs) and recovery wells (RWs) [*Annable et al*., 1998]. A suite of alcohol tracers, including a non-partitioning tracer and a number of partitioning tracers, is injected and recovered [*Jin et al*., 1995]. As the tracers flow through the swept volume, the partitioning tracers are delayed or retarded versus the non-partitioning tracer arrival at the RWs. The breakthrough curves are analyzed by the method of moments to yield the mean arrival time of each tracer. From the difference in the mean arrival times of the partitioning and conservative tracers, the saturation of NAPL can be estimated for the region interrogated by the tracers [*Jin et al*., 1995; *Annable et al*., 1998]. Assumptions made for a PITT include: (1) the NAPL is essentially insoluble and is the only sorbent of partitioning tracers; (2) NAPL is present in low saturations such that it has a negligible effect on non-partitioning tracers; (3) equilibrium, linear, reversible partitioning occurs; and (4) dispersion is negligible over the short time frame of the tracer test [*Jin et al.,* 1995; *Annable et al*., 1998; *Enfield et al*., 2005].

The ratio of the concentration of the partitioning tracer in the NAPL phase (C_p) to the concentration of the tracer in the aqueous phase (C_w) is the NAPL – water partition coefficient (K_{Nw}).

$$K_{Nw} = \frac{C_p}{C_w} \tag{1-4}$$

The retardation factor (R) is the ratio of the mean arrival times of the partitioning tracer (τ_p) to the non-partitioning tracer (τ_n).

$$R = \frac{\tau_p}{\tau_n} \tag{1-5}$$

The selection of the tracers is based on each being nontoxic, nondegrading, having low volatility, and being easily quantifiable [*Annable et al*., 1998]. The K_{Nw} values determine the amount of

time the partitioning tracer will spend in the subsurface. Tracers should be chosen to provide adequate retardation, but not so that the test is unreasonably long. The recommended retardation factor is between 1.2 and 4 [*Jin et al*., 1995].

The mean arrival times are calculated from the method of moments [*Jin et al*., 1995; *Annable et al*., 1998; *Jawitz et al*., 2003; *Jawitz*, 2004]. The injection pulse is maintained at constant concentration, and the MLS or RWs are sampled frequently. The resultant break through curves (BTCs) are then be plotted and analyzed by the method of moments. The *N*th absolute moment (M_N) of a distribution is described by:

$$M_N = \int_0^\infty t_N C(t) dt \tag{1-6}$$

The first normalized moment (μ_1) is determined by dividing M_1 by M_o.

$$\mu_1 = \frac{\int_0^\infty tC(t)dt}{\int_0^\infty C(t)dt} \tag{1-7}$$

One half of the tracer pulse duration (t_o) is subtracted from the first normalized moment to get the *i*th tracer mean arrival time, τ_i.

$$\tau_i = \mu_1 - \frac{t_0}{2} \tag{1-8}$$

The average NAPL saturation (S_N) in the swept volume is then calculated from the difference in the mean arrival times of the non-partitioning and partitioning tracers.

$$S_N = \frac{\left(t_p - t_n\right)}{\left[t_p - t_n\left(K_{Nw} - 1\right)\right]} \tag{1-9}$$

The effective pore volume (V_e) for each RW is determined from the mean arrival time of the non-partitioning tracer and the RW extraction rate, Q_i.

$$V_e = Q_i t_n \tag{1-10}$$

The NAPL saturation and the effective pore volume are used to calculate the volume of NAPL (V_N) in the area swept by the tracers.

$$V_N = \frac{S_N V_e}{1 - S_N} \tag{1-11}$$

Summing up the NAPL volumes from the RWs will determine the total volume of NAPL in the region swept by all the tracers. For the field test, RW pre and post-remedial PCE saturations were determined using this method [*Sillan*, 1999; *Jawitz et al*., 2000]. However, since MLS tubes are not continuously pumped, the effective pore volume cannot be exactly determined, thus volume of the NAPL for the tracer swept zone for the MLS was not determined in this work.

