Development and Application of Analytical Methods to Evaluate DNAPL Remediation Using a Brine Based Remediation Technology

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ABSTRACT

Patrick Sanderson: Development and Application of Analytical Methods to Evaluate DNAPL Remediation Using a Brine Base Remediation Technology
(Under the direction of Cass T. Miller)

With the general inability of existing groundwater remediation techniques to efficiently remove dense non-aqueous phase liquids (DNAPLs) from the subsurface, a novel strategy known as the Brine Barrier Remediation Technique (BBRT) has been proposed as a potential alternative to currently used remedial strategies. However, there are still numerous open issues concerning this new technology including the complexities it introduces into contaminated systems that cause the analytical methods commonly used for system characterization to fail.

New analytical methods were developed that were compatible with BBRT, and capable of quantifying the common groundwater contaminant, perchloroethene (PCE), chlorinated degradation products, and two surfactants, MA-80 and Triton X-100 often employed in remediation techniques. The developed methods were subsequently used to calculate mass balances for PCE and surfactant recovery within a field-scale implementation of the BBRT. Supplemental experiments were conducted to more closely examine the fate of unrecovered surfactants in the field system.

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LIST OF ABBREVIATIONS AND SYMBOLS

4-BFB	4-bromofluorobenzene
BBRT	Brine barrier remediation technique
Bgal/d	Billion gallons per day
^0C	Degrees Celsius
c-1,2-DCE	cis-1,2-dichloroethene
$CaBr_2$	Calcium bromide
$CaCl_2$	Calcium chloride
C/C_0	Effluent concentration to influent concentration ratio
CF	Correction factor
CMC	Critical micelle concentration
cm	Centimeter
cm/s	Centimeters per second
CO_2	Carbon dioxide
C_S	Aqueous surfactant concentration (mg/L)
DI	Deionized
DNAPL	Dense nonaqueous phase liquid
DNTS	Dover National Test Site
ECD	Electron capture detection
EPA	Environmental Protection Agency
FID	Flame ionization detection
f_{OC}	Organic carbon fraction
ft/day	Feet per day

g	gram
GC	Gas chromatography
H_2O_2	Hydrogen peroxide
HLB	Hydrophilic-lipophilic balance
HPLC	High performance liquid chromatography
IFT	Interfacial tension
IPA	Isopropanol
K_d	Soil-water partitioning coefficient
K_F	Freundilich sorption coefficient
kg	Kilogram
K_H	Henry's constant
$KMnO_4$	Potassium permanganate
K_{OW}	Octanol-water partitioning coefficient
$K_{PCE/W}$	PCE-water partitioning coefficient
L	Liters
L*atm/g	Liters times atmospheres per gram
L/kg	Liters per kilogram
LNAPL	Light nonaqueous phase liquid
m	Freundlich coefficient
m	Meter
M	Molarity (moles/Liter)
MA-80	Sodium dihexyl sulfosuccinate
MCL	Maximum contaminant level

MDL	Method detection limit
mg	Milligram
mg/kg	Milligrams per kilogram
mg/L	Milligrams per Liter
mL	Milliliter
mL/hr	Milliliters per hour
mL/min	Milliliters per minute
MLS	Multi-level Sampler
$MnO_2(s)$	Magnesium oxide
NaCl	Sodium chloride
NAPL	Nonaqueous phase liquid
nm	Nanometers
O_3	Ozone
PAH	Polycyclic aromatic hydrocarbon
PAT	Pump and treat
PCE	Perchloroethene
PDA	Photodiode array
PTFE	Polytetrafluoroethylene
PV	Pore volume
q	sorbed surfactant (mg/kg)
QC	Quality control
R^2	Correlation coefficient
R_f	Retardation factor

RPD	Relative percent difference
rpm	Revolutions per minute
SOM	Soil organic matter
SVE	Soil vapor extraction
TBA	tert-butyl alcohol
TCE	Trichloroethene
TCVOC	Total chlorinated volatile organic contaminants
Triton X-100	Polyoxyethylene octylphenol
USGS	United State Geological Survey
UV	Ultraviolet
VC	Vinyl chloride
VOA	Volatile organic analysis
VOC	Volatile organic compound
v/v	Volume per volume
μL	Microliter
μm	Micrometer
ρ	Density (kg/L)
ρ_S	Solid phase density (kg/L)

1. INTRODUCTION

During the past 50 years, groundwater has become an exceedingly important source of drinking water for much of the national population. Presently, groundwater supplies approximately half of the US population with drinking water from domestic and public wells, and an even higher percentage in rural areas (Alley 1999). In 2000, average daily withdrawal rates for drinking water supply were 3.5 Bgal/d from domestic wells, and 16 Bgal/d from public wells, increases of 60% and 100% respectively since 1965 (Hutson 2004). With this dramatic increase in groundwater consumption, several problematic issues have increased in magnitude as well. Issues such as aquifer depletion and saltwater intrusion have become more prevalent due to groundwater consumption trends. Another considerable problem is groundwater contamination stemming primarily from population increases and industrialization. Contamination control is an extremely daunting task due to the broad range of contaminant species that currently exist in natural systems.

There are many important contaminant classifications identified by the United States Geological Survey (USGS). The major classes include pesticides and excess nutrients, primarily used in agricultural practices, trace elements such as arsenic, and volatile organic contaminants (VOCs), which consist of a variety of contaminants including solvents, hydrocarbons, disinfection byproducts, and fumigants (Zogorski 2006). Each class has a variety of sources, and cause direct and indirect human health effects on many levels. However, all classes mentioned similarly lead to a decrease in overall drinking water quality.

The severity of quality depletion depends upon the contaminants present and their respective concentrations within groundwater systems.

The class of VOCs in particular presents a uniquely hazardous problem for a number of reasons. One prevalent characteristic of many VOC species is their ability to exist as a separate phase in groundwater systems due to their low aqueous solubility. These separate phases are defined as Non-Aqueous Phase Liquids, more commonly known as NAPLs. NAPLs can be divided into one of two subcategories: LNAPLs, which include gasoline hydrocarbons, and DNAPLs including polycyclic aromatic hydrocarbons (PAHs) and chlorinated solvents. LNAPLs by definition are less dense than water, which consequently causes them to float on top of the water table and remain in the vadose zone (Fitchett 2004). DNAPLs in contrast have densities lower than that of water, and therefore tend to sink within the saturated zone until they reach a layer of low permeability, forming DNAPL pools, or are trapped as disconnected ganglia by capillary forces. The tendency of DNAPLs to migrate downward prevents the efficient removal of these contaminants from the subsurface.

Historically, tetrachloroethylene or PCE has been utilized for textile finishing, dry cleaning, and as a degreasing solvent (Zogorski 2006). PCE is currently used in 80 percent of commercial dry cleaners in the U.S. (McDaniel 2004). Although industrial use of chlorinated solvents has decreased sharply since the 1970's due to increasing health concerns (Pankow and Cherry 1996), PCE and trichloroethylene (TCE) are still among the VOC species posing the greatest potential concern for groundwater contamination. In 2006, the USGS reported PCE as the second most common VOC behind chloroform found in public and domestic wells in the U.S., and 75 percent of the wells exhibiting VOC concentrations exceeding MCL levels were due to the presence of either PCE or TCE (Zogorski 2006). In addition, TCE and

PCE were found in over 50 percent of the national priority sites for groundwater identified by the U.S. Environmental Protection Agency (EPA) (McDaniel 2004).

Once PCE enters the subsurface, it tends to be very recalcitrant. If it exists as a separate phase, it is extremely difficult to remove. Free-phase PCE exhibits a high interfacial tension with water, thus resisting mobilization from groundwater advection alone. At the same time, if mobilization does occur, the high density of PCE (ρ = 1.62 kg/L) most likely results in downward migration of the NAPL phase into previously uncontaminated areas. Another characteristic contributing to the ability of PCE to remain in the subsurface is its low aqueous solubility, which is commonly reported between 150 mg/L and 240 mg/L (CRC 2006). Solubilities in this range present a two-sided dilemma. First of all, PCE aqueous solubility is orders of magnitude higher than the maximum contaminant level (MCL) of 0.005 mg/L set by the EPA, so groundwater systems containing PCE routinely exceed maximum contaminant levels (Sabatini 2000). On the contrary, because the aqueous solubility is thousands of times less than the density of free-phase PCE, NAPL phase does not solubilize quickly into water, and typical plume life is expected to be on the order of hundreds or thousands of years in the absence of reactions (Heron 2005).

The problems associated with PCE contamination in the subsurface convey the need for remediation techniques in order to reclaim contaminated aquifers as useable groundwater sources. The pump and treat (PAT) strategy was the first method employed as an aquifer remediation technique for NAPL contaminated systems, and until the early 1990's, was the prescribed treatment at approximately two thirds of existing Superfund sites (Travis and Doty 1990). The basic theory behind PAT strategy involves pumping clean water into a contaminated system allowing the NAPL phase to solubilize into the injected water, and then

collecting the contaminated water for treatment. However, this technique has proven to be very inefficient for attaining drinking water standards in a reasonable amount of time.

Several reasons have been suggested as to why PAT methods have functioned so poorly. In addition to the low aqueous solubility of PCE, flowing water may not reach all contaminated areas. Any dissolved or free phase NAPL located in regions of low hydraulic conductivity are frequently inaccessible to advective flow due to the formation of preferential flow paths that bypass regions of low permeability. It is known that the permeability of unsaturated soils can vary by many orders of magnitude over a spatial scale of centimeters or meters, so preferential flow is a common occurrence in groundwater systems (Buettner & Daily 1995). Solvents such as PCE are also capable of extensive sorption to soils in some situations depending primarily upon the organic content of the soil. Furthermore, the process of PCE interphase exchange between either soils or NAPL and the aqueous phase can be rate limited, which slows PCE removal even more (Rabideau 1994). Consequently, in PAT field implementations, the process generally reaches a point where system effluent is nearly constant and well below PCE solubility, but still well above MCL levels. This characteristic of the PAT technique renders it a very inefficient remediation technique. Attempts have been made to improve upon PAT such as intermittent or "pulsed" pumping to allow equilibration between phases and alleviate rate limitations. Still, these enhancements have proven unable to decrease remediation times in systems with high spatial heterogeneity, which are often present in natural systems (Rabideau 1994).

The shortcomings of PAT technology have revealed the need to further develop enhanced remediation techniques in order to effectively remove PCE and other organic contaminants from subsurface systems. Desired techniques should concentrate upon

addressing the issues that cause the PAT method to be inefficient. For example, enhancing the physical characteristics of PCE by increasing aqueous solubility or decreasing the interfacial tension between PCE and the aqueous phase would potentially increase PCE removal from groundwater systems. PCE can also be chemically oxidized or reduced under certain conditions to form harmless end products such as CO_2 or ethylene. Several techniques that have been developed are discussed more thoroughly in the background section.

2. BACKGROUND

This section will provide brief introductions for existing remediation techniques used for PCE removal from the subsurface, including a novel technology known as the Brine Barrier Remediation Technique or BBRT. The work detailed herein revolves around the implementation of BBRT in a confined field setting, and thus the open questions regarding utilization of this remedial technique will be highlighted as well. BBRT issues include the complexity of such a system as well as the analytical obstacles that must be overcome in order to quantify overall contaminant removal in this particular implementation of BBRT.

2.1. Soil Vapor Extraction (SVE)

In the process of SVE, air is circulated through the soil via an applied vacuum (Buettner & Daily 1995), and this technique has proven to be a reliable, safe, and robust physical treatment (Thomson 2000). As air pushes through the system, compounds volatilize into the advective air flow and are removed from the system. In this manner, SVE capitalizes on the high vapor pressures exhibited by volatile species such as chlorinated solvents. Experimental results suggest that mass transfer into the air phase is not a major limitation in SVE due to the fact that pulsed pumping SVE strategies to allow equilibration rarely result in higher removal rates (Farhan 2002). Nevertheless, there are exceptions as mass transfer rates are largely dependent upon the system (Thomson 2000). Another potential benefit of SVE is that it adds oxygen to the system, which can enhance oxidation and aerobic degradation for many VOC species (Heron 2005).

Although SVE has greater removal potential for PCE than water flushing, (Thomson, 2000 describes a study succeeding in 63% PCE removal), removal rates over time often follow a pattern analogous to the PAT strategy previously described. Contaminant removal is close to ideal initially with effluent air concentrations typically on the order of air saturation levels. This is followed by a rapid decline in removal rate, which ultimately exhibits an asymptotic tailing to some residual saturation above MCL limits, which often has a direct relationship to system heterogeneity (Thomson 2000). For this reason, successful SVE implementation has been limited to soil systems with relatively high and uniform hydraulic conductivities between 10^{-2} and 10^{-3} cm/s (Farhan 2002). However, natural systems often contain layers or lenses possessing much lower hydraulic conductivities than this. A further limitation of vapor extraction methods is that they are only operative in the unsaturated zone, meaning the system has to be fully drained in order to reach the entire contaminant zone. This is a problem because even when fully drained, low permeability regions typically have very high water residual saturations, which can severely restrict regions accessible by SVE.

2.2. Thermal Remediation Techniques

Another common alternative to PAT involves heating the contaminated system through addition of hot water, steam, or soil heating using heat blankets, thermal wells, or low frequency electrical heating (Heron 1998), with steam injection and electrical resistance heating being the most commonly employed techniques (McGuire 2006). By increasing the temperature in groundwater systems, several physical forces responsible for NAPL entrapment are lessened, and NAPL removal becomes more efficient. Aqueous solubility, soil desorption, vapor pressure, and diffusion coefficients all increase with elevated temperatures, which all contribute to more efficient NAPL removal (Imhoff 1997, Heron

1998, 2005). Furthermore, elevated temperatures increase mass transfer rates from the NAPL phase due to decreases in interfacial tensions, which results in a larger interfacial area for mass transfer into the aqueous phase to occur (Imhoff 1997). Overall, thermal strategies to date have been very effective for DNAPL removal, showing median reductions of 95% or greater at DNAPL contaminated sites (McGuire 2006).

2.2.1. Hot Water and Steam Injection

Hot water flooding historically has been used in the petroleum industry to improve recoveries of viscous oils by enhancing oil mobility (Imhoff 1996). This remediation technique is typically designed to mobilize NAPL for systems with high free-phase residual saturations (Davis 1993), but can be expected to increase NAPL solubilization rates as well as aqueous solubility. However, it has been reported that over the temperature range of 20 to 80 ^{0}C, the PCE/aqueous interfacial tension decreases by only 7%, which at typical PCE residual saturations should not be sufficient to induce substantial PCE mobilization (Imhoff 1996). Naturally cool groundwater temperatures (Freeze & Cherry 1979, Imhoff 1996) may also inhibit PCE removal from hot water or steam injection in terms of overall cost.

Therefore, the most effective method of PCE removal from hot water flooding is likely through solubilization. Unfortunately, this technique has not demonstrated the ability to dramatically increase aqueous solubility at elevated temperatures either. Stephenson (1992) reports a PCE aqueous solubility of 520 mg/L at 92 ^{0}C. This represents just above a 100% increase from water at 20 ^{0}C, and other chlorinated solvents such as TCE and cis-1,2-dichloroethylene (c-1,2-DCE) increase solubility between 50% and 100% over the same range (Heron 1998). Experimental data has shown the PCE rate of dissolution increases by

about 400% in controlled laboratory experiments (Imhoff 1997), yet this is still not a dramatic improvement over conventional PAT methods.

The use of steam injection is somewhat similar to hot water flushing, but has greater overall enhancement potential. First of all, steam injection can potentially raise the system temperature more than hot water, which will further enhance the physical conditions needed for PCE removal (Heron 2005). In this technique, NAPL contaminants are displaced at the steam front by vaporization due to increased vapor pressures (Schmidt 2002). The vapor pressure increases markedly as steam injection temperature increases, between 10- and 30-fold for most VOC species when the temperature is increased from 20 ^{0}C to 100 ^{0}C (Udell 1996). Also, if temperatures of 100 ^{0}C are exceeded, thermal destruction of contaminants may occur (McGuire 2006). In past studies, steam injection has removed between 85% and 99% of total chlorinated solvents (She and Sleep 1999, Heron 2005).

Nonetheless, there still exist several problems with steam injection. Probably the most severe drawback of steam injection is that it may lead to downward migration of DNAPL pools (Schmidt 2002). As the steam front comes into contact with DNAPL residual, it is volatilized and later condenses at the steam front as the steam cools (Hunt 1988). DNAPL continues to collect and move with the steam front in this manner, and once a sufficient amount of DNAPL has condensed at the steam front, it can potentially migrate vertically due to gravitational forces. Attempts to negate vertical migration such as injecting steam below the contaminated area and injecting a mixture of steam and air have been suggested, but have not been extensively explored at this point (Schmidt 2002). The cost of steam techniques can be a major limitation for large systems as well (Heron 1998).

Although employing hot water or steam as the flushing fluid is preferred over classic PAT methods for increasing mobilization, mass transfer rates, and solubility of DNAPLs, many serious problems persist. Though to varying extents, soil systems with large spatial heterogeneities pose problems for both hot water and steam flushing. In heterogeneous systems, the flushing fluid continues to form preferential flow paths around low conductivity regions, and as a result NAPL located in these regions will remain mostly unaffected from recovery attempts (Buettner and Daily 1995, Heron 1998). This limitation is a major drawback as VOCs will concentrate and remain in low permeability areas due to increased capillary tension and soil adsorption (Buettner and Daily 1995).