The site hydrogeology and DNAPL architecture can cause errors in PITT estimation of DNAPL content. Media heterogeneity and the resultant non-uniform DNAPL distribution are expected at field sites. This results in hydraulic constraints in tracers accessing DNAPL which causes underestimation of free phase DNAPL saturation [*Rao et al*., 2000]. These limitations can be overcome by sufficient tracer injection volume and adequate test time to fully record tracer tailing [*Meinardus et al*., 2002]

The administration of a post-remedial PITT allows the determination of the amount and location of DNAPL remaining [*Jin et al*., 1995] and thus when compared to the pre-PITT, and assessment of remedial performance [*Jin et al*., 1995; *Annable et al*., 1998]. At Sages, the pre and post-remedial PITTs allowed the evaluation of ethanol flushing for aggressive source removal [*Sillan*, 1999; *Jawitz et al*., 2000]. However, the comparison of source depletion and subsequent concentration response was not previously published. The results of pre and post flushing PCE saturations for both RW and MLS wells affords the calculation of NAPL reduction. This can be compared to aqueous concentration changes, another metric for remedial

performance. From the results of NAPL removal and concentration changes, the site can be compared to other alcohol flushing remedial actions.

1.9 Bioremediation

At sites with the required conditions, monitored natural attenuation of DNAPLs may be an alternative to other remediation methods [*USEPA*, 1999]. However, when these requirements are not met, other means of controlling, removing, or destroying the source may be appropriate. Although enhanced volatilization, solubilization, and mobilization are methods of removal, bioremediation is the destruction of DNAPL by microbes in the subsurface [*NRC*, 2005]. In-situ bioremediation (ISB) of DNAPL source zones refers to the stimulation or augmentation of biological processes to accelerate contaminant mass removal or to control downgradient plume migration [*ITRC*, 2005]. This can be achieved by biostimulation, providing the conditions to promote colonization of indigenous reductive dechlorinating bacteria, or by bioaugmentation, the introduction of microbes capable of destroying chlorinated solvents [*ITRC*, 2005]. Although several recent studies have demonstrated the ability of biological species to survive in the high concentration of source zones, combined source removal and residual treatment is recommended for PCE saturated source zones [*Yang and McCarty*, 2000, 2002; *NRC*, 2005]. The long term monitoring of ISB sites is called enhanced monitored natural attenuation [*ITRC*, 2005].

Proper choice of remediation technology can facilitate the depletion of significant source mass and it can also enhance the sites natural ability to attenuate the residual contamination [*Rao et al*., 2002; *NRC*, 2005]. Dissolution is limited at sites with very low groundwater velocities because the aqueous phase reaches equilibrium with the NAPL phase, hindering further dissolution [*Chu et al*., 2004]. It has been demonstrated that DNAPL biodegradation can also enhance dissolution of chlorinated solvents [*Cope and Hughes*, 2001; *Yang and McCarty*, 2000,

2002]. Biological enhancement of PCE solubility occurs by biological transformation of dissolved PCE to its more soluble daughter products, TCE and DCE. At the NAPL water boundary, this allows additional PCE mass transfer to the aqueous phase [*Carr et al*., 2000]. This has the advantage of decreasing source zone longevity [*Yang and McCarty*, 2000]. Increased dissolution creates greater aqueous phase DNAPL, thus greater accessibility for microbial use [*Carr et al*., 2000].

1.10 Solvent Extraction Residual Biotreatment

During standard bioremediation methods, the biostimulation or bioaumentation agents are delivered to the source or plume to provide the necessary requirements for biodegradation. Mixing and contact with DNAPL are the limiting processes. Source zone depletion only occurs at the DNAPL-water interface, so the agents must be delivered to this region if this is the goal. One of the distinct advantages of the solvent extraction residual biotreatment (SERB) technology is that the mixing and contact of biotreatment agents with contaminants is achieved directly during the flushing event [*Mravik et al*., 2003]. The limitation of all flushing technologies is that the remedial fluids primarily flow through zones of higher hydraulic conductivity. Thus, even in the SERB method, there will be lack of contact in lower permeable zones where DNAPL tends to accumulate [*Sewell et a*l., 2006]. The mixed areas will stimulate bioremediation as the flushing agent can act as the electron donor and the DNAPL can act as the electron acceptor. If electron donors, electron acceptors and dechlorinating microbes are present, the environment may be suitable for reductive dechlorination to occur [*Sewell et al*., 2006].

As a result of this pilot alcohol flushing test, some ethanol was not able to be recovered at the RWs. This residual ethanol serves as an electron donor and PCE will be the electron acceptor. Of the 34 kL of ethanol injected into the source zone, 92% was recovered leaving a

residual ethanol of 2.72 kL in the subsurface [*Mravik et al*., 2003]. The post flushing groundwater samples indicate increasing byproducts of reductive dehalogenation of PCE over time, demonstrating enhanced natural attenuation of residual PCE [*Mravik et al*., 2003; *Sewell et al*., 2006].

1.11 Mass Flux and Mass Discharge

Although quantifying the source mass or volume is important in determining the size of the source and the best method for remediation, the amount of mass leaving the source in dissolved form may be more important [*Feenstra et al*., 1996]. The risk to a downgradient well has less to do with the mass of the source and more to do with the hydrogeologic conditions at the site. A site with little or no groundwater flow maybe of little risk to receptors downgradient, however an area with high flow through a contaminated site, may create an extensive plume of dissolved contaminants stretching for miles [*Einarson and McKay*, 2001].

The assessment of contaminant source strength is completed by calculating the mass leaving the source area in dissolved form [*EPA*, 2003]. The groundwater flux (q_i) is also called the Darcy flux, and is a measure of the flow per unit area of a region. It is calculated from the product of the saturated hydraulic conductivity (K_s) and the hydraulic gradient (j) [*USEPA*, 2003; *Basu et al*., 2006].

$$q_i = -K_s j \tag{1-12}$$

The hydraulic gradient is the change in head (dh) per change in distance (dl). By measuring or estimating the groundwater flux, the contaminant flux can be calculated when combined with the concentration in the respective groundwater samples The contaminant mass flux (J_i) is the product of the water flux and concentration of the contaminant in that water $\left[M / L^2 T \right]$ [*USEPA*, 2003; *Falta et al*., 2005; *Guilbeault et al*., 2005; *Basu et al*., 2006;].

$$J_i = q_i C_i \qquad (1\text{-}13)$$

Both the water flux and mass flux require a cross sectional area (i), or control plane. This is best illustrated in Figure 1-2.

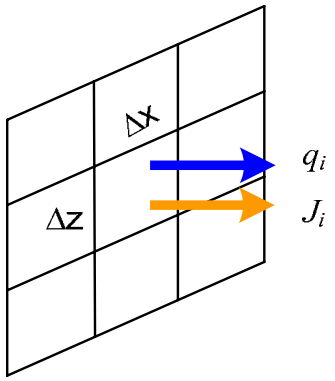

Figure 1-2. Water flux (q_i) and contaminant flux (J_i) across a control plane. ΔX and ΔZ are the cross sectional distances and the cross sectional area A_i is the product of these two lengths.

In the field, there have been a number of new technologies developed recently for assessing in-situ mass flux. One of these is the University of Florida passive flux meter (PFM) [*Hatfield et al.,* 2004; *Annable et al*., 2005; *Basu et al.,* 2006]. This downhole device allows the simultaneous measurement of groundwater flux and contaminant flux across a control plane of wells. Another new method for flux measurement is the integral groundwater investigation method (IGIM) or integral pump test [*Bockelmann et al*, 2001; *Bockelmann et al*, 2003; *Bauer et al*., 2004; *Jarso et al*., 2005]. A modification of this method has been utilized by Guilbeault et al. [2005] at several sites to simultaneously pump a control plane of wells continuously, capturing the entire contaminant plume, and affording an estimation of mass flux.

Finally, we can determine the mass discharge for the source area, a full measure of the source zone strength. This is the mass leaving the source area per unit time. The product of the total cross sectional area with the contaminant mass flux (J_i) is the mass discharge (M_d) [*USEPA*, 2003].

$$M_d = \sum J_i A_i = \int_A J_i dA \qquad (1\text{-}14)$$

This can be also thought of as the spatial integration of contaminant flux across the control plane [*Basu et al*., 2006]. The units of contaminant mass discharge are mass per time [M/T].

Stroo et al. [2003] identified the need for field data of mass discharge at sites undergoing source removal. Estimates of the mass discharge across the source zone and downgradient transects will be evaluated over a six-year period following the 1998 ethanol flood and presented in Chapter 3 of this thesis.

1.12 Benefits of DNAPL Source Depletion

Mass flux may be more important than the actual mass in the source zone [*Rao et al*., 2002; *USEPA*, 2003; *NRC*, 2005]. Through a contaminant source region of very slow groundwater velocity, the mass flux maybe very small due to the low Darcy flux. However, a small mass of residual PCE can produce a long plume of contaminated groundwater in a region of high groundwater velocity. Large reductions in mass discharge from remedial efforts should produce significant decreases in concentrations reaching downgradient receptors, and decrease site longevity [*Rao et al*., 2002]. In the past decade several alcohol flushing field tests have demonstrated the ability to reduce a field source zone DNAPL mass [*Rao et al*., 1997*; Jawitz et al*., 1998; *Sillan*, 1999; *Jawitz et al*., 2000*; Falta et al*., 1999*; Brooks et al*., 2003]. Although aggressive source removal rarely will achieve total site groundwater concentrations below maximum contaminant limits (MCLs), contaminant flux reductions have been demonstrated. This has spawned considerable debate on the benefits of source depletion [*Sale and McWhorter*, 2001; *Rao et al*., 2002; *Rao and Jawitz*, 2003]. Due to a shift in consideration to the downgradient receptors of a contaminant source's plume, risk based corrective action (RBCA)

was developed to provide the framework for assessing downgradient risks to people and the environment [*ASTM*, 2002].