2.2.2. Soil Heating

In this remediation scenario, the entire system is heated by electrical or resistance heating. While injection of thermally enhanced air or water only reaches relatively permeable subsurface regions, resistance heating over the entire system may be able to more efficiently affect the entire zone (Buettner and Daily 1995, Heron 1998, Heron 2005). In addition to heating the system more evenly giving way to more uniform contaminant removal, resistance heating has further advantages over heating via injected fluids. Whereas injected fluids such as hot water and steam flow only through high permeability regions, potentially bypassing large contaminant residuals in heterogeneous zones, electric current is more efficiently conducted through low permeability soils because of higher water and clay content contributing to a higher overall charge density (Buettner and Daily 1995, Heron 1998). This results in a pressure gradient theoretically driving contaminant from clays and fines into more permeable regions that can then be accessed by air, steam, or other remedial fluids

(Buettner and Daily 1995). Residual water in the unsaturated zone will evaporate more quickly as well, leading to more NAPL phase exposure to the advecting fluid.

Resistance heating has been successfully employed prior to SVE or steam treatment in past studies, and such studies have demonstrated the ability to remove NAPL contaminants very effectively. Field studies combining resistance heating and SVE or steam treatment frequently exceed 95% removal of DNAPLs (McGuire 2006), and in one instance, an 88% increase in removal was observed when electrical heating was applied to an ongoing SVE study (Heron 2005). This example stresses the potential advantages of adding electrical heating to previously existing remediation techniques. A major concern with soil heating is cost, but this may be offset by decreases in waste generated and total remediation times (Heron 1998).

2.3. In-situ Oxidation

VOCs such as benzene, xylene, toluene as well as chlorinated solvents PCE, TCE, and vinyl chloride (VC) undergo oxidation to carboxylic acids and eventually to CO_2 (Amarante 2000). Although it is naturally a slow process, oxidation can be catalyzed by the addition of oxidizing agents such as Fenton's reagent, O_3, H_2O_2, or $KMnO_4$ to the system (Schnarr 1998, Amarante 2000, MacKinnon 2002, McGuire 2006). There are several benefits to remediation through oxidation partially because contaminants are destroyed in-situ, so no extraction or excavation is required with the exception of monitoring. Moreover, once parent compounds (PCE or TCE) undergo oxidation, the intermediates formed degrade very quickly to carboxylic acids (Yan & Schwartz 2002). Treatment with $KMnO_4$ has become the most popular oxidant for remediation, because it is non-toxic to microorganisms and does not form any harmful byproducts (Amarante 2000, Waldemer 2006). Chemical oxidation has shown

promise at several field sites. A compilation of field study results reported that sites where chemical oxidation was utilized have median reduction rates of 88% for all DNAPLs, and 72% for chlorinated solvents in particular (McGuire 2006). In addition, recovery is often greater than 90% for sites where large DNAPL pools are absent (Amarante 2000, MacKinnon 2006).

Given this apparent success, as of yet there is no documentation of oxidation techniques yielding greater than 50% recovery in heavily contaminated sites containing free phase DNAPL. Slow dissolution into the aqueous phase and areas of low permeability hinder oxidizing agents from contacting large amounts of free phase contaminant (Schnarr 1998). Also, the deposition of $MnO_2(s)$, a product of oxidation reactions, can decrease the system hydraulic conductivity by a factor of five, thereby decreasing contaminant removal efficiency as well (MacKinnon 2002). Another problem especially apparent within oxidation implementations is rebound or increases in contaminant concentrations that are often observed after studies are complete (McGuire 2006). The exact reason for this phenomenon is unknown, but is possibly caused by the inhibition of ambient microbial activity stemming from residual oxidant or organic carbon depletion (McGuire 2006). This decrease in organic carbon would result in release of previously sorbed contaminant, and in the process would increase aqueous contaminant concentrations. Oxidative removal for PCE in particular is a very slow process even in laboratory experiments. The chemical structure of PCE slows oxidation reaction rates due to electron withdrawing chlorine atoms that sterically hinder the formation of intermediate species, and thus PCE oxidation is ten times slower than for TCE (Yan and Schwartz 2000).

2.4. In-Situ Bioremediation

Bioremediation of chlorinated solvents is accomplished through microbial mediated reductive dehalogenation. This process reduces chlorinated solvents in a stepwise manner from PCE to TCE to c-1,2-DCE to vinyl chloride, and finally to ethylene. Natural attenuation of chlorinated solvents can be enhanced by the addition of dehalogenating microorganism strains, which is known as bioaugmentation (Adamson 2003, 2004), or through supplementation of the subsurface with excess nutrients and electron donors such as acetate, lactate, or pyruvate that speed up the dehalogenation process (Cupples 2004, Adamson 2003, Devlin 2004). Enhanced bioremediation is an appealing technology in that contaminant removal is completed by a natural process, which is relatively inexpensive to implement (Devlin 2004). Besides ultimately reducing PCE and TCE to ethylene, a harmless end product, each successive reduction results in a less chlorinated product, which exhibits increased aqueous solubility and mass transfer rates over its predecessor (Chu 2004, Cope & Hughes 2001). Thus, flushing techniques coupled with bioremediation can more effectively remove chlorinated compounds through solubilization. McGuire (2006) reports 62% removal of total chlorinated VOCs (TCVOCs) among 26 cleanup sites employing enhanced bioremediation techniques, and supplementary studies have claimed up to 95% removal of total chlorinated hydrocarbons (Witt 2002). Still, bioremediation has been chiefly used in the past for removal of dissolved phase contaminants (McGuire 2006).

At this point, it is unclear how well bioremediation works on areas where large DNAPL pools are present. PCE and TCE are only accessible to dehalogenating organisms in the aqueous phase, so total contaminant removal through bioremediation is limited by mass

transfer processes when DNAPL phase is present. Furthermore, when large mass fractions of PCE or TCE originally exist, c-1,2-DCE and VC concentrations persist for long periods of time, because dehalogenating microbes favorably breakdown PCE and TCE over c-1,2-DCE and VC (Adamson 2004). This accumulation of c-1,2-DCE and VC at remediation sites is not desirable. Although c-1,2-DCE and VC have greater aqueous solubilities than either PCE or TCE, VC is a known human carcinogen with the lowest MCL levels (0.001 mg/L) of all chlorinated solvents (Cupples 2004). For this reason, some field strategies periodically switch between anaerobic conditions, needed for PCE degradation, and aerobic conditions to stimulate aerobic degradation of c-1,2-DCE and VC (Witt 2002). Bioremediation is also a very slow process relative to other strategies as enhanced bioremediation sites have an average duration of nearly two years (McGuire 2006). More importantly, remediation below MCL levels is highly unlikely through enhanced bioremediation. Dechlorination can produce significant amounts of hydrochloric acid, greatly reducing system pH levels, which can be detrimental to dehalogenating microbial communities (Adamson 2004).

2.5. Cosolvent Flushing

Cosolvent flushing with short chain alcohols that are completely miscible with water is another groundwater remediation option (Ladaa 2001). Cosolvent addition results in PCE solubility increases as well as the potential for free-phase mobilization from interfacial tension reductions. PCE solubility increases approximately 40 times in a 60% methanol solution over ambient aqueous concentrations with a parallel decrease in interfacial tension by a factor of four (Imhoff 1995). Thus, using cosolvents carries with it the unwanted potential of downward DNAPL migration and breakthrough into previously uncontaminated regions if interfacial tensions decrease enough. However, breakthrough into underlying

confinement layers did not occur experimentally at cosolvent concentrations of less than 60% even with very small variations in hydraulic conductivity (Van Valkenburg 2002). Moreover, past field experiments using 95% ethanol as the flushing fluid have found no evidence that any such migration occurred (Jawitz 2000, Brooks 2004). The use of alcohols will also increase subsurface drainage efficiency if desired for subsequent vapor extraction techniques.

It is not clear whether cosolvents that partition favorably into the DNAPL phase such as tert-butyl alcohol (TBA) will help or hinder the remediation process. Though solubilities show greater increases when TBA is added to systems in comparison to other commonly used cosolvents, it has been hypothesized that TBA addition will both increase and decrease downward mobility of DNAPLs. Because TBA partitions into PCE, the density will decrease, and thus gravitational migration may be hindered (Van Valkenburg 2002). However, it is also suggested that interfacial tension decreases from TBA will cause greater downward mobility (Imhoff 1995).

In field studies using cosolvent flushing, PCE recovery was less than 70% for all cases, and removal efficiencies were only 1-2 orders of magnitude better than PAT methods (Brooks 2004). While this shows improvement over conventional methods, cosolvent flushing with these results will not attain MCL levels for PCE within realistic temporal and economic constraints. Spatial heterogeneities will not only result in preferential flows that bypass NAPL in areas of low permeability, but they can also enhance downward mobility once cosolvent is added (Imhoff 1995). Because contaminant bypass occurs, and the fact that PCE solubilities do not increase sharply until the aqueous phase contains 10-20% cosolvent by weight in most cases (Ladaa 2001), large amounts of cosolvent must be used for each contaminated site. Therefore, it is not surprising that cosolvent flushing is among the most

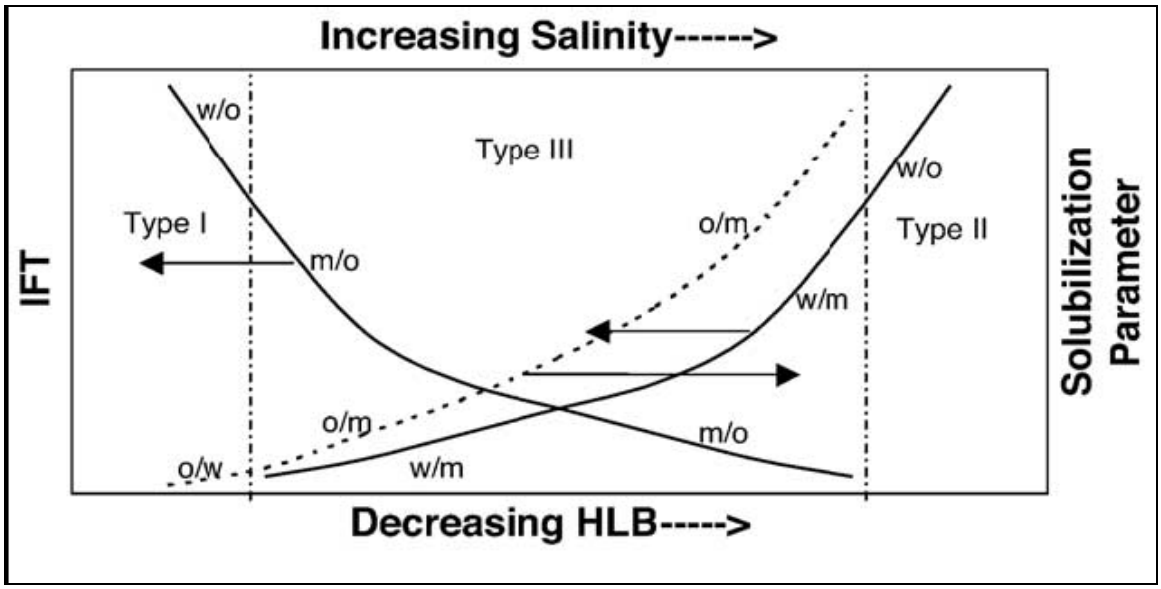
expensive remediation methods in existence (Brooks 2004). Waste management can also be a problem due to increases in Henry's constants, which causes air stripping of contaminants from effluent waste to be very inefficient for removing chlorinated solvents (Ladaa 2001).

2.6. Surfactant Flushing

Surfactants are a group of compounds with both hydrophilic (polar) and hydrophobic (apolar) regions, making them soluble in a variety of media. This allows surfactants to form micelles or aggregations of surfactant molecules with similar polar and apolar orientation (Sabatini 2000). In other words, surfactant molecules form spheres with a polar or non-polar exterior and the opposite type of interior depending upon the media. Micelles can only be formed when surfactant concentrations exceed a threshold known as the critical micelle concentration (CMC). Micelles in the presence of PCE or other free-phase NAPLs can result in trapping large amounts of NAPL in the hydrophobic center of the aggregate, while remaining water soluble due to the hydrophilic exterior (Taylor 2001, Sharmin 2006). Thus, surfactants essentially solubilize large amounts of contaminant at concentrations much lower than required for cosolvents. For example, in a surfactant screen test, PCE solubility was increased up to 700,000 mg/L for some surfactant solutions, which is greater than a three order magnitude increase over aqueous solubility (Childs 2004). It should be noted however that aqueous phase supersolubilized with PCE can increase substantially in density, possibly inducing the remedial fluid to sink within the saturated zone (Taylor 2001).

Surfactant mixtures can be customized to enhance solubility, mobilization, or a number of other variables for a particular system (Acosta 2002, Jayanti 2002). Based on what the desired process is, the hydrophilic-lipophilic balance (HLB), which is a measure of which micelle orientation will dominate in the presence of both aqueous and nonaqueous phase

liquids, can be altered to enhance the desired process by electrolyte or salt addition. Micelles with a hydrophilic exterior, known as Winsor Type I solutions, form in low electrolyte concentrations, and micelles with hydrophobic exteriors, known as Winsor Type II solutions, form when high electrolyte concentrations are present. Balance between the two phases will result in the greatest interfacial tension reductions, and thus offer the greatest potential for mobilization (Childs 2006). Solutions formed in this balance are known as Winsor Type III solutions, which result in mixed micelle systems of both orientations. For illustration, the Winsor phase diagram is shown in Figure 2.1 below.



In addition to achieving minimal IFT's, Winsor Type III solutions also tend to form microemulsion phases with very high contaminant and surfactant concentrations. Surfactant and electrolyte solutions can be efficient at mobilizing DNAPL pools, yet as discussed before, this may not be desirable (Taylor 2001).

In cases where solubilization without mobilization is warranted, the HLB can be shifted to a Winsor Type I solution where surfactant micelles preferably form polar exteriors,

and NAPL is effectively solubilized into the aqueous phase (Dwarakanath 2000). By operating near the Type I/Type III interface shown as the solid line to the left in Figure 2.1, high contaminant solubilities are achieved while minimizing vertical migration potential (Childs 2004). Cosolvents are frequently added to surfactant mixtures as well to prohibit gel formation in the subsurface, reduce fluid viscosity, and lower equilibration times with the contaminant although they also reduce overall PCE solubilities (Dwarakanath 2000). With so many additives in surfactant solutions, the successful utilization of these remediation strategies requires careful balancing of the physicochemical fluid properties.

The surfactant solution selected for a given application must also be carefully selected based upon the system, for surfactant strategies often fail where full subsurface characterization is not completed prior to implementation (Abriola 2005). There exist numerous surfactant families to choose from for remediation, which will respond to natural systems in a variety of ways. Generally, surfactants are divided into three main categories: anionic, cationic, and nonionic, with anionic and nonionic the most popular for groundwater remediation (West and Harwell 1992). Both of these categories have advantages and disadvantages, and either could perform better in a certain situation. Anionic surfactants do not readily sorb to most soils, do not form gels, and have very quick solubilization rates (Childs 2004). However, anionics also tend to form precipitates in many field settings (Childs 2004, Dwarakanath 2000). Nonionics on the other hand show high increases in PCE solubilities and have not been shown to form precipitates. However, they are more likely to be considered toxic, preferentially sorb to organic soil matter, and can partition favorably into free-phase NAPL (Sharmin 2006). Many times multiple surfactants are combined to

form synergistic mixtures that relax negative aspects found within single surfactant solutions (West and Harwell 1992).

The major problems for surfactant use are regrettably the same characteristics that make them appealing. Though there are several means of improving surfactant performance through adding cations, cosolvents, or other surfactants, each component adds more complexity to the system. This translates to more time and money expended to discover the best mixture for a particular system, which may perform poorly for other contaminated sites. For this reason, surfactant techniques are among the most expensive remedial techniques to implement (McGuire 2006). The complexity of surfactant mixtures is conveyed in the wide range of success reported in field studies. Past attempts have yielded recoveries from over 99% in relatively homogeneous systems to very small recoveries in others (Abriola 2005). Furthermore, by injecting surfactants into a natural system, surfactant recovery as well as the original contaminant becomes an issue (Okuda 1996). Recent studies have shown surfactant recovery over 90% (Ramsburg 2004a, Childs 2006), but surfactants showing the potential for extensive sorption should be studied in depth before utilization in the field.

2.7. Brine Barrier Remediation Techniques (BBRT)

BBRT is a novel technique just recently developed exhibiting great potential for removing large amounts of DNAPL residual. This technology calls for the initial injection of a high density salt solution into the system exceeding the density of the DNAPL to be removed (Miller 2000). Theoretically, this brine solution then works as a barrier at the bottom of aquifers halting downward migration caused by mobilization (Miller 2000, Hill 2001, Johnson 2004). After a brine layer is established, surfactant flushing with a solution aimed at DNAPL mobilization is initiated, which should result in DNAPL migration until it

reaches the brine where DNAPL will remain due to buoyancy forces (Johnson 2004). Because location of the brine layer can be monitored by density measurements, the DNAPL pools formed should be easier to locate and remove from the system. This can be a very attractive situation in that most of the DNAPL removed will exist in a very concentrated form, and thus removal and waste treatment increases in efficiency.