Recently several researchers have altered focus to the RBCA framework, studying the effects of DNAPL source depletion on contaminant mass flux [*Lemke et al*., 2004; *Annable et al.,* 2005; *Guilbeault et al*., 2005; *Jawitz et al.,* 2005; *Wood et al*., 2005; *Fure et al.,* 2006*; Newman et al.,* 2006]. Because traditional plume control methods tend to be costly due to the high insolubility of DNAPLs, leading to long term maintenance and operation expenses [*MacKay and Cherry*, 1989; *Mayer et al.*, 2002], aggressive source zone depletion measures are attractive. While active remediation rarely achieves source zone clean up to regulatory limits, the benefits of reduction in source mass have been predicted in models through decreases in mass flux, source longevity, and associated maintenance costs [*Rao et al*., 2002; *Falta et al*., 2005; *Jawitz et al*., 2005]. In 2-D heterogeneous physical models, aqueous dissolution experiments determined that NAPL architecture was the primary control of the mass depletion, flux response relationship [*Fure et al*., 2006]. Although simple uniform flow field models have predicted that most of the mass needs to be removed to result in significant flux reduction, field sites are not this simple [*Sale and McWhorter*, 2001]. Even small natural heterogeneities in media result in much greater heterogeneity in the groundwater velocity field [*Kueper et al*., 1993]. Further Lagrangian steamtube modeling has demonstrated that as heterogeneity of aquifer properties and the subsequent NAPL heterogenous architecture increase, more favorable flux responses will follow source zone depletion [*Jawitz et al*., 2005]. This type of situation better represents field conditions.

The relationship of mass reduction to flux reduction has been modeled by many researchers recently [*Rao et al*., 2001; *Rao and Jawitz*, 2003; *Parker and Park*, 2004; *Jawitz et al.*, 2005; *Falta et al*., 2005a,b; *Enfield et al*., 2005; *Wood et al*., 2005; *Basu et al.,* 2006]. A modified version of this is described in Eq. 1-15, where fractional mass reduction (1-M/M_0) is plotted against fractional flux reduction (1-C/C_0).

$$\left(1-\frac{C}{C_0}\right)=\left[1-\frac{M}{M_0}\right]^{1/\beta} \tag{1-15}$$

Figure 1-3 presents the relationship described in Eq 1-15.

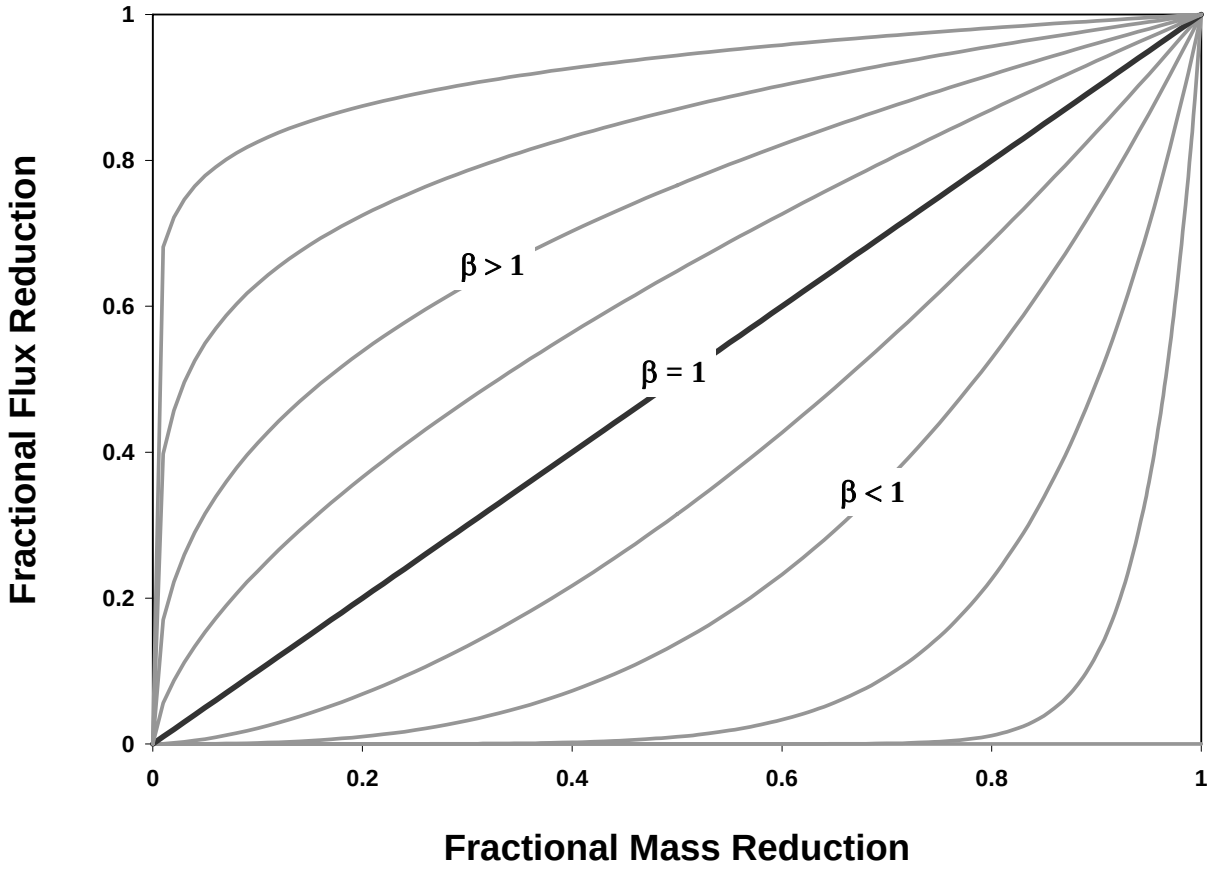

Figure 1-3. Flux reduction to mass reduction relationship. The black line down the middle (β = 1) represents a situation where equal amount of flux reduction is produced from a mass reduction. The lines to the right (β < 1) indicate the conditions where larger amounts of mass must be removed to realize reductions in flux. In the left region (β > 1) smaller mass reductions produce greater flux reduction.

In this figure, conditions where very large mass reductions are required to create significant flux reductions ($\beta << 1$) are considered unfavorable for remediation [*Sale and McWhorter*, 2001]. However, this type of condition has not been demonstrated in alcohol flushing field tests [*Rao et al.,* 1997*; Falta et al,* 1999*; Brooks et al.,* 2004]. Although the initial field tests were performed in highly sandy aquifers, sufficient homogeneity of media has not been found to create such an unfavorable situation.