In this case, surfactant solutions that reduce IFT's to a minimum are preferred as they are most likely to produce DNAPL mobilization. Focusing on mobilization eliminates problems associated with mass transfer limited solubilization, which decreases remediation times and flushing volumes (Hill 2001). Past studies have shown that a one pore volume (PV) flush of a highly mobilizing surfactant solution results in greater than 90% PCE removal from experimental heterogeneous systems (Miller 2000). These solutions also assist in higher water desaturation of the system, which is an ideal condition for SVE techniques to remove any remaining PCE after surfactant flushing (Miller 2000). In a documented experiment utilizing such a strategy, greater than 99% of the initial PCE residual was removed from the system after SVE was completed (Johnson 2004). BBRT strategies have the potential to become an efficient contaminant removal technique for subsurface systems, though much experimental work remains to answer open questions.

2.8. BBRT Open Issues

While BBRT strategies have shown promise in small-scale experimental settings, there are several open issues that must be attended to before BBRT can be considered a viable option for groundwater remediation. The addition of high brine and surfactant concentrations can lead to very complex interactions within the contaminated system. For example, increases in salinity due to brine addition lead to solubility decreases for PCE and

surfactants, which can cause anionic surfactant precipitation and nonionic surfactant partitioning into free-phase PCE. Although interactions among brine, surfactant, and PCE have been studied extensively in lab settings, it is difficult to test for all component combinations that may arise during a large-scale remedial process. Due to the complexities created, brine and surfactant removal efficiency after remediation is complete are also largely unknown (Johnson 2004). In addition, further unexpected issues may arise due to ambient chemical and biological communities as well as system heterogeneity in field-scale implementations.

Another open question involves what analytical methods can be appropriately employed for such a system. The complexities found in BBRT systems eliminate most conventional analytical methods for VOCs from consideration. Furthermore, depending on the surfactant flushing solution used for a particular situation, the applicability of analytical methods could vary for each separate BBRT implementation.

2.8.1. Field Scale Issues

Though BBRT has proven very effective in one-, two-, and three-dimensional experiments (Miller 2000, Hill 2001, Johnson 2004), there is still the necessity for field experiments to verify that such a strategy will be successful in contaminated natural systems. Laboratory experiments are an important and necessary step in the formulation of groundwater remediation strategies as they are needed initially to test the technology in question under various controlled conditions. However, it is impossible to recreate a virtual field setting complete with representative soil heterogeneities at the micro- and macro-scales, microbial communities, and naturally occurring physical and chemical components. Natural systems are bound to reveal several problems unforeseen from lab work, because it is so

complicated to completely characterize any natural system. Experiments including only brine and surfactant in a PCE contaminated cell with homogeneous packing are very expensive and time consuming (Miller 2000), and more combinations or complexities will increase the time and costs involved. The next logical step in acceptance of BBRT as a practical remediation alternative is examination of its performance in a field setting. Consequently, our lab group embarked on a field-scale implementation of BBRT at Dover National Test Site (DNTS) in Dover, DE from December, 2005 to June, 2006.

Site Description. DNTS covers approximately 3.5 acres of a grassy field with minor topographic undulations of less than 2 feet. The Columbia Formation contains an underground aquifer that varies in depth from 36-47 feet (RETEC 2005). It is comprised of fine-to-medium sands with occasional discontinuous clay and silt lenses exhibiting very low organic content of 0.025% (Witt 2002). The depth to the water table of the Columbia Aquifer is approximately 24-26 feet below ground surface. Pumping tests have yielded a vertically averaged hydraulic conductivity of 8.5 ft/day, vertically averaged horizontal transmissivity of 129 ft^2/day, specific yield of 0.27, and storativity of 0.0003 ft^{-1} (RETEC 2005). Underlying the Columbia Formation is the Calvert Formation, which consists of gray, firm, dense marine clays. This confining layer is approximately 20 feet thick and has a hydraulic conductivity of $8.4*10^{-3}$ ft/day (Childs 2006). Under the Calvert Formation is the locally confined Fredrica Aquifer. Analyses indicate the soils range from slightly to moderately acidic, ranging in pH from 4.9 to 6.4. Microbial evidence of anaerobic metabolism and denitrifying enzyme activity were low (RETEC 2005).

There are three confined test cells on site at DNTS that have been used to conduct various PCE remediation studies. Test Cell 3, the cell used for the current experiment, has

been used to conduct three prior studies. These studies included a cosolvent study, a surfactant study using sodium dihexyl sulfosuccinate (MA-80), and a complex sugar flushing strategy using cyclodextrin. As of June, 2001, approximately 35.6 L of PCE remained in Test Cell 3 (RETEC 2005). Based on the recovery of cyclodextrin from the prior study, cyclodextrin concentration was approximately 35,000 mg/L at the end of that study (Tick 2003). Low levels of MA-80 surfactant and several alcohols used in PCE tracer tests were present as well.

Field Experiment Schedule. The successful implementation of the BBRT in a field setting required several steps during implementation. This was due to the fact that addition of PCE, brine, and surfactant must be administered to the system in a stepwise manner to attain the desired results. Additional steps were also required because several different contaminant removal methods were employed as well. With each successive species addition, the system increased in complexity, which required intensive matrix sampling during all stages of the study in order to monitor the behavior of all analytes within the system.

Stages 1-3 were primarily for pre-characterization of the test cell to quantify the distribution of PCE, degradation products, and MA-80 initially present as well as the ambient draining characteristics of the subsurface. Stage 4 involved the delivery of PCE to the cell, resulting in a free-phase PCE residual of approximately 100 L. The PCE was further distributed throughout the cell during Stage 5 in which the water table was raised by pumping water back into the system. The brine was injected in Stage 6, and once the brine barrier was established, Stage 7, surfactant flushing, commenced. The cell was dewatered in Stage 8 to prepare for free-phase PCE removal in Stage 9 and SVE implementation in Stage 10. Finally, the brine was removed, and the water table was returned to initial conditions

during Stages 11 and 12. The scheduled stages within this field experiment are summarized in Table 2.1 including the intent of each stage as well as the species of interest present at that time.

Stage	Stage Description	Primary Analytes Present
Stage 1	Test Cell Pre-characterization	PCE, MA-80, degradation products
Stage 2	Preliminary Dewatering and SVE	PCE, MA-80, degradation products
Stage 3	Equilibration	PCE, MA-80, degradation products
Stage 4	PCE Delivery	PCE, MA-80
Stage 5	Water Table Adjustment	PCE, MA-80
Stage 6	Brine Injection	PCE, brine, MA-80
Stage 7	Surfactant Addition	PCE, brine, MA-80, Triton X-100, IPA
Stage 8	Dewatering	PCE, brine, MA-80, Triton X-100, IPA
Stage 9	PCE Removal and Final Dewatering	PCE, brine, MA-80, Triton X-100, IPA
Stage 10	Brine Flushing and SVE	PCE, brine, MA-80, Triton X-100, IPA
Stage 11	TDS Reduction and SVE	PCE, brine, MA-80, Triton X-100, IPA
Stage 12	Return to Starting Water Level	PCE, brine, MA-80, Triton X-100, IPA

Table 2.1: Summary of Proposed Stages during Field Experiment.

2.8.2. System Complexity Issues

A 52% calcium bromide ($CaBr_2$) solution with a density of 1.7 kg/L was selected to act as the dense brine barrier in the current experiment. A solution of this density should halt gravity driven migration of even the densest chlorinated solvent, PCE (ρ =1.62), if the brine barrier is successfully established. This is based upon the assumptions that 1) a low lying aquifer confinement of sufficiently low hydraulic conductivity capable of supporting a dense brine layer exists, and 2) that soil heterogeneities do not prevent a stable, uniform brine layer throughout the lower reaches at or near a density of 1.7 kg/L from forming. Failure to achieve these constraints may result in loss of PCE or brine from the system. The brine has a very high viscosity, which may increase the time and amount needed to establish a uniform layer. This high viscosity could cause brine recovery problems at the end of the study as well (Johnson 2004). Additionally, as brine mixes with groundwater, the aqueous solubility of PCE and surfactant will decrease with increasing calcium bromide concentrations. Although

this is not likely a major problem for PCE overall removal in this situation as solubilization is not heavily relied upon as method of removal, the surfactant solubility reduction may lead to precipitation of anionic surfactants, and increased sorption of nonionics.

After extensive experimentation, the surfactant solution selected consisted of 1.575% polyoxyethylene octylphenol (Triton X-100) surfactant, 1.425% MA-80 surfactant, 1.4% calcium chloride ($CaCl_2$), and 3% isopropanol (IPA) by weight. MA-80 is an anionic surfactant subject to precipitation in the presence of salt. Thus, Triton X-100 was added, which is a nonionic surfactant that when mixed with MA-80 reduces precipitation. However, some Triton oligomers are potentially toxic, and partition favorably into free phase PCE (Sharmin 2006). Calcium chloride was included in the surfactant mixture to shift the resultant solution to a Winsor Type III, resulting in the highest mobility potential for PCE and the development of microemulsions with very high PCE and surfactant concentrations. IPA was added to the solution in order to reduce fluid viscosity and lower equilibration times with PCE. It remains to be seen if microemulsion phase or free-phase PCE pools can be removed from natural systems without problems associated with increased viscosity, and this could pose problems for removal efficiency of both PCE and surfactants. Also, the addition of IPA decreases overall PCE solubility and adds complexity to the system.

The potential system complexities going into the study include brine, surfactants, and possibly a significant amount of cyclodextrin from past studies that likely lead to very complex PCE phase behavior. Each component alone markedly affects PCE solubility and potentially mobility, which makes it difficult to track contaminant movement during the study. Furthermore, the system complexity will alter air-water partitioning coefficients, and

complete cell dewatering may be hampered by viscosity increases. These aspects of BBRT systems as well as residual surfactant may later cause SVE performance to vary drastically.

2.8.3. Analytical Issues

In the experimental system described, the primary analytes of interest are MA-80, Triton X-100, PCE, and any chlorinated daughter products formed by microbial degradation including TCE, c-1,2-DCE, and VC. Various analytical methods exist for each species, though not previously in a system of this complexity. Ideally, a method capable of quantifying each analyte in a single injection would be adopted. Unfortunately, such a method does not currently exist. Past methods used to quantify the analytes of interest are highlighted below, as well as problems that may surface due to the presence of brine, cyclodextrin, and other system complexities.

PCE and Daughter Products. Chlorinated solvents are typically quantified by gas chromatography (GC) methods coupled with either flame ionization (FID) or electron capture detection (ECD). GC-FID and GC-ECD systems are both very commonly used for PCE detection, and sometimes are used simultaneously (Ramsburg 2004). FID detectors are more reliable over a wide concentration range for chlorinated solvents, but ECD detectors give lower detection limits by a factor of approximately 10. The high electron density of chlorine atoms makes ECD a very attractive method for PCE and daughter products at concentrations near MCL levels. However, PCE concentrations are several orders of magnitude above MCL's at most remediation sites, and hence FID may be the preferred quantitation method in such situations. In fact, nearly every field study examined that utilized GC methods used FID detection with a few employing ECD as well (Dwarakanath and Pope 2000, Brooks 2002, Ramsburg 2003, Childs 2004, Ramsburg 2004b). The one exception

utilized liquid:liquid extraction methods followed by dilution to levels accurately measured by ECD (Rivett 2005).

Three common method types specified by the EPA exist for detection of PCE and other VOC species: direct injection, headspace, and purge-and-trap analysis. Direct injection as the name implies calls for sample injection directly onto the GC column head. This method is relatively simple and may result in shorter run times. However, because of incompatibilities with water, direct injection with FID may not work well with aqueous samples. Headspace analysis methods take advantage of the volatility exhibited by chlorinated solvents by allowing a known sample volume to equilibrate with a known volume of headspace in a predetermined amount of time. Once the equilibration time is complete, a sample is taken from the headspace. Headspace analysis is very popular for field samples because it avoids the issue of analyte losses due to volatilization, and also removes many potential interference compounds that are left behind in the aqueous phase. The main fault of this technique is its reliance upon air-water partitioning or Henry's constant (K_H). If any species are present in the original aqueous samples that change the partitioning behavior of the analyte, quantification will be inaccurate. The purge-and-trap technique also samples the headspace, but the aqueous sample is first purged with air for an amount of time necessary to transfer essentially all of the analyte into the air phase. Purge-and-trap is an effective option, although purge times can be very long for PCE analysis in complex systems.

Because of the complicated system created by BBRT methods, conventional GC analytical methods for chlorinated solvents cannot be used. The wide range of surfactant, brine, and cyclodextrin concentrations expected throughout this study will cause K_H to vary from sample to sample, rendering GC headspace methods very unreliable. Past remediation

studies making use of surfactants have evaded this problem by either adding excess surfactant up to a uniform concentration (Childs 2004), or diluting samples below surfactant CMC levels, where surfactant presence should not affect PCE partitioning behavior, prior to analysis (Sabatini 2000). While both methods should work to a degree, each will cause significant rises in detection limits. The former method increases detection limits because increased surfactant concentrations result in lower PCE partitioning into the headspace, the latter because the original sample must be diluted to low concentrations. Additionally, the proposed experimental system contains two surfactants, which can result in a lower effective CMC than either surfactant displays alone (West and Harwell 1992), and thus requiring greater dilutions to attain surfactant CMC levels, which will result in even higher method detection limits (MDL). Brine presence is expected to complicate PCE partitioning even further. Aside from the problems evident in headspace analysis, purge-and-trap methods also suffer interferences caused by surfactant foam or brine precipitation created in samples from extensive air purging. Finally, GC direct injection was shown experimentally to fail in PCE quantification due to interference with IPA at high concentrations, which are expected within the test cell.

High performance liquid chromatography (HPLC) methods with ultraviolet (UV) detection are occasionally used for chlorinated solvent analysis in field experiments (Field and Sawyer 2000, Chen 2004). In most instances though, GC methods are preferred over HPLC because of lower detection limits, and species volatility is more of an issue in liquid samples. This is reiterated in the fact that an EPA standard method does not exist for chlorinated solvent analysis via HPLC. Plus, UV maximum sorption for all chlorinated solvents is around 210 nm, which is at or near the max sorption for a number of other

compounds, hence increasing potential for peak interference. One benefit from HPLC analysis is its universality. HPLC methods are capable of quantifying a number of various compounds in a single run if the mobile phase is prepared correctly. Also, unlike GC headspace methods, HPLC quantification methods are not reliant upon the species K_H, which is nearly impossible to judge in systems containing high concentrations of surfactants and salts. However, PCE recovery via HPLC may vary due to the presence of brine and surfactants.

Surfactants. In contrast to chlorinated solvents, both MA-80 and Triton X-100 have very low volatility, and are not easily quantified by GC headspace methods. As previously mentioned, surfactants are incompatible with GC purge-and-trap methods due to their tendency to produce large amounts of foam that will likely interfere with VOC analysis. In past studies, some form of liquid chromatography is most commonly used for both surfactant compounds.

Triton molecules contain a phenyl group, so UV detection works well for Triton and spectrophotometric absorbance measurements will suffice in simple systems (Sharmin 2006). Triton X-100 quantification in complex systems on the other hand has proven very burdensome. First of all, Triton X-100 is not a pure compound, and is rather a mixture of oligomers with ethoxy chains varying in length from 1 to 16 carbon members (Kamiusuki 1999). When run through a C18 adsorption HPLC column, these oligomers will split into several peaks representing separate oligomers that are very hard to resolve. Complete oligomer separation has been accomplished with UV and fluorescence detection, but run times vary between 4 and 5 hours (Kamiusuki 1999), which eliminates high sample throughput while employing such a method. If individual oligomer quantification is not

required, Triton X-100 can be eluted as a single peak with a high organic content mobile phase in less than 5 minutes (Medvedovici 2001). This will increase potential for interferences, but the advantages gained through run time decrease may outweigh this setback for some applications.

MA-80 has been quantified in the past by ion exchange chromatography (Childs 2004), titrimetric methods, conductivity measurements (Childs 2006), and HPLC with UV detection (Field and Sawyer 2000, Ramsburg 2004). Titrimetric methods have numerous interferences and are very time consuming, so analyzing numerous samples in a complex system is problematic. Simple conductivity measurements may be reliable in simple systems, but systems containing large amounts of salt as in our system can cause significant background interference. Ion exchange chromatography followed by conductivity detection could work well for field samples as MA-80 is an anionic surfactant. This method is dependent upon whether MA-80 can be chromatographically separated from other ions. HPLC using a C18 adsorption column with subsequent PDA detection can be accomplished, but detection limits are high as the max absorbance of MA-80 is relatively low.

2.9. Overall Objectives

Given the incompatibility of classical analytical methods with the complexities presented by BBRT methods, the objective of this project is to develop analytical methods capable of quantifying the primary analytes found in such systems including PCE, chlorinated daughter products, MA-80, and Triton X-100. The methods developed will be validated through a series of quality control (QC) checks later discussed, and then utilized to measure mass balances for PCE, MA-80, and Triton X-100 in order to evaluate contaminant and remedial fluid recovery efficiencies for Brine Barrier Remediation Techniques.

3. METHODS DEVELOPMENT

3.1. Analytical Method Selection

Taking into account the failure of conventional PCE analytical methods and the fact that both MA-80 and Triton X-100 have been successfully quantified in the past using HPLC methods, it was decided to concentrate efforts on developing an HPLC method hopefully capable of quantifying each analyte simultaneously, while not sacrificing greatly in terms of detection limits.