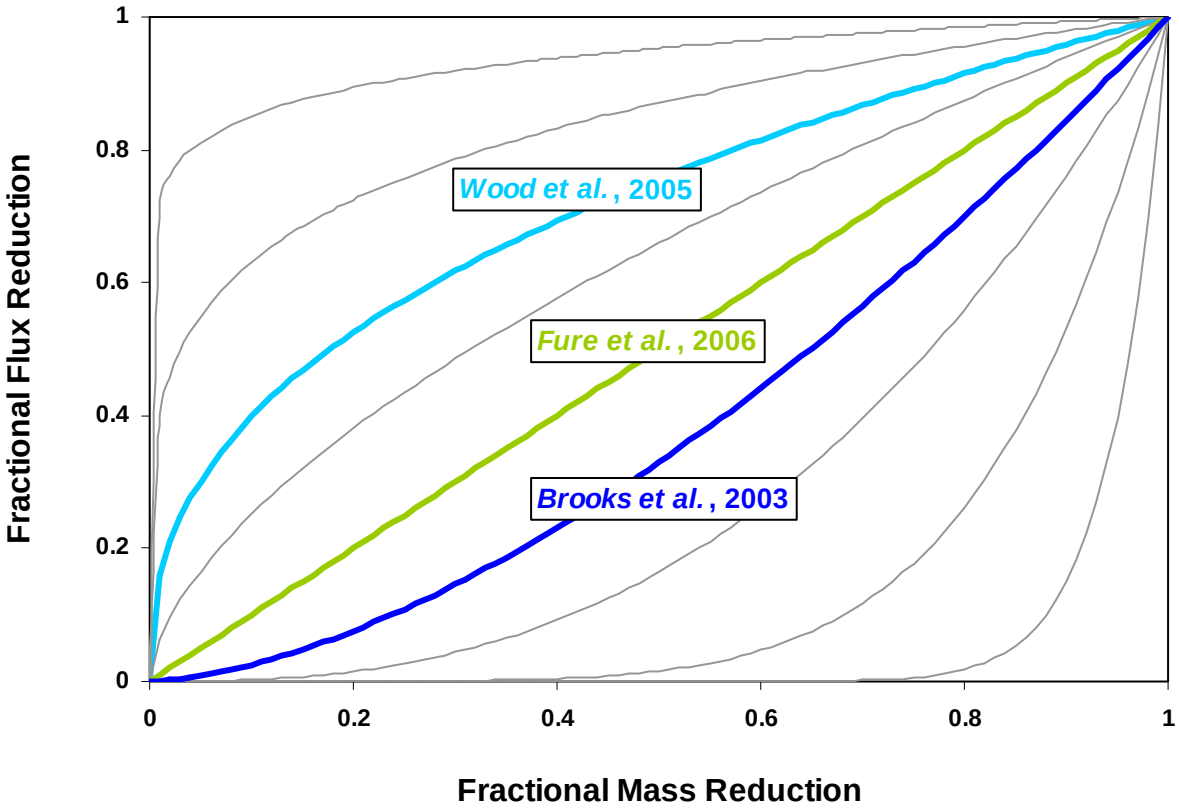

Figure 1-4. Approximate alcohol flushing test results of source zone depletion and subsequent flux reduction [*Brooks et al.*, 2004; *Wood et al*., 2005; *Fure et al*., 2006].

More often, both laboratory and field tests of alcohol flushing has produced relationships from $\beta = 0.5$ to $\beta = 2.5$ as in Figure 1-4. Recent laboratory experiments with 2-D box physical models have confirmed that media heterogeneity leads to near 1:1 mass reduction to flux

reduction relationship ($\beta = 1$) for DCA and TCE [*Fure et al*., 2006]. In a controlled release of PCE at Dover AFB, Brooks et al. [2004] reported favorable mass reduction to flux reduction ratios for the extraction wells after an ethanol flushing field test. Another field test at Hill AFB OU1, in a field test inside a sheet pile test cell, alcohol flushing was performed and the results yielded even more favorable flux response to source removal ($\beta > 1$)[*Wood et al*., 2005].

These results forecast that in-situ alcohol flushing can be successful in both source zone depletion and decreasing contaminant flux. The relationship described above was applied to the ethanol flood results for both RW and MLS wells and will be reported later in this paper.

After thorough site characterization, an understanding of DNAPL dissolution, cosolvency, bioremediation, mass discharge, and the benefits of source depletion, this work can now transition to the analysis of the 1998 ethanol flushing and its long term effects on the Sages site.

CHAPTER 2
REMEDIAL FLOW FIELD

2.1 Flow Field Design

From the site characterization, computer modeling and pumping tests, the design of the remedial system was for hydraulic containment of both extracted contaminant and remedial fluids. Around the perimeter of inferred PCE source zone, six recovery wells were installed. In the middle of the source zone, three injection wells were deployed to deliver the PITT and remedial fluids. The injection wells were screened from 7.6 to 9.9 m bgs, while the recovery wells were screened from 7.9 to 9.6 m bgs. The design was to reduce the risk of downward mobilization of PCE by forcing slight upward gradient flow of remedial fluids [*Lunn and Kueper*, 1999; *Sillan*, 1999; *Jawitz et al*., 2000]. Figure 2-1 shows the locations of the wells in and around the PCE source zone.