In order to minimize analyte losses from volatility that is inevitable when using HPLC methods, dissolve any free-phase PCE present in samples, and to increase the overall sample holding time, all samples were diluted by a 1:1 ratio with an appropriate cosolvent. Following a cosolvent screen study including methanol, ethanol, and IPA, the conclusion was reached that dilution with IPA results in the smallest percent loss of analyte and the greatest solubilizing capacity of free-phase PCE. Values from the literature support our finding as PCE solubility in 50% IPA is nearly 3 and 10 times the reported values for 50% ethanol and methanol respectively (Ladaa 2001, Imhoff 1995). Volatility should also decrease as PCE solubility increases. Aside from increasing PCE solubility and decreasing volatility, sample dilution with IPA minimizes any PCE sorption to the septa of sample vials and the HPLC vial plastic caps. Cosolvent addition should also minimize the effects of brine and surfactant on PCE recovery as it should break up any surfactant micelles present and dissolve any precipitates caused by brine. This dilution step will obviously decrease detection sensitivity

by a factor of two, but the advantages of cosolvent addition will likely outweigh this drawback.

Despite the fact that all samples were to be diluted 1:1 (v/v) with IPA, recovery losses from sample preparation and analysis were still expected. For this reason, a surrogate spike was sought to serve as QC to field samples. Though surrogate spikes have not been well documented for HPLC methods, it is frequently used as a QC measure for environmental samples analyzed by GC methods (Foreman 2000, Schumacher 1997, Harlin 1994). In order to correctly utilize a surrogate spike, a volatile compound not commonly found in the environment is added to each sample that theoretically mimics losses apparent in chlorinated solvents due to sample prep and instrument drift during analysis. The percent recovery of the known surrogate concentration can then be used to calculate a correction factor, which in turn can be used to predict the original sample concentration of each chlorinated compound. The surrogate 4-bromofluorobenzene (4-BFB) was selected because it has been identified as a potential quantitation reference compound for chlorinated solvents in that it exhibits similar air-water partitioning behavior (Schumacher 1997). Another surrogate, d-toluene was found to be a better reference compound for PCE in particular, but this compound exhibited high detection limits and toluene currently exists at low concentrations in Test Cell #3 that could cause background interference. Further experimental work showed that 4-BFB was detectable by HPLC methods, and was separable from all analytes of interest, which makes 4-BFB an appealing surrogate standard for HPLC methods.

3.2. Standards Preparation

Stock standards of 5,000 mg/L were prepared gravimetrically in HPLC grade IPA supplied by Burdick and Jackson for each volatile species to be analyzed with neat PCE and TCE solutions from Fisher Scientific, c-1,2-DCE from Supelco, and 4-bromofluorobenzene

(4-BFB) from Arcos Organics. These stock standards were subsequently used to generate two working standards containing 1,000 mg/L and 50 mg/L of all volatile species in IPA. Separate MA-80 and Triton X-100 stock standards of 100,000 mg/L were prepared gravimetrically from samples supplied by Cytec (80% sodium dihexyl sulfosuccinate, 5% IPA) and Acros organics respectively. Similarly, these stock solutions were used to make up separate working standards for each surfactant of 20,000 mg/L and 1,000 mg/L in 100% IPA. Stock and working standards were sealed with parafilm and stored at 4 ^{0}C, and were stable for up to three months.

Both chlorinated solvent and MA-80 stock and working standards were combined to form a series of 11 calibration standards in 100 mL volumetric flasks brought up to volume in a 50:50 (v/v) solution of DI water and IPA with the following components:

Standard	MA-80 (mg/L)	Working Std. Used	Amount(mL)		PCE (mg/L)	Working Std. Used	Amount(mL)
1	15000	Stock	15		400	Stock	8
2	10000	Stock	10		200	1	20
3	4000	1	20		100	1	10
4	2000	1	10		50	1	5
5	400	1	2		20	1	2
6	200	2	20		10	2	20
7	100	2	10		5	2	10
8	60	2	6		2	2	4
9	40	2	4		1	2	2
10	20	2	2		0.5	2	1
11	0	NA	0		0.25	2	0.5

Table 3.1: List of Individual MA-80 and Chlorinated Solvent Calibration Standard Components.

A separate set of seven calibration standards for Triton X-100 were made up in the same solution with target concentrations similar to MA-80 concentrations in standards 2, 3, 4, 5, 6, 7, and 9. Calibration standards were sealed with parafilm, stored at 4 ^{0}C when not in use, and remade every month. In addition, a 15,000 mg/L stock solution of 4-BFB was prepared in IPA to serve as a surrogate spike to field samples. The solution was changed to 60,000 mg/L

for periods in the study where PCE concentrations were very high and sample injection volumes were appropriately decreased.

3.3. Sample Handling and Preparation

Samples taken at DNTS for HPLC analysis were collected in 30 mL EPA volatile organic analysis (VOA) screw cap vials with Teflon lined septa and zero headspace. These samples were shipped on ice to UNC-CH where they were stored at 4 ^{0}C until ready for analysis. Holding times for samples prepared as such with minimal headspace were experimentally determined to be stable for at least 14 days. However, once diluted in IPA, chlorinated solvent concentrations were stable for up to one month

Once ready for preparation, samples were removed from storage, and allowed to equilibrate to room temperature. Using a 50 μL air-tight glass syringe, 50 μL of 4-BFB stock solution was drawn, and immediately added to each sample for a target concentration of 12.5 or 50 mg/L depending on the stock solution used. The samples were then inverted several times to completely mix. Once spiked, samples were poured through a glass funnel into a pre-rinsed 60 mL Qorpak Boston Round bottle containing approximately 10 mL IPA prior to sample addition. The sample vial, cap, and funnel were subsequently rinsed several times with IPA, and all washes were added to the 60 mL bottle, and the bottle was completely filled with IPA. Samples were then inverted several times and gently shaken to thoroughly mix the sample with IPA. At this point, samples were either prepared further for analysis, or stored at 4 ^{0}C until analysis could be completed.

Samples were next allowed to equilibrate to room temperature if not already equilibrated. Using 5 mL Luer-Loc syringes, approximately 5 mL of sample were removed from 60 mL bottles. A PTFE filter tip was placed on the syringe to remove particulates in the sample, and 3-4 mL of sample were passed through the filter before collecting roughly 1 mL

of sample in Fisher HPLC vials for analysis. The remaining sample was stored at 4 ^{0}C in case duplicate runs were later required.

3.4. HPLC Method Overview

All analyses were performed by a Waters HPLC system, including a Waters 717 Plus autosampler, a 616 pump, 606S controller, and a Waters 996 photodiode array detector (PDA). A 25 X 4.6 cm, 5 μm particle size Supelco C18 adsorption column was used for the separation of PCE, PCE daughter products, 4-BFB, and MA-80 in an HPLC method adopted from a method previously documented by Field and Sawyer (2000) used for TCE and MA-80 analysis with some slight variations due to the presence of brine and Triton X-100. The same column was also used in a supplementary method developed exclusively for the separation and quantification of Triton X-100.

3.4.1 MA-80, PCE, and Daughter Products Method Description

Depending upon the field experiment stage, either 10 or 50 μL samples were injected at a flow rate of 0.8 mL/min, and the flow rate was increased to 1.0 mL/min 0.2 minutes into the run. The mobile phase initially consisted of 70% 0.003 M NaCl in HPLC grade DI water attained from Sigma-Aldrich, and 30% HPLC grade acetonitrile from Burdick and Jackson. At 3.0 minutes, the mobile phase sharply stepped to 50% 0.003 M NaCl, 50% acetonitrile, which eluted the MA-80 and was a sufficient amount of time to give complete separation from the brine peak, which was very large and eluted at the column void volume. Then, using a concave gradient beginning at 3 minutes, the mobile phase was slowly shifted to 20% 0.003 M NaCl, 80% acetonitrile over 30 minutes in order to separate the PCE and Triton X-100 peaks, which interfered with one another if the Field and Sawyer method was used without alteration. Initial mobile phase conditions were restored after 31 minutes, and 4 minutes were allowed for column equilibration between samples, giving a total run time of 35 minutes.

Cleanup steps consisted of a 60 minute flush with a 50:50 acetonitrile:DI water solution at 1.0 mL/min to dissolve any precipitated brine in the system followed by a 60 minute flush with a 95:5 acetonitrile:DI water solution at 0.1 mL/min to mobilize any organic species remaining on the column.

MA-80, PCE, and daughter products were detected at 220 nm as opposed to 210 nm, which had been used in the Field and Sawyer method. This modification was due to the fact that many compounds display maximum absorbance at or near 210 nm, and thus potential for interference was greater at this detection wavelength. Quantification of all analytes was accomplished by a six point linear calibration regression (R^2 values > 0.995 for acceptance) calculated at the beginning of each sample set from the calibration standards described in Section 3.2. The standards used to form the calibration curve depended upon the stage of the field study as well as characteristic effluent PCE and surfactant concentrations at the time of analysis. The MA-80 eluted at approximately 8.3 minutes, cis-1,2-DCE eluted at 12.2 minutes, TCE at 18.4 minutes, 4-BFB at 20.8 minutes, and the PCE peak appeared at 25.8 minutes. In field samples, a series of broad, unresolved peaks appeared shortly after PCE representative of Triton X-100 oligomers if present. A sample chromatogram a standard analyzed by this method is shown in Figure 3.1, and real field samples are shown in Figures 3.2 and 3.3. It was observed that the retention time for each analyte with the exception of MA-80 increased by as much as 1 minute as the HPLC column age increases. The MDL was determined to be 20.0 mg/L for MA-80, 0.1 mg/L for PCE, TCE, and 1.0 mg/L for cis-1,2-DCE as described in Standard Methods.

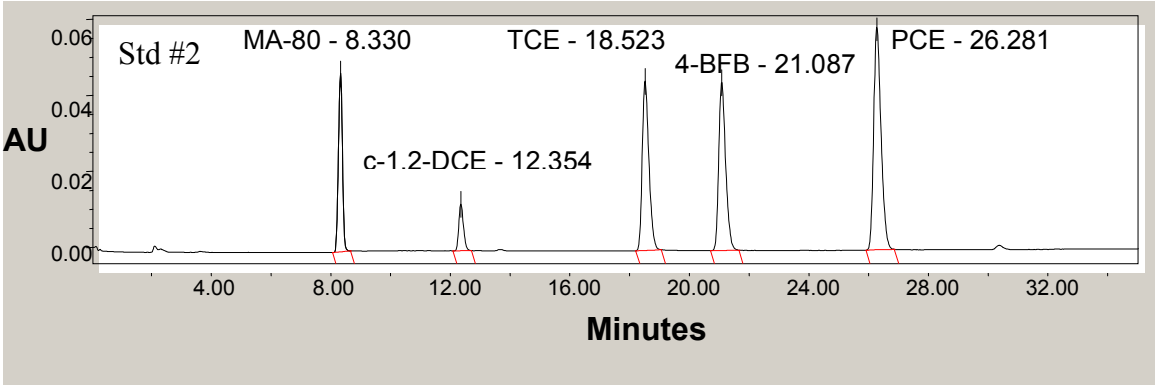


Figure 3.1: Sample chromatogram of 10 µL injection of calibration standard containing 200mg/L cis-1,2-DCE, TCE, 4-BFB, PCE, and 10,000 mg/L MA-80.

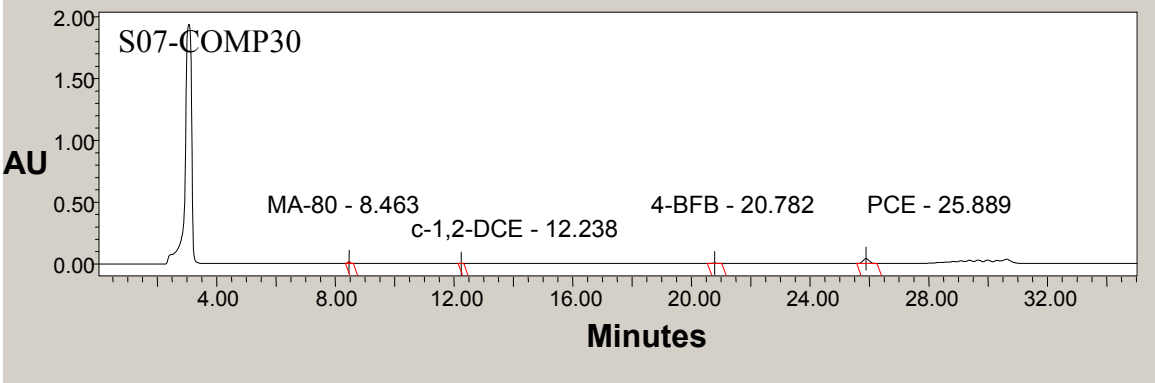


Figure 3.2: 10 µL Injection, full scale chromatogram of field sample S07-COMP30.

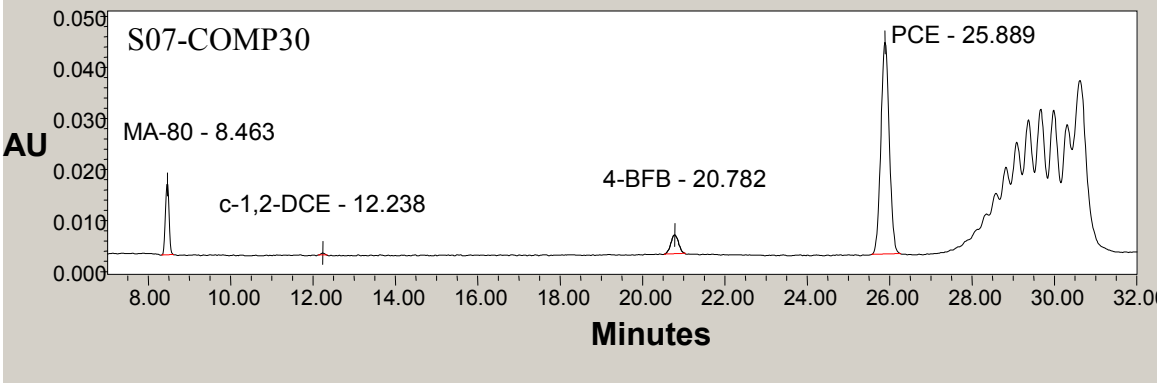


Figure 3.3: Chromatogram of field sample S07-COMP30 zoomed in on species of interest.

As with any new method, the method just depicted has several shortcomings associated with it. For instance, EPA standard GC methods boast detection limits two orders of magnitude lower than the method developed. Therefore, determining contaminant removal below MCL concentrations would require an alternative method. At this detection

wavelength, vinyl chloride has a very high MDL, and thus was unable to be quantified by this method. Although VC was not likely to be a major contributor to total chlorinated compound concentrations, quantification would still be beneficial. Furthermore, this method is incapable of quantifying species of subsidiary interest such as IPA, ethanol, and cyclodextrin that would ideally be available. This method also does nothing to remove the high concentrations of brine potentially present in samples. Although this has not proven to be an interference problem during sample runs, brine exposure over time may cause failure of internal HPLC parts due to brine precipitation and corrosion.

3.4.2. Triton X-100 Method Description

In this method, 50 μL of sample were injected onto the column at a flow rate of 1.0 mL/min. The elution was isocratic, using an 85:15 acetonitrile:DI water mobile phase. The high organic content of the mobile phase succeeded in eluting all Triton oligomers as a single peak, which made the total Triton quantifiable.

Although Triton gave a higher response, and thus a lower detection limit at 220 nm, detection is performed at 277 nm, where a local maximum absorbance exists. This avoided interference from PCE, which under these mobile phase conditions eluted at the same time as Triton X-100. Quantification of Triton X-100 was accomplished by a seven point linear calibration regression (R^2 values > 0.995 for acceptance) calculated from the Triton calibration standards described in the Standards Preparation section. The total run time was 10 minutes, with Triton X-100 eluting at approximately 7.4 minutes, although the retention time was dependent upon the relative amounts of each oligomer present. Triton standard and field sample chromatograms are displayed in Figures 4 and 5 respectively. The shift in retention time can be discerned somewhat in Figure 3.5 due to a dominance of shorter ethoxy chain Triton oligomers, which is obvious from Figure 3.3.

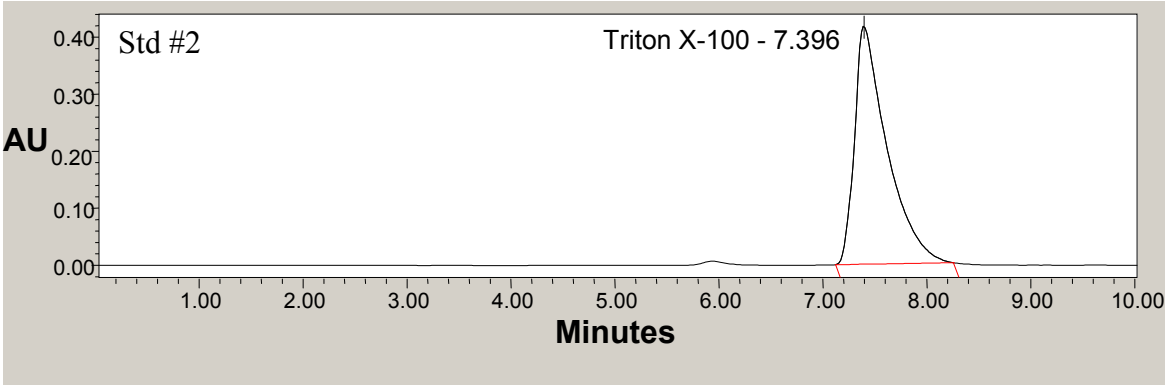


Figure 3.4: 50 µL injection, sample chromatogram of calibration standard containing 10,000 mg/L Triton X-100.