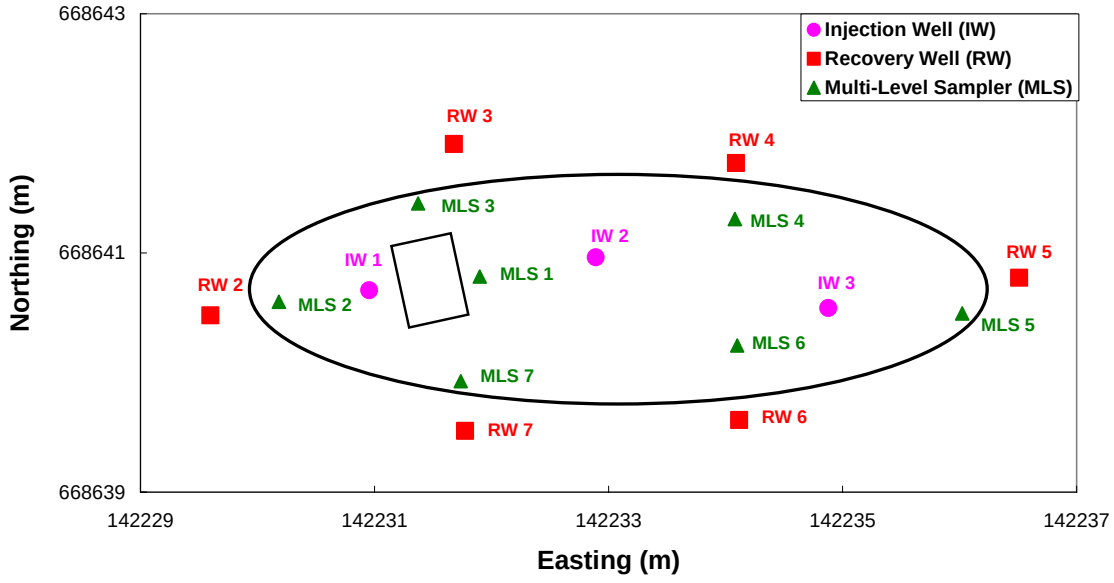

Figure 2-1. Map View of well locations for 1998 remedial flow field (units are Florida State Plane Coordinate System).

To achieve the desired 2:1 extraction to injection rate, the flow rate used for the three injection wells was 5.03 L/min. The central recovery wells (3, 4, 6, 7) were pumped at 5.91 L/min and the outer recovery wells (2, 5) were pumped at 3.4 L/min. This created the induced remedial flow field from the inner injection region of the source zone to the outer recovery wells. These rates were employed for the pre-remedial PITT, the ethanol flood, and the post-remedial PITT.

Referring to Figure 2-2 below, the fluid velocity of each depth at each well was estimated from the distance from the nearest IW to the MLS, and the mean arrival time of the conservative tracer (τ_n) from Eq. 1-12 from the pre-remedial PITT. This delivers an estimation of linear fluid velocity in [L/T] units for each MLS well depth.