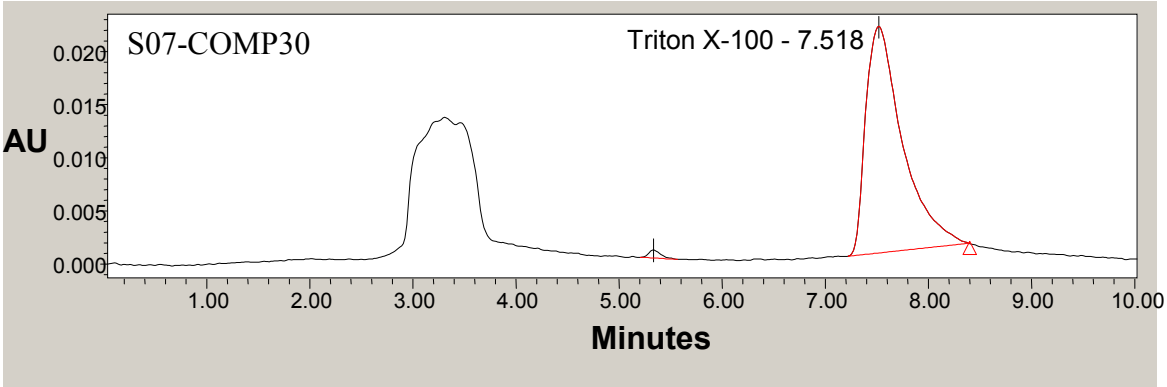


Figure 3.5: 50 µL injection, sample chromatogram of field sample S07-COMP30 using Triton X-100 method.

The potential disadvantages of Triton X-100 quantification by this method included the inability to get accurate measurements at PCE concentrations greater than 5,000 mg/L, lower sensitivity than at 220 nm, and increased peak spreading at concentrations approaching CMC levels. Contrarily, peak spreading caused a much higher detection limit for Triton, around its CMC of 130 mg/L (Zhu 2003). This was especially problematic in later stages of the study when effluent concentrations fell below CMC levels. High PCE concentrations were generally not a problem as concentrations of 5,000 mg/L were rarely seen in field samples.

3.4.3 Method Performance Criteria

The detection limits determined for all VOC analytes with the exception of TCE were considered appropriate for a majority of the study due to the relatively large concentrations of each species initially present. During later stage, c-1,2-DCE concentrations dropped below the MDL. TCE and c-1,2-DCE masses were very small when compared to PCE mass though, and hence this was not considered a problem with method performance. However, because MCL values are well below the MDL for all chlorinated solvents, alternative methods will be required to monitor contaminant removal below the MCL. The concentrations of both surfactants injected on the other hand were three orders of magnitude higher than detection limits, and thus the calculated MDL were considered acceptable for mass balance calculations of both surfactants.

The accuracy and precision desired for this experiment were hard to define initially because of the complex matrix found within the system. In addition, percent recovery of VOC analytes in all environmental samples is highly variable and is often considered acceptable at ± 30% of expected values due to volatility issues(Laconto 2006). However, ± 30% is considered a maximum limit for acceptance, and a higher degree of accuracy was desired for chlorinated solvent recovery in all QC samples. Initial tests for PCE recovery yielded an average of approximately 85% of original concentrations over the range of 0.2 – 200 mg/L. Thus, a control range of ± 15% was established for all QC samples. Spiked blank samples to be described later were expected to yield lower recoveries, and thus an 80% recovery control limit was used for these samples.

For simplicity, a 15% relative percent difference (%RPD) was also adopted as the criteria for measuring the precision between duplicate samples. However, this limit is

somewhat arbitrary in that the expected %RPD between duplicate samples in a highly variable and complex sample matrix was not established prior to the field experiment. Ideally, several duplicate sets at different PCE concentrations should have been analyzed beforehand to attain such control limits.

4. RESULTS AND DISCUSSION

4.1. Data Validation

An integral component required for approval of data generated through any analytical method rests in the method's validation through various quality control (QC) processes. QC programs can involve many types of checks aimed to test the accuracy, precision, and reproducibility of the method. Although numerous other QC measures exist, QC programs typically include sample blanks, spiked blanks, and sample duplicates in some capacity. The QC steps taken within the Dover field study included 1) surrogate spikes of all field samples upon arrival at UNC, 2) check standards and 3) PCE lab spikes of known concentrations prepared at UNC, 4) field blanks, trip blanks, and spiked blanks prepared onsite at DNTS, 5) duplicate field samples, and 6) split samples analyzed by an outside lab for the analytes of interest. Each QC step mentioned provided a measure of accuracy and/or precision to the generated data as well as overall method performance. One deficiency in method validation is the underutilization of the developed methods in other labs. As of yet, no outside laboratories have adopted the exact methods developed here for analysis of chlorinated solvents or either surfactant, and thus true validation tests of the newly developed methods were absent.

4.1.1. Surrogate Spikes

By spiking each field sample with a known amount of 4-bromofluorobenzene, we were able to correct for potential variations in volatile analytes due to instrumental drift or

sample preparation. A correction factor (*CF*) was calculated for each sample in the following manner:

$$CF = \frac{\text{Actual (4-BFB)}}{\text{Expected (4-BFB)}} \qquad \textbf{(4.1)}$$

In the equation, Actual (4-BFB) represents the 4-BFB concentration quantified analytically, and Expected (4-BFB) equals the 4-BFB concentration expected based on the concentration and added volume of the 4-BFB spiking solution. After a *CF* was calculated for each sample, concentrations for each chlorinated solvent were then corrected by the following equation:

$$\text{Corrected (VOC)} = \frac{\text{Actual (VOC)}}{CF} \qquad \textbf{(4.2)}$$

Assuming that the behavior of 4-BFB during sample analysis roughly reflects that of PCE, TCE, and c-1,2-DCE, dividing reported chlorinated solvent concentrations by the calculated *CF* will result in corrected values that are more representative of the original solvent concentrations in field samples. The average *CF* of all field samples calculated from 4-BFB recovery was 0.918 with a standard deviation of 0.043. Although variations in surrogate recovery might have been anticipated in different stages of the study due to the presence of brine and/or surfactant, 4-BFB recovery remained fairly constant in the majority of samples between Stages 4 and 9, which included brine injection (Stage 6) and surfactant injection (Stage 7) as shown in Figure 4.1. The average *CF* calculated in Stages 4-9 was similar to the overall study average at 0.914, but the standard deviation dropped to 0.021. The only major change was seen in Stage 10, where surrogate recovery increased drastically, ultimately resulting in an average *CF* of 1.116. This means quantified 4-BFB concentrations routinely exceeded the concentrations expected during this stage. This change in surrogate recovery was not altogether surprising, as the increase coincided with HPLC autosampler

failure and injection volumes were highly variable. Obviously, this could be a major source of not only the increase in average recovery, but also the variability increase seen here as the standard deviation for surrogate recovery in Stage 10 was 0.190, which is over 4 times greater than the standard deviation for surrogate recovery over the entire study.

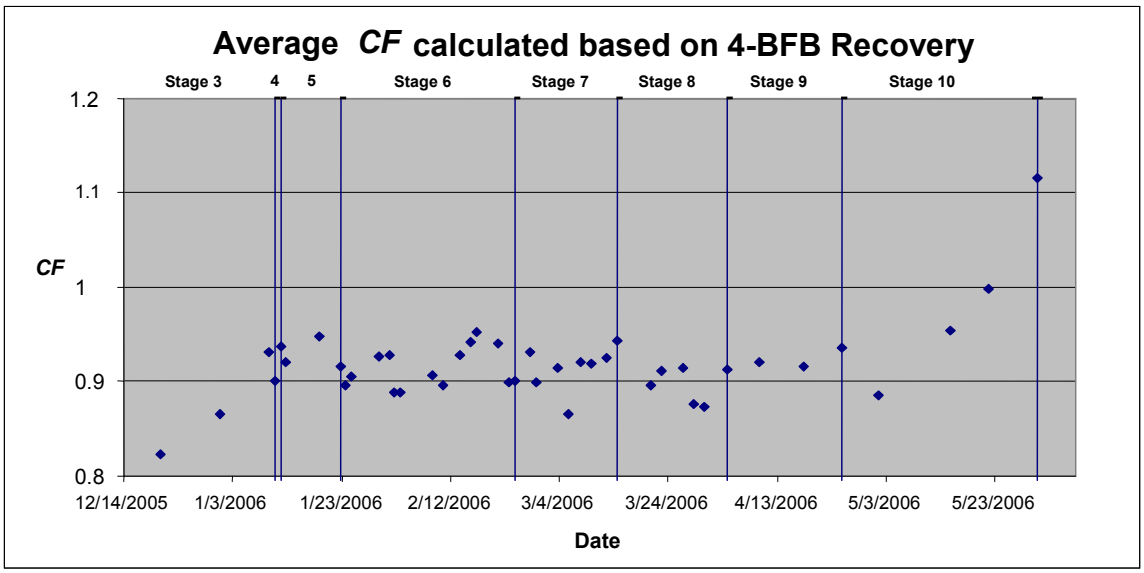


Figure 4.1: Average recovery of surrogate 4-BFB for each sample set during the study.

4.1.2. Check Standards

Check standards made up in 50:50 IPA and DI water of known concentrations for all analytes were included every ten samples in each sample set. Initially, check standards were prescribed with the intention of measuring any instrumental drift affecting detection that may arise during sample runs. However, it quickly became apparent that significant VOC losses were occurring throughout sample sets. Check standards run immediately after instrument calibration returned an average recovery of 101.5% ± 5.3% for PCE, 100.3% ± 8.0% for TCE, and 105.5% ± 2.2% for c-1,2-DCE, which are all well within the set control limits of 85 and 115%. In contrast, VOC losses frequently greater than 15% occurred in check standards quantified after 20-30 sample runs. This trend is not a major surprise, because as

the time between HPLC sample preparation and analysis increased, the total amount of solvent volatilized should have increased as well. Furthermore, with sample run times of 35 minutes there was a major difference in the time for volatilization to occur between Sample 1 and Sample 30. Still, volatilization alone was not likely to cause these drops in recovery. As stated before, once diluted in IPA, samples were stable for more than two weeks. The losses are thought to be caused primarily from sorption of chlorinated solvents onto the plastic HPLC vial caps once volatilized, which served as a sink for chlorinated solvents in the sample. PCE is known to sorb extensively to plastic surfaces, and if this method is used in the future, plastic vial caps should be replaced with a surface that chlorinated solvents do not preferentially sorb to.

With this in mind, check standard results were also used to measure percent recovery of each VOC relative to 4-BFB recovery, because ultimately each field sample was quantified based on the *CF* calculated from 4-BFB recovery. By calculating a recovery for PCE, TCE, and c-1,2-DCE relative to 4-BFB, we can then estimate how well *CF'*s functioned in yielding accurate VOC concentrations in field samples. Overall average PCE, TCE, and c-1,2-DCE recoveries from check standards relative to 4-BFB were 98.4% ± 5.9%, 99.5% ± 7.5%, and 99.5% ± 2.7% respectively. From these results, we can deduce that 4-BFB recoveries from check standards reflect the recoveries for all chlorinated solvents in question very well. However, this particular surrogate more closely mimics TCE and c-1,2-DCE behavior in this situation than PCE, with which a prior study agrees (Schumacher 1997). The Henry's Law Constant (K_H), an indicator of volatility, for 4-BFB (0.014 L*atm/g) is less than the K_H for all chlorinated solvents, but more closely resembles that of c-1,2-DCE (0.049 L*atm/g) than TCE (0.075 L*atm/g) and PCE (0.107 L*atm/g). However, the octanol-

water partitioning coefficient (K_{OW}) for 4-BFB (1200), which should be an indicator of sorption tendencies, is on the same order of PCE (2500), and is much higher than TCE (260) or c-1,2-DCE (200) (Toxnet 2004). Recovery issues for chlorinated solvents were probably caused by a combination of these physical forces.

Also, because volatilization and sorption are rate limiting processes, relative recoveries of each analyte should change with time. Because PCE was the primary contaminant, the most important recovery relationship for this particular study is between PCE and 4-BFB. The relative recovery of PCE to 4-BFB in check standards is shown over time in Figure 4.2. From this plot, it is evident that relative PCE recovery steadily decreased with increasing number of sample runs.

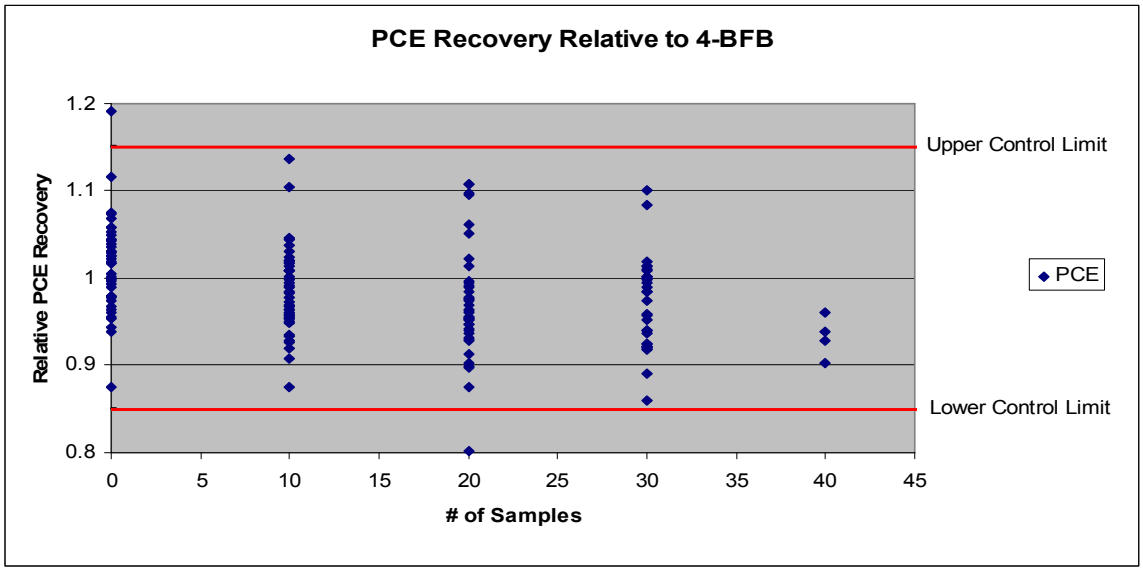


Figure 4.2: PCE recovery relative to 4-BFB of check standards vs. sampling time during run.

Although 98.1% of PCE check standards fell within the control limits of 85% and 115% of expected recovery, the average recovery decreased from 101.5% at the beginning of sample sets to 93.3% after 40 samples have been previously run. Consequently, analytical corrections based solely upon 4-BFB recovery may not be accurate for samples analyzed later in very large sample sets.

One method of avoiding such a problem is to generate a linear regression from this relationship for each chlorinated compound, and subsequently use the linear equation as a correction factor for quantification. In Figure 4.3, the average check standard recoveries relative to 4-BFB after 0, 10, 20, 30, and 40 sample runs for cis-1,2-DCE, TCE, and PCE are plotted, and linear regressions fitted for each compound to show correlation between relative recovery and check standard sequence within a sample set. The figure shows that relative recovery of c-1,2-DCE ($R^2 = 0.5927$) increased with sample run length, TCE ($R^2 = 0.3612$) recovery decreased very slightly with run length, and PCE ($R^2 = 0.9450$) recoveries dropped the most over time. The high R^2 value for PCE does imply that there was a significant correlation between PCE recovery relative to 4-BFB and the sequence in which samples were run. Although the results of this study were not treated as such, fitting regressions like this one to correct for VOC losses is likely a more rigorous method than simply generating *CF*'s based on surrogate recovery. It can also be concluded that 4-BFB best served as a reference compound for TCE in this field study.

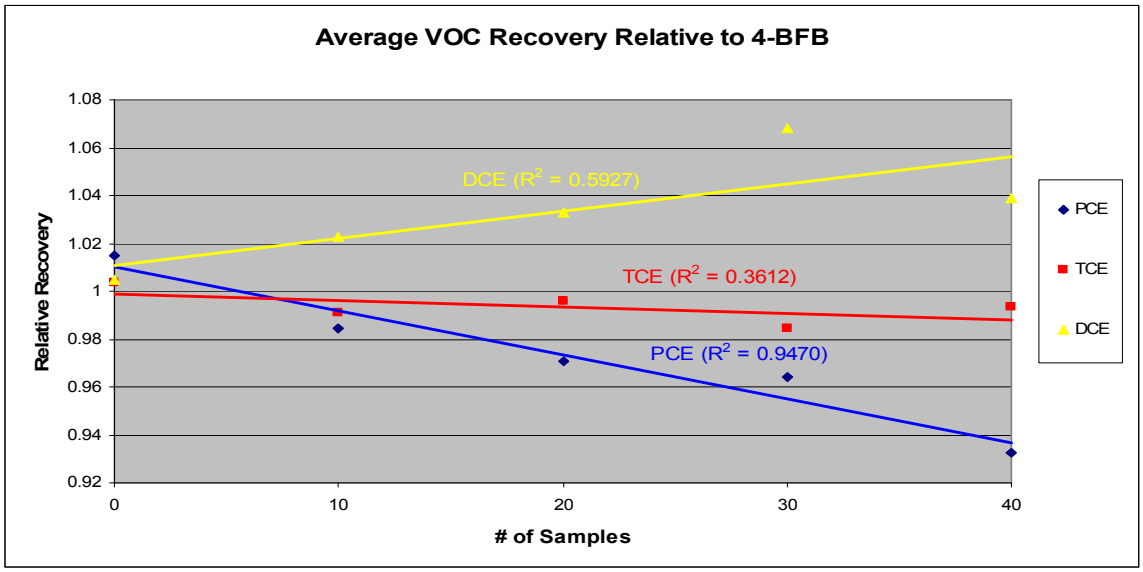


Figure 4.3: Average recovery for PCE, TCE, and c-1,2-DCE relative to 4-BFB over time and fitted linear regressions for each compound.

While chlorinated compound check standards were used to validate 4-BFB as a reliable surrogate spike, surfactant check standards served to measure variations in detection due to instrumental drift. Both surfactants are non-volatile species, and thus surfactant check standards should have given precise results unless variations occurred due to HPLC instrumental problems. Though only MA-80 checks were performed prior to the surfactant flush due to MA-80 already in the system from a prior study (Childs 2006), check standards for both surfactants were included for a majority of the study. Overall, MA-80 checks gave results on average 101.7% ± 8.2% of expected values, while Triton X-100 checks were on average 98.4% ± 5.9% of expected values. As expected, recoveries for neither surfactant were dependent upon their sequence in sample runs, which is conveyed in Figures 4.4 and 4.5 below.

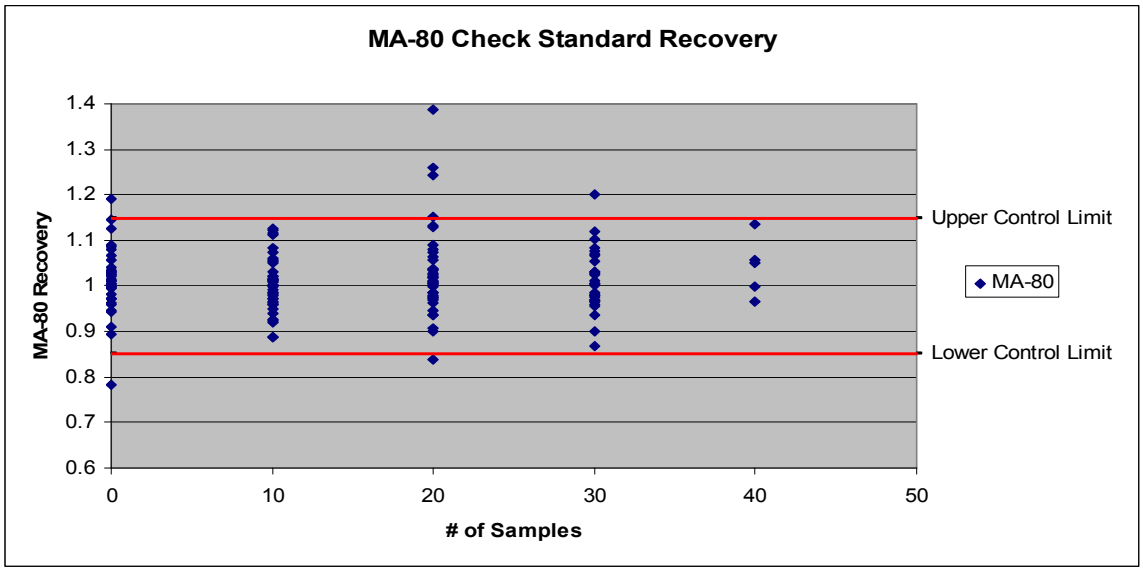


Figure 4.4: MA-80 check standard recovery vs. sequence in sample run.

Due to the consistency of surfactant recovery from check standards throughout sample sets, it can be inferred that instrumental drift during sample sets did not significantly affect analyte detection. Most of the surfactant checks fell within the control limits specified of 85% and

115%, which are the red lines shown in Figures 4.4 and 4.5, of expected concentrations with 98.7% of MA-80 and 93.0% of Triton X-100 checks within these limits. Most outliers occurred late in Stage 10 when the HPLC autosampler was malfunctioning. However, surfactant concentrations were very low at this point in the study, and should not have had major effects on the mass balances calculated.

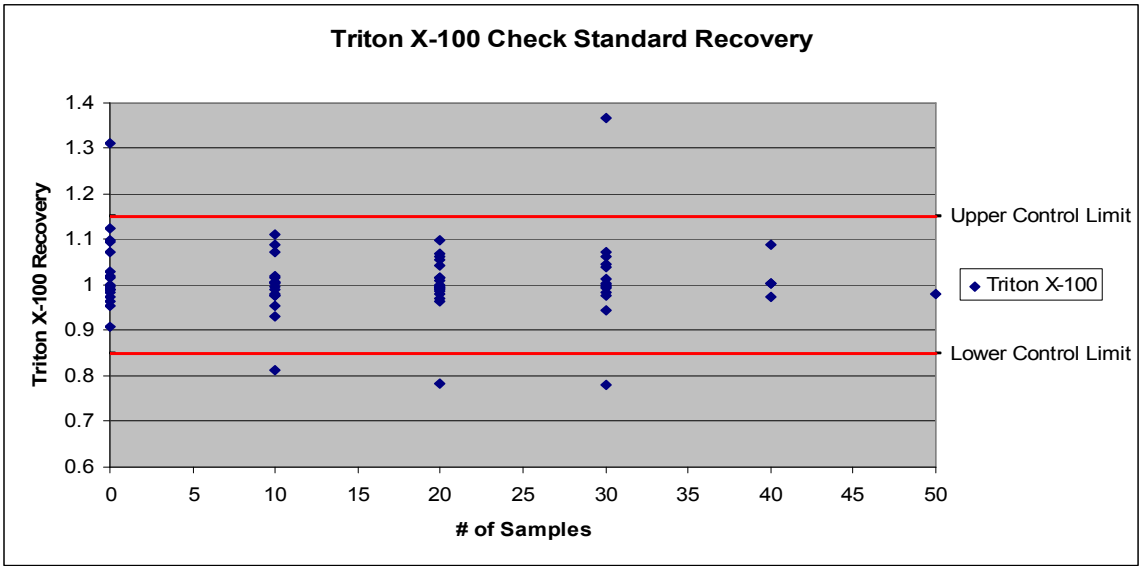


Figure 4.5: Triton X-100 check standard recovery vs. sequence in sample run.

4.1.3. Lab Spikes

Lab spikes prepared at UNC consisted of a 30 mL VOA vial filled with DI water that was spiked with a known volume between 0.1 and 1.0 mL of a separately prepared 5,000 mg/L PCE stock standard made up in IPA immediately before sample preparation. The spiked samples were then prepared and analyzed by the exact method used for field samples. Thus, PCE concentrations in lab spikes were corrected based on surrogate recovery as well. In general, a lab spike was run every 10 samples, although in some sample sets lab spikes were not run due to time constraints. The purpose of these samples was to observe any major

PCE recovery issues that arise from sample preparation steps, and to see whether PCE losses were similar to those observed in check standards for samples analyzed later in sample sets.

The overall average PCE recovery from lab spikes after correction was 101.2% ± 6.8% of expected values, a significant improvement over the average uncorrected recovery of 90.6% ± 6.5%. Furthermore, 96.7% of lab spikes were within 15% of expected PCE concentrations once corrected, while only 85.1% of raw results fell within the same range. PCE recovery from lab spikes versus the sequence in sample sets is shown in Figure 4.6 with upper and lower control limits shown in red. A trend similar to that in PCE check standards was also discernible in lab spikes, as PCE recovery normalized by the correction factor decreased for spikes run later in the sample set. Figure 4.7 shows PCE recovery in lab spikes after 10, 20, and 30 samples analyzed, and the calculated linear regression from that relationship. The high R^2 value of 0.9762 of the fitted regression further supports the potential use of a linear regression to more accurately calculate PCE concentrations in field samples.

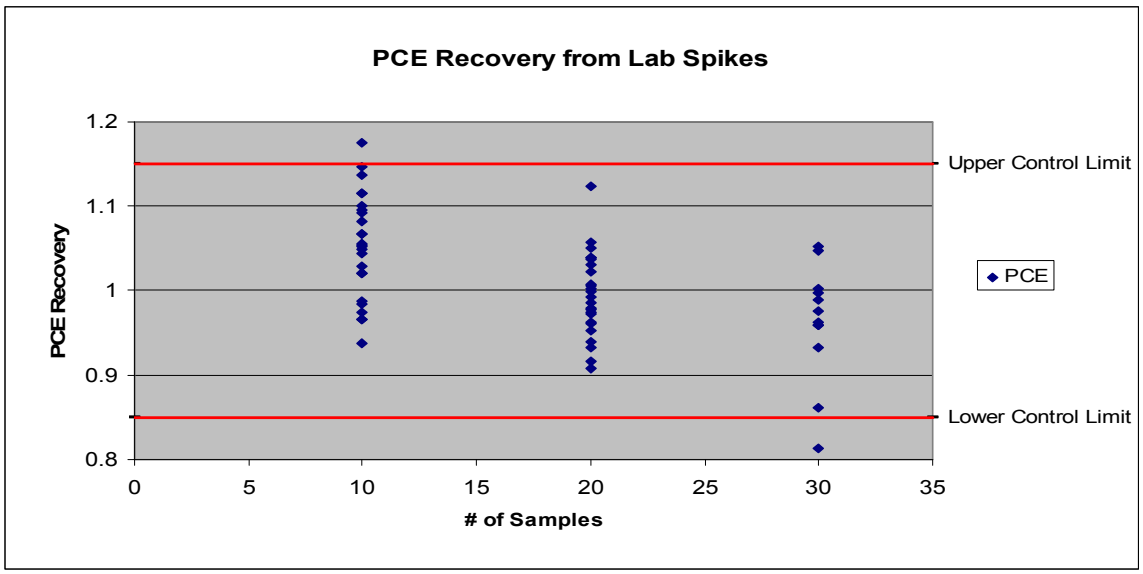


Figure 4.6: Corrected PCE recovery from lab spikes.

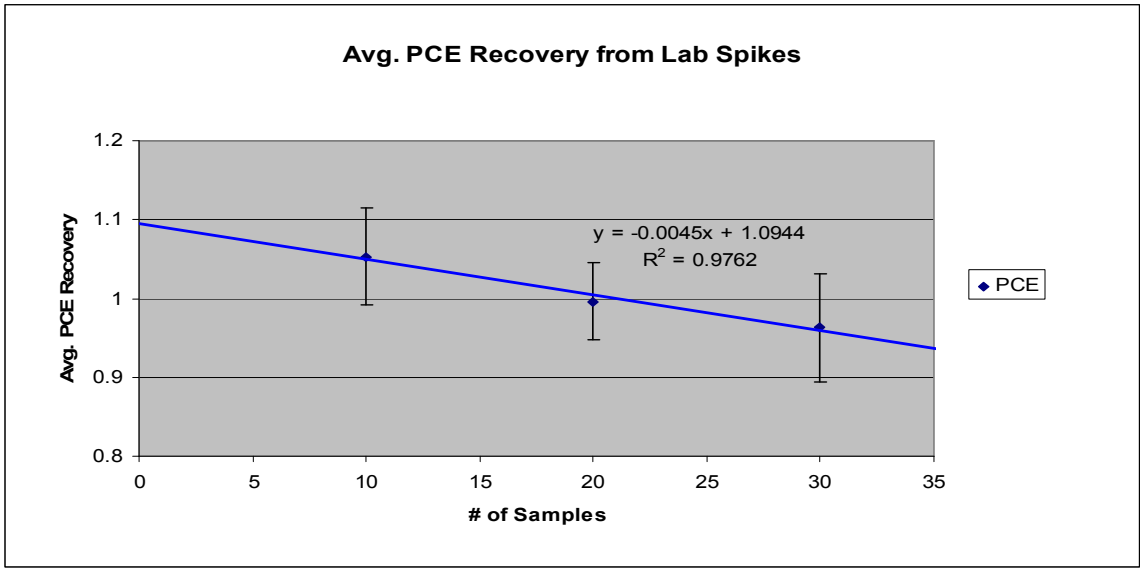


Figure 4.7: Average PCE recovery from lab spikes after 10, 20, and 30 samples, and the fitted linear regression.

Predictions from the regression in Figure 4.7 yielded a steeper slope than in the regression calculated from check standard recoveries. PCE recoveries from lab spikes after 10 samples were on average 1.05 times the surrogate recovery, and yielded higher recovery than 4-BFB in 76% of lab spikes ran after 10 samples. This trend, which is exclusively seen in lab spikes, may stem from the surrogate spike itself. Unlike check standards, 4-BFB was injected into lab spikes during sample preparation similar to field samples, and this supplementary step increases the chance of error in results. Furthermore, upon injection into lab spikes, the surrogate often formed a white residue that clung to the sides of the vial, making it difficult to completely dissolve the injected 4-BFB into the sample. This observation is supported by the fact that the average 4-BFB recovery in lab spikes was 3.7% lower than the overall average 4-BFB recovery, which could explain the 5 percent increase in PCE recovery seen in initial lab spikes. The resistance of 4-BFB to dissolve in lab spikes may have been due in part to the sample matrix used for lab spikes. Whereas field samples contained a complex mixture of chlorinated solvents, alcohols, cyclodextrin, brine, and

surfactant, lab spikes contained only DI water, which may not have been as conducive to 4-BFB dissolution. However, recovery problems with 4-BFB did not occur in blank field samples, which contained only DI water as the sample matrix, so the sample matrix did not appear to be the problem. Also, lab spikes were prepared with a slightly different type of vial and cap, and though these vials were recommended for use with VOC's and Teflon lined caps were used, the surrogate was observed to cling to the walls more often in these vials than in field sample vials. In retrospect, a uniform type of vial and cap should have been used for all samples analyzed.

4.1.4. Field, Trip, and Spiked Blanks

Field, trip, and spiked blanks were prepared at DNTS and one of each was shipped with every delivery of samples to UNC. Field and trip blanks were nothing more than a VOA sample vial completely filled with DI water. The two differed only in that field blanks were opened to the air during the time in which field samples were collected for that shipment, whereas trip blanks remained closed after the vials were filled. Thus, the purpose of field blanks was to measure any contamination that occurred due to air exposure near the Test Cell, and trip blanks measured any contamination that occurred during shipping.

Neither trip blanks nor field blanks ever contained analytes above method detection limits. Although some degree of contamination should occur in field blanks due to air exposure, the amount of contamination was too small to adversely affect analyte quantification in field samples. Both types of samples also served to show that cross contamination among samples did not occur to any measurable degree during sample preparation or HPLC analysis. Figure 4.8 shows a sample chromatogram typical of field and trip blanks analyzed during the experiment.

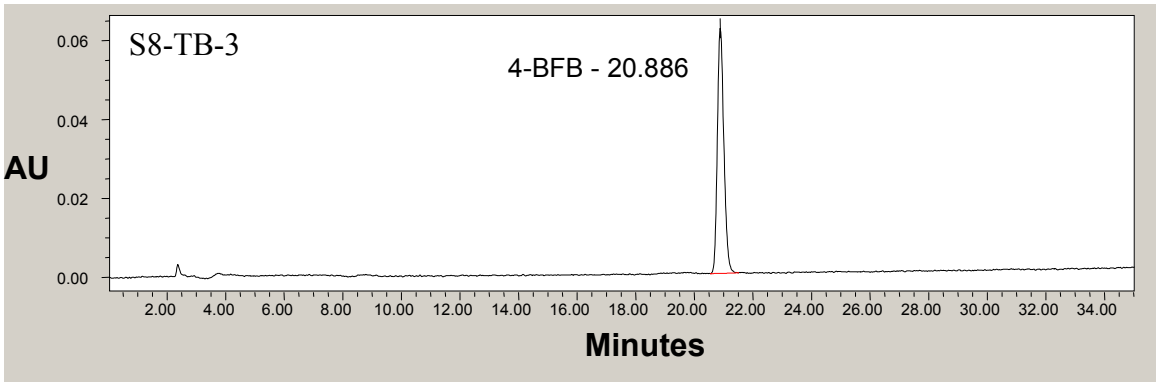


Figure 4.8: Sample chromatogram of a trip blank in Stage 8.

Spiked blanks as the name implies were samples of DI water spiked with varying amounts of a PCE stock standard made up in methanol. These samples were similar to lab spikes prepared at UNC, but the PCE target concentration was unknown to the analyst. Therefore, spiked blanks not only revealed PCE losses from sample preparation, but also ensured that reported results were unbiased in that PCE concentrations were unknown. In addition to any PCE losses suffered from sample preparation and analysis, spiked blanks also accounted for losses from shipment and prolonged storage at UNC if necessary.

The average PCE recovery in spiked blanks after correction was 86.0% ± 10.1%, which was within the control limit of 85% recovery. Still, the high standard deviation shows that PCE recovery was highly variable within the spiked blanks. This variability was in part due to the fact that several spiked blanks were of PCE target concentrations within a factor of 10 of the method detection limit, and as concentrations approach detection limits, variability inherently increases. If those samples with very low PCE concentrations are removed, the average recovery decreased slightly to 85.2% but the standard deviation is reduced to 8.2%.

Corrected PCE recovery from Spiked Blanks is shown graphically in Figure 4.9.