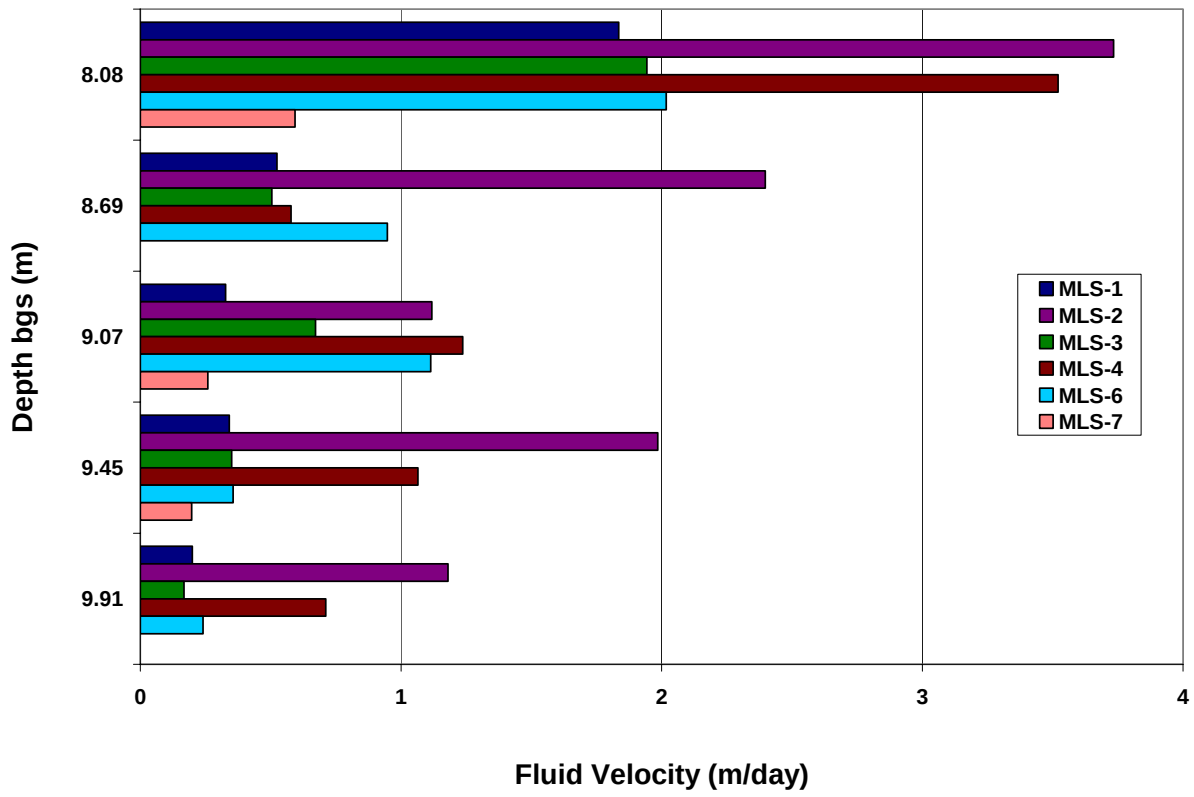

Figure 2-2. Estimated linear fluid velocities of each MLS well at each respective depth during Sages 1998 field test.

The general pattern was that the upper interrogated region (8.08 m bgs) demonstrated higher hydraulic conductivity than the depths below. In the mid-levels there were lower velocities at a depth of 8.69 m bgs in MLS-1, MLS-3, MLS-4, and MLS-6. In every case but MLS-1, fluid velocity increased slightly at the next depth of 9.07 m and then continually decreased to their lowest values at 9.91 m bgs. The low value at MLS-6 at 8.69 m bgs was almost double the value of MLS-1 and MLS-3. This is further evidence of a low permeability layer in the upper middle zone around these wells, which might have caused PCE to collect and spill off to the next finer grained strata. However, at MLS-2 the mid-level lower fluid velocity was observed at 9.07m bgs and the lower depths were slightly higher. At the lowest depth, MLS-6 showed the lowest velocity. This is the region that the highest PCE saturations were observed indicating the presence of finer grained, low permeability media. In all depths of MLS-5 and several depths of MLS-7, sufficient tracers did not arrive at the sampling location to compute mean arrival times, thus an estimated velocity was not determined. MLS-7 displayed the same trend of decreasing fluid velocity with depth.

Previous studies at the Sages site estimated decreasing hydraulic conductivity as depth increased [*Sillan*, 1999; *Jawitz et al*., 2000]. Furthermore, borehole flow meter tests by Mravik et al. [2003] determined hydraulic conductivities of 4 m/d at 8 m bgs, decreasing to less than 1 m/d at 9 m bgs.

2.2 Tracer Selection

The field test included both pre and post-remediation PITTs to identify the NAPL saturation and volume in the suspected source area. In the pre-PITT, methanol (MeOH) was the conservative tracer and n-hexanol (HexOH), 2,4-dimethyl-3-pentanol (DMP), and 2-ethyl-1-hexanol (E-HexOH) were used as the partitioning tracers. In the post ethanol flood PITT,

HexOH was used as the non-partitioning tracer and DMP and E-HexOH were used as partioning tracers. Methanol was not employed as the conservative tracer due to known problems of interference with residual ethanol [*Cho et al*., 2003]. Furthermore, TBA was injected as a conservative tracer, but ethanol analytical interference occurred. Thus, HexOH, with a very low K_{Nw} was used. A summary of the tracer pulse injections, the tracers and their PCE partitioning coefficients is provided in Table 2-1 [*Sillan*, 1999; *Jawitz et al*,. 2000].

Table 2-1. Sages tracers for 1998 PITTs.

Tracer	C_o (mg/L)	K_{Nw}	(t_o) Pulse Duration (hours)
Pre-PITT			
Methanol (MeOH)	2199	0	3.8
n-hexanol (HexOH)	822	5.58	3.8
2,4-dimethyl-3-pentanol (DMP)	436	20.4	3.8
2-ethyl-1-hexanol (E-HexOH)	487	81.23	3.8
Post-PITT			
t-butanol (TBA)	1105	0.17	3.7
n-hexanol (HexOH)	473	5.58	3.7
2,4-dimethyl-3-pentanol (DMP)	354	20.4	3.7
2-ethyl-1-hexanol (E-HexOH)	457	81.23	3.7

2.3 Breakthough Curve Analysis

From the pre and post-flushing PITTs, the S_N was estimated for each MLS well and depth, using the method of moments. For the temporal breakthrough curves (BTCs) where the end of the tail of each tracer did not reach the MLS well, exponential extrapolation was performed to estimate S_N using the method developed by Helms [1997] and utilized by Annable et al. [1998]. This procedure was also employed for all BTCs to reduce fluctuations or noise in the tail regions. Each BTC was then numerically integrated using the trapezoidal rule in the