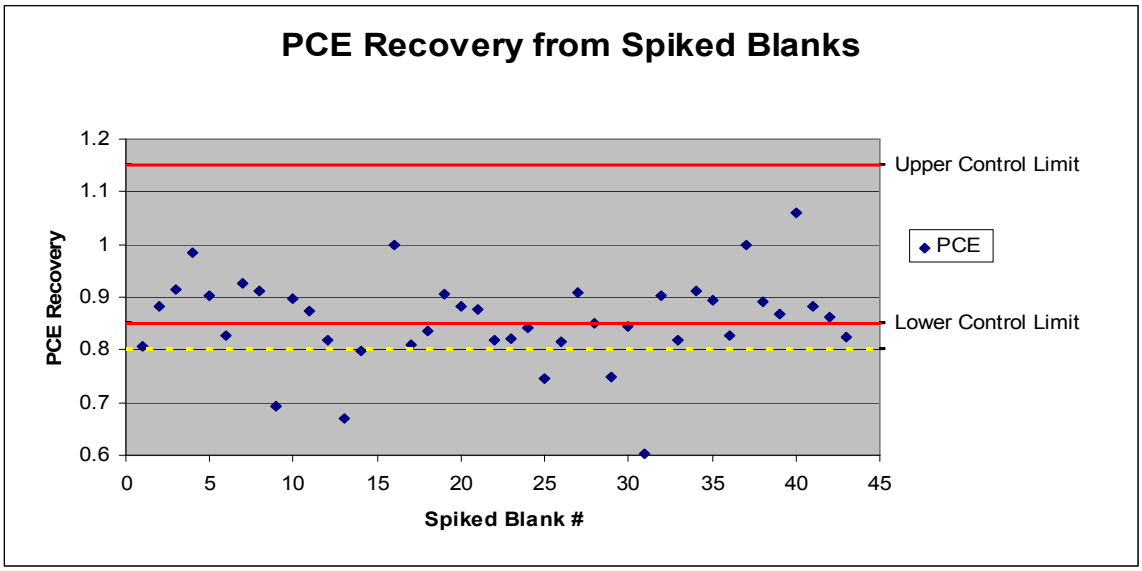


Figure 4.9: PCE recovery from spiked blanks throughout the study. The dotted line represents 80% recovery.

Only 58.1% of the samples gave results greater than 85% of expected PCE concentrations after correction based on surrogate recovery, which was a significant discrepancy from recovery seen in lab spike samples. However, spiked blanks provided recoveries greater than 80% of expected concentrations consistently as 88.4% of spiked blanks achieved at least this level of recovery.

The difference in results between PCE recovery in spiked blanks and lab spikes should be expected to some extent. Although both types of sample were prepared in a similar way by adding small amounts of a PCE stock standard into DI water in volumetric flasks, the stock standard used for spikes was made up in methanol, while the stock standard used for lab spikes was made up in IPA. Though this seems like a small difference, initial cosolvent screen tests reported lower PCE recovery for samples diluted in methanol than in IPA. Also, whereas lab spikes were immediately poured into sample vials, prepared, and analyzed, spiked blanks contrarily were immediately poured into sample vials after preparation, but then had to be shipped and possibly stored for up to one week at UNC before dilution in IPA.

The total elapsed time between the making of spiked blanks and dilution with IPA, typically 10 days, could have led to VOC volatilization into any existing vial headspace and potentially sorption onto the Teflon lined septa as well. Although the vials and septa were thoroughly rinsed with IPA during sample preparation, rinsing may not have been sufficient to collect all PCE if extensive sorption had occurred. In hindsight, lab spikes and spiked blanks should have been prepared in the same types of vials with similar stock standards in order to achieve better agreement.

4.1.5. Duplicate Samples

Duplicate samples were field samples that once collected were subsequently split into two separate samples. The purpose of duplicates was to measure the precision of the analytical methods by comparison of the duplicate results. One duplicate sample set was included for roughly every 10 field samples, and it was unknown to the analyst which field samples were accompanied by duplicates to eliminate any potential bias.

Once duplicate samples were revealed, the relative percent difference (%*RPD*) was calculated for all analytes in each duplicate sample pair by the following equation:

$$\%RPD = \left(\frac{|X1 - X2|}{\overline{X}} \right) \times 100\% \qquad \textbf{(4.3)}$$

Here, $X1$ and $X2$ represent the analyte concentration in each duplicate sample, and $\overline{X}$ equals the average of $X1$ and $X2$. To summarize, 78.1% of PCE, 71.4% of TCE, 75.0% of c-1,2-DCE, 67.5% of MA-80, and 78.4% Triton X-100 duplicate sample concentrations displayed a %*RPD* less than 15% between duplicate pairs, which is used to indicate method precision. Ideally, a higher %*RPD* would be attained for all analytes, but there are several possible explanations for the discrepancies reported between duplicates. For example, all analytes of

interest with the exception of PCE were near or below method detection limits at some point in the study, which undoubtedly led to increased %*RPD* between duplicates. For example, if duplicates having concentrations within a factor of 10 of the MDL for a particular analyte are eliminated from the sample pool, 78.8% of TCE, 79.1% of c-1,2-DCE, 79.0% of MA-80, and 82.5% of Triton X-100 concentrations in duplicate samples yield %*RPD* values less than 15%. This point is further emphasized in Figure 4.10, which depicts the %*RPD* calculated for each surfactant in duplicate samples during each stage. Stages 1 through 5 are not shown because very few duplicate samples were taken during this part of the study. In Stage 6, prior to surfactant injection, MA-80 was present at very low concentrations, and %*RPD* fluctuated greatly. Then, when large concentrations of both surfactants are injected in Stage 7, %*RPD*s decreased sharply as 93.9% of MA-80 and 96.8% of Triton X-100 duplicate results were within 15% during Stage 7. Low %*RPD* values persisted until the middle of Stage 8, when surfactant concentrations in effluent samples quickly decreased. This decrease in concentrations was also the most probable cause for large %*RPD* values in Stages 9 and 10, although HPLC autosampler problems likely contributed as well.

A similar pattern can be seen in duplicate PCE results from Figure 4.11, although a higher number of duplicate pairs possess a %*RPD* less than 15%, and %*RPD* variability was not as large as for the surfactants. Nonetheless, the large drop in PCE effluent concentrations was presumed to be the primary cause of increased average %*RPD* values, going from over 90% within the 15% limit in Stages 6-7 to under 60% in Stages 8-10.

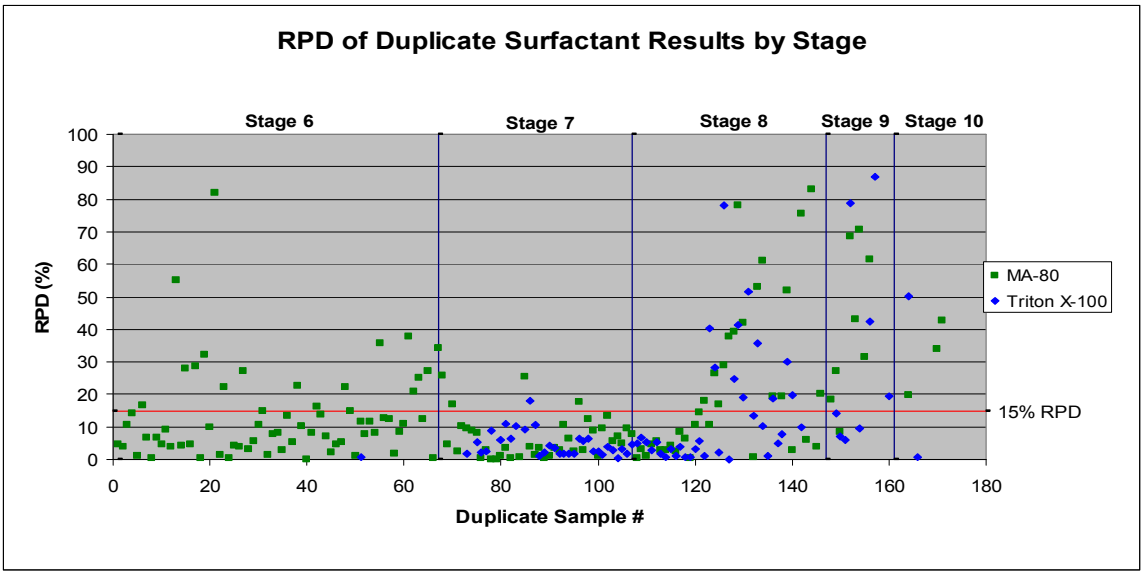


Figure 4.10: Relative percent difference of MA-80 and Triton X-100 concentrations in duplicates divided into stages.

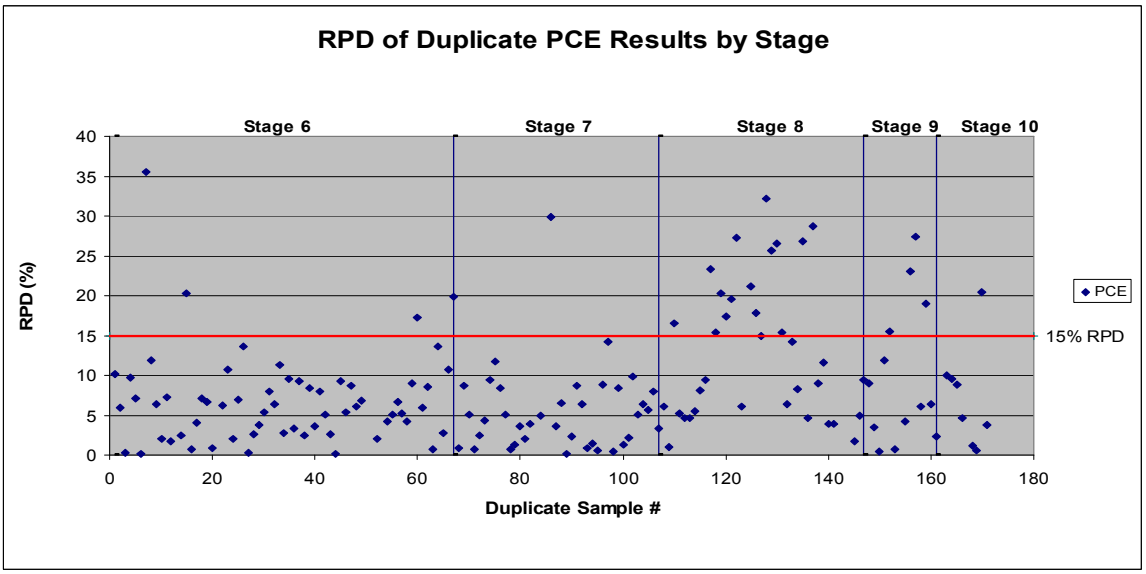


Figure 4.11: Duplicate results for PCE divided into stages.

4.1.6. Split Samples

In addition to duplicate samples sent to UNC, 10% of all field samples were analyzed by an outside lab for chlorinated solvents, MA-80, and Triton X-100. Although analyzed by completely different methods than the ones described previously, split samples served as a check of accuracy for the data generated by the developed HPLC methods.

All split samples were analyzed for chlorinated solvents on site at DNTS by a GC headspace sampling method coupled with ECD detection, which is a vastly different method than the one used at UNC. Samples analyzed by DNTS reported on average 18.5% higher recovery for c-1,2-DCE, 485% for TCE, and 17.2% for PCE. For c-1,2-DCE analysis, 61.1% of all split samples showed less than 15% difference between the pairs, TCE split sample concentrations were only within 15% of each other 2.4% of the time, and 39.3% of PCE concentrations in split samples showed less than 15% difference. The agreement between DNTS and UNC samples was very poor throughout the study for TCE. However, split samples reported good agreement for PCE in certain periods of the study, and also trends exist in the data that may help explain the apparent lack of agreement between samples analyzed by DNTS and those by UNC.

TCE concentrations were very low throughout the study with a maximum concentration of 3 mg/L, which partially explains the especially poor agreement for TCE between split samples. In addition, split samples taken early in the study were collected as separate samples rather than taken as a single sample that was later split. Samples collected in this manner are not true split samples, and can lead to higher variation. The % difference calculated for these split samples not only reflects the variation between the two analytical methods, but also the inherent variability due to sampling in small volumes from a spatially heterogeneous system. Only 46.7% of c-1,2-DCE concentrations and 18.2% of PCE concentrations were within 15% for split samples collected as separate samples.

The % difference calculated between split samples varied greatly in different stages of the study as well. In Stage 6, 67.3% of c-1,2-DCE results and 64.3% of PCE in all split samples fell within the control limit of 15%, showing slightly better agreement for c-1,2-

DCE than in Stage 7 or Stage 8 where 62.5% and 57.9% were within the control limit respectively, but much better agreement for PCE as only 20.3% of split samples were within the control limit for Stage 7 and 25.8% for Stage 8. Because these variations between stages were more apparent for PCE, the % difference between split samples for PCE is plotted below in Figures 4.12 and 4.13 based on the stage in which the sample was collected for effluent and waste samples. In both figures, % difference is not calculated as an absolute value as for *%RPD* calculations so it can be shown whether DNTS or UNC yielded higher sample recovery represented by positive or negative % difference values respectively. Also, Stages 1-5 and 9-10 are not included because very few split samples were collected in the earlier stages, and split sample data has not yet been compiled from the later stages. A potential reason for the increase in c-1,2-DCE differences is that c-1,2-DCE concentrations steadily decrease from Stage 6 to Stage 8 to levels approaching the method detection limit. Concentrations at these levels will increase variability in results.

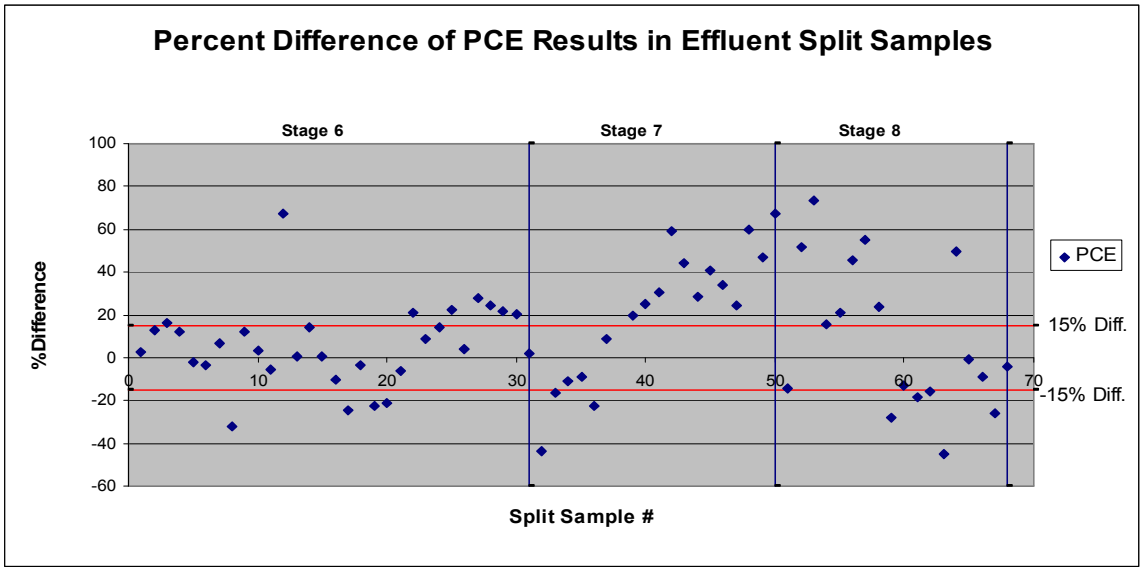


Figure 4.12: Calculated %*RPD* between split effluent samples analyzed by UNC and DNTS.

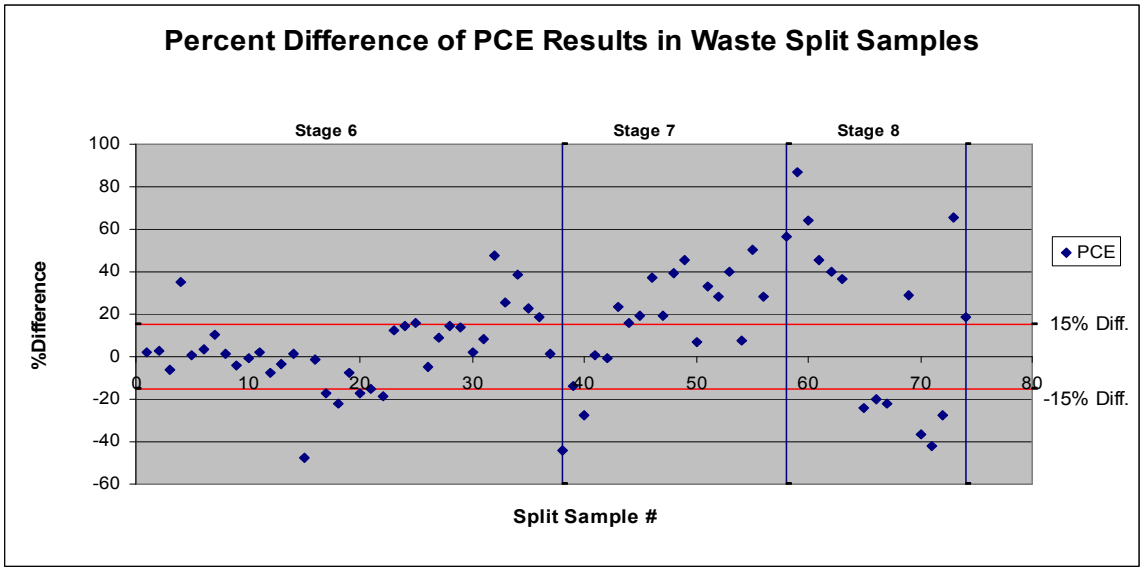


Figure 4.13: %*RPD* between split waste samples analyzed by UNC and DNTS.

In contrast, PCE waste and effluent concentrations increased sharply in Stage 7, and although they dropped in Stage 8, PCE levels were well above detection limits for all of Stage 7 and 8. Thus, there must be some other explanation for the increased variability of %*RPD* for PCE in split samples likely stemming from the different method used for VOC analysis at DNTS.

The GC headspace method utilized by DNTS is dependent upon the air-water partitioning behavior of each analyte for quantification, and this behavior will change with the addition of components to the system that decrease PCE solubility such as brine, or increase solubility such as surfactants. Therefore, we should expect increased DNTS sample recovery relative to UNC in Stage 6 from an increased K_H due to brine injection, followed by decreases in Stage 7 due to surfactant addition and a resultant decreased K_H. However, the presence of brine in Stage 6 did not seem to affect PCE recovery in DNTS samples as split samples in this stage displayed the best agreement of any period in the study for both effluent and waste samples. Plus, DNTS recoveries did not increase in Stage 6 over earlier stages as expected, and in fact they decreased relative to recoveries seen in UNC samples from an

average difference of 14.0% greater in DNTS samples in Stages 1-5 to only 2.8% greater in all Stage 6 samples.

The variability of split samples increased dramatically in Stage 7, but it should also be noted that samples analyzed by DNTS yield consistently higher results than those analyzed at UNC throughout Stage 7 and the beginning of Stage 8. This trend is the opposite of what was originally expected. PCE recovery in DNTS samples should theoretically have decreased due to decreased K_H constants in the presence of surfactant. Nevertheless in samples containing greater than 5000 mg/L total surfactant, DNTS consistently reported greater than 20% higher concentrations relative to UNC analysis in split samples. This trend is illustrated in Figure 4.14. It can also be inferred that at surfactant concentrations less than 1000 mg/L, neither DNTS nor UNC analysis reports consistently higher values for PCE.

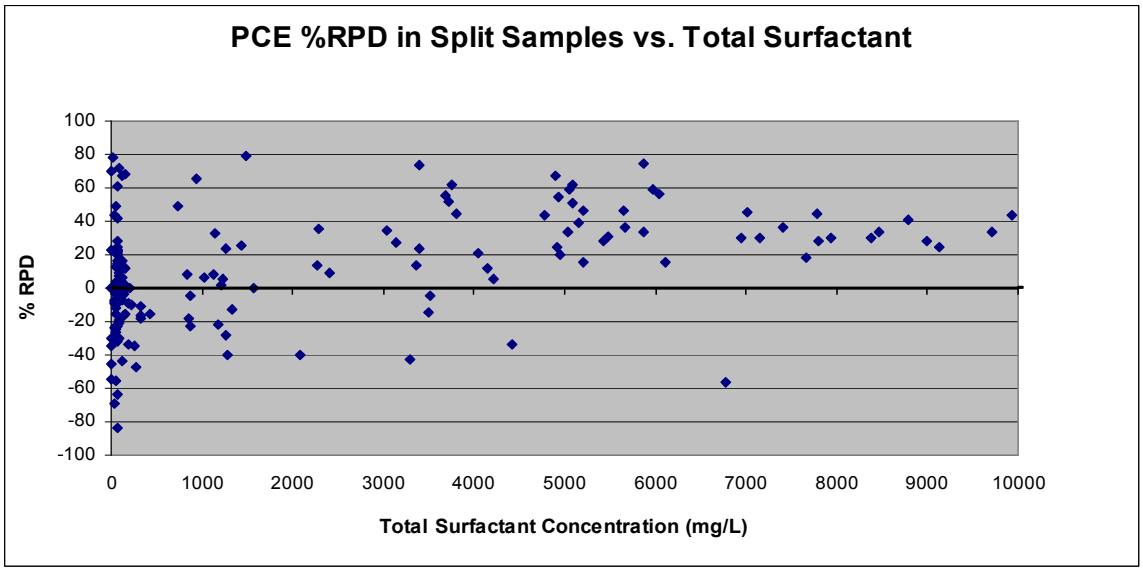


Figure 4.14: % difference of PCE concentrations in split samples against MA-80 and Triton X-100 concentrations combined.

This trend is somewhat puzzling as we expected the opposite to occur in samples with high surfactant concentrations. A possible explanation that has been discussed is the potential

for surfactants to cause interference with PCE detection, which could increase apparent PCE concentration in DNTS samples. In an earlier remediation study conducted at DNTS, MA-80 was determined to cause interference with PCE detection. Though both surfactants were screened beforehand to test their compatibility with the headspace method utilized, at repeated runs with very high MA-80 concentrations, interference may again have become a problem resulting in abnormally high apparent PCE concentrations for samples analyzed at DNTS.

Split samples are to be analyzed for both MA-80 and Triton X-100 by the ChemCore at UNC by an HPLC method similar to the ones described previously. At this time, the samples have not yet been analyzed and/or reported. Hence, no data comparison for surfactant split samples can be completed at this time.

4.2. Experimental Results

4.2.1. PCE Recovery

Cumulative recovery of all TCVOC's is shown throughout the study in Figure 4.15. Of the estimated 160 kg of PCE in Test Cell #3 at the beginning of the study, approximately 6.24 kg of total chlorinated solvents were recovered in the aqueous phase effluent, which translates to only 3.9% removal of PCE through solubilization. Breaking it down by individual species, 4.06 kg of this total was removed as PCE, 0.02 kg as TCE, and 2.16 kg as c-1,2-DCE. These results, corrected via surrogate recovery, displayed an increased recovery of 4.3% for TCVOCs, 4.8% for PCE, 5.3% for TCE, and 4.6% for c-1,2-DCE, over the recoveries calculated from raw data. Although the recovery increases were insignificant for the current study, where large amounts of PCE remain in the system, such corrections could

prove substantial in calculating accurate recoveries for studies with low initial contaminant levels, or in studies that attain residual contaminant concentrations approaching MCL levels.

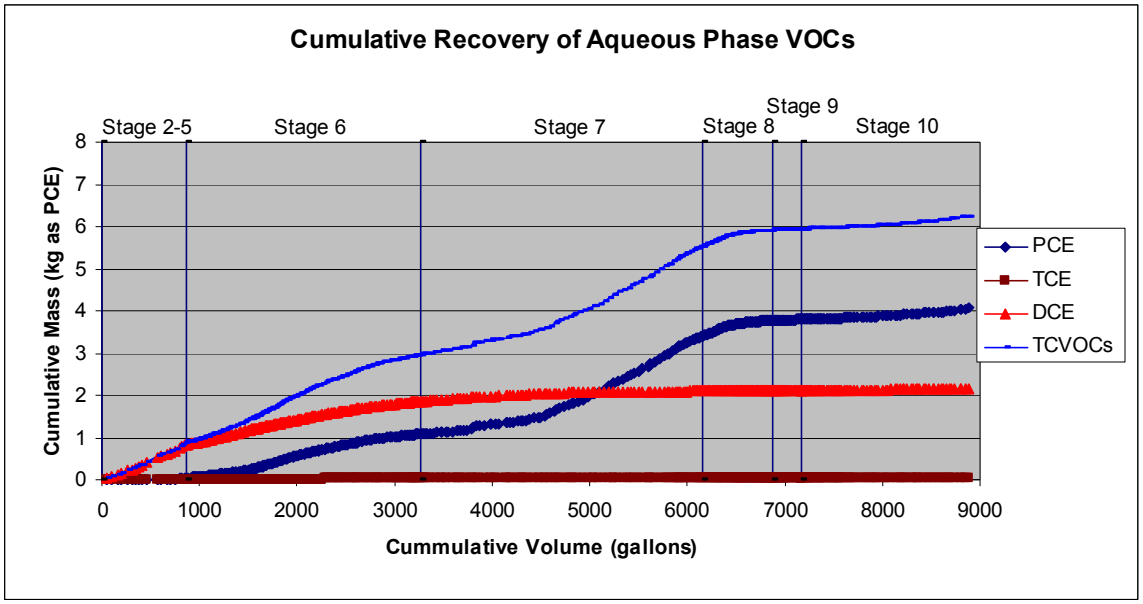


Figure 4.15: Estimated cumulative recovery of PCE, TCE, c-1,2-DCE, and TCVOCs from surrogate corrected data throughout the study.

Though much lower than originally expected, the PCE recovery calculated from aqueous phase concentrations does not reflect the vinyl chloride mass recovered in the aqueous phase, PCE removed through SVE techniques implemented in Stage 9, nor PCE removed as free-phase DNAPL during the study. Furthermore, it is believed that the initial estimate for PCE residual in the test cell of 160 kg was too high. This value was a very rough approximation made by adding the estimated PCE initially in the cell to what was added during Stage 4 in the study. A more thorough PCE mass balance for the study taking into account vinyl chloride recovery predicted from GC analysis as well as SVE and free-phase recovery will be completed in the future.

PCE spatial profiles generated from multi-level sampling (MLS) wells are highly variable based on location yet do show an interesting trend in local PCE concentrations throughout the cell. PCE concentrations of MLS wells sampled both prior to brine and

surfactant injection and after completion of the study are summarized in Table 4.1. While MLS samples taken at depths shallower than 12.0 m were significantly less, exhibiting an average decrease of 88.8% in local PCE concentrations, samples at or below 12.0 m all showed increases in PCE concentrations at the experiment's end. Overall, 61.1% of MLS depths sampled above 12 m before and after show decreases in PCE concentrations of greater than 90%.

MLS Well	Depth (m)	Conc. (1/10) mg/L	Conc. (6/4) mg/L	% Decrease
S10-112-2	11.20	67.5	5.9	91.2
S10-114-3	11.49	247.7	4.0	98.4
S10-114-4	11.79	608.9	69.7	88.6
S10-116-4	11.73	20.2	2.0	90.0
S10-121-2	11.00	219.0	2.5	98.9
S10-121-4	11.59	323.9	15.1	95.3
S10-123-4	11.64	4.0	0.7	83.1
S10-125-4	11.71	205.1	15.0	92.7
S10-132-4	11.79	197.8	6.1	96.9
S10-134-3	11.49	114.8	6.3	94.5
S10-134-4	11.79	4.3	1.0	76.3
S10-136-4	11.76	11.8	0.0	100
S10-141-2	11.02	172.1	0.8	99.5
S10-143-4	11.64	161.4	14.1	91.2
S10-145-5	11.97	17.0	0.4	97.6
S10-152-3	11.50	99.4	18.8	81.1
S10-152-4	11.80	7.6	2.3	70.1
S10-154-4	11.79	20.2	6.6	67.5
S10-161-4	11.59	48.9	12.9	73.6

Table 4.1: PCE concentrations at MLS depths < 12.0 m found prior to surfactant and brine injection and after study completion. The final column on the right represents the amount of decrease seen at each MLS sampled.

The decreases in PCE concentration at shallower MLS depths and the subsequent increases at depths of 12.0 m, which is near the confining clay layer of the cell, implies that PCE mobilization likely did occur throughout the cell to a some extent. PCE profiles throughout the study at 12.0 m for MLS wells where sufficient data existed are shown in Figure 4.16. At a majority of MLS locations sampled, greater than 90% local reductions in PCE were witnessed, which was predicted in previous experimental studies (Miller 2000, Johnson 2004). Presence of free-phase DNAPL in the bottom of the cell is evident during the final stages because of the very high PCE concentrations seen at 12.0 m throughout the cell

at this point. Still, despite the apparent mobilization of PCE, the experiment was largely unsuccessful at removing large amounts of free-phase PCE from the subsurface. This shortcoming may have been caused by increased fluid viscosity from surfactant and brine presence as well as gravitational forces that impeded horizontal movement of DNAPL towards extraction wells. Future research should address developing efficient removal techniques once the DNAPL phase is mobilized and collected at the brine barrier.

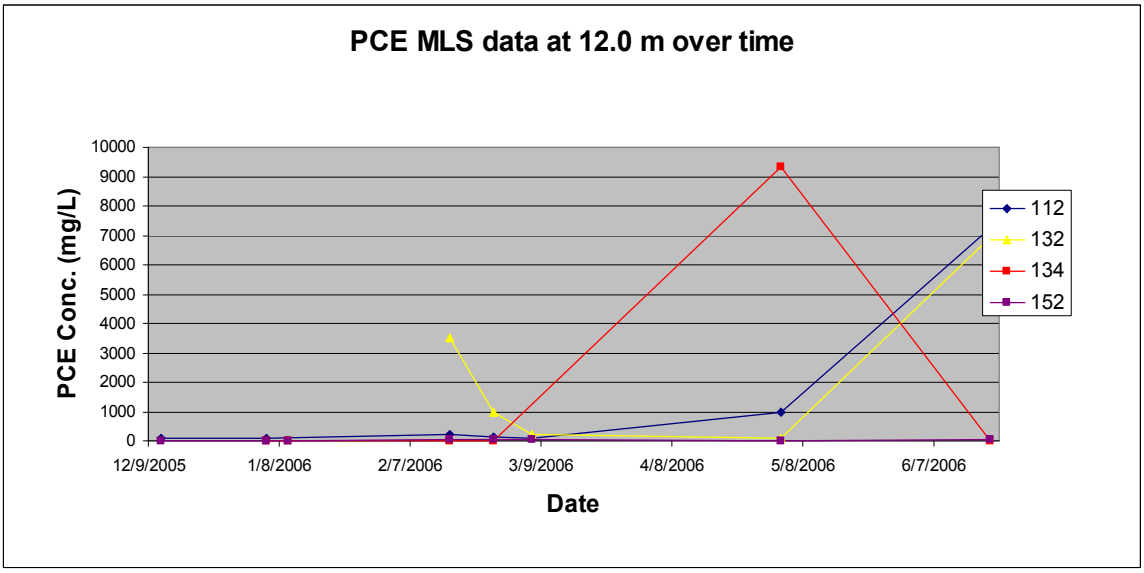


Figure 4.16: PCE Concentrations at 12.0 m for Select MLS Wells Over Time.

4.2.2. MA-80 and Triton X-100 Recovery

Based on analysis of the injected surfactant solution, approximately 119 kg of MA-80 and 146 kg of Triton X-100 were injected into Test Cell #3 during the study. Of the amounts added, 27.6 kg of MA-80 and 28.5 kg of Triton X-100 were recovered from the cell, which translates to 23.2% recovery of MA-80 and 19.4% recovery of Triton X-100 in the extracted fluid. Figure 4.17 depicts the cumulative recovery of each surfactant. No substantial recovery of either surfactant transpired after Stage 8, though based on effluent samples, a considerable amount of each surfactant remained in the cell.

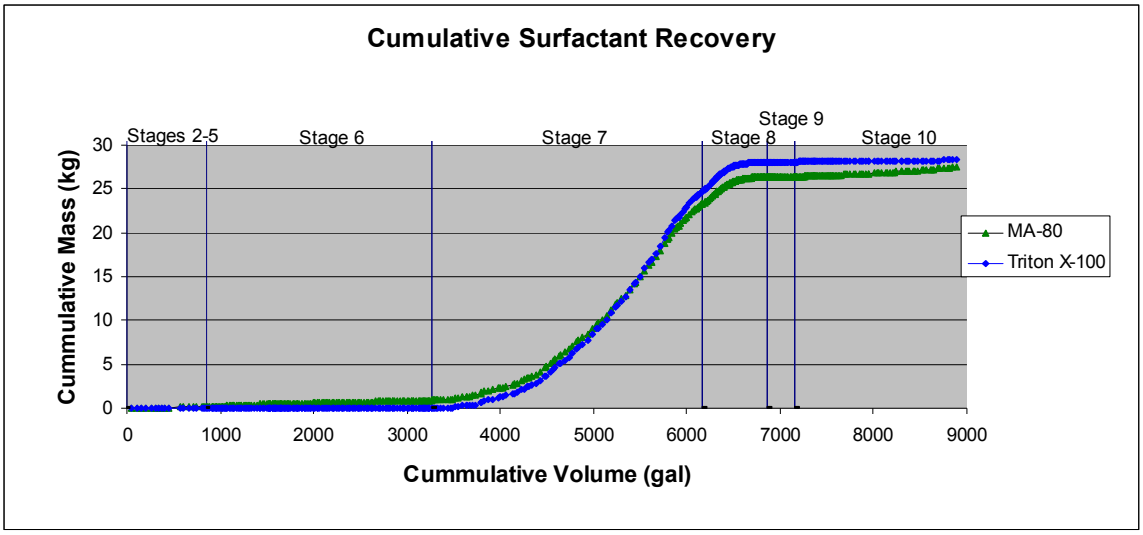


Figure 4.17: Cumulative surfactant recovery through the duration of the experiment.

Effluent sample MA-80 and Triton X-100 concentrations are shown in Figure 4.18 illustrating the overall surfactant breakthrough. It can be observed that increases in surfactant concentrations coincided with increased effluent PCE concentrations (Figure 4.19), which exceeded 400 mg/L late in Stage 7. The maximum PCE concentrations seen in the field study agreed well with laboratory batch studies, which resulted in surfactant mixture PCE concentrations of 395 mg/L in equilibrium with free phase PCE. However, maximum PCE concentrations were transient, and they quickly decreased concurrently with both surfactants during Stage 8 as the cell was drained in preparation for SVE. Slight increases in surfactant concentrations occurred late in Stage 10 when the water table was again raised after the conclusion of SVE, but the increase was small compared to the overall surfactant residuals in the cell and thus did not drastically affect calculated mass balances for either surfactant. Based on the cumulative recovery from effluent samples, 96.4 kg of MA-80 and 117.7 kg of Triton X-100 that were originally injected into the cell remain unaccounted for. This is potentially problematic because Triton oligomers with low numbers of ethoxy units are likely toxic and non-biodegradable (Kibbey and Hayes 2000), and though MA-80 is non-toxic, it

exhibits low degrees of biodegradability by natural microbial communities (Franzetti 2006). The low volume of flushing conducted at the end of the study likely led to such inefficient surfactant recovery. However, a combination of increased aqueous phase viscosity due to brine and surfactant complexities, trapping in areas of stagnation due to soil heterogeneities, and surfactant sorption to the solid phase also probably contributed to surfactant retention.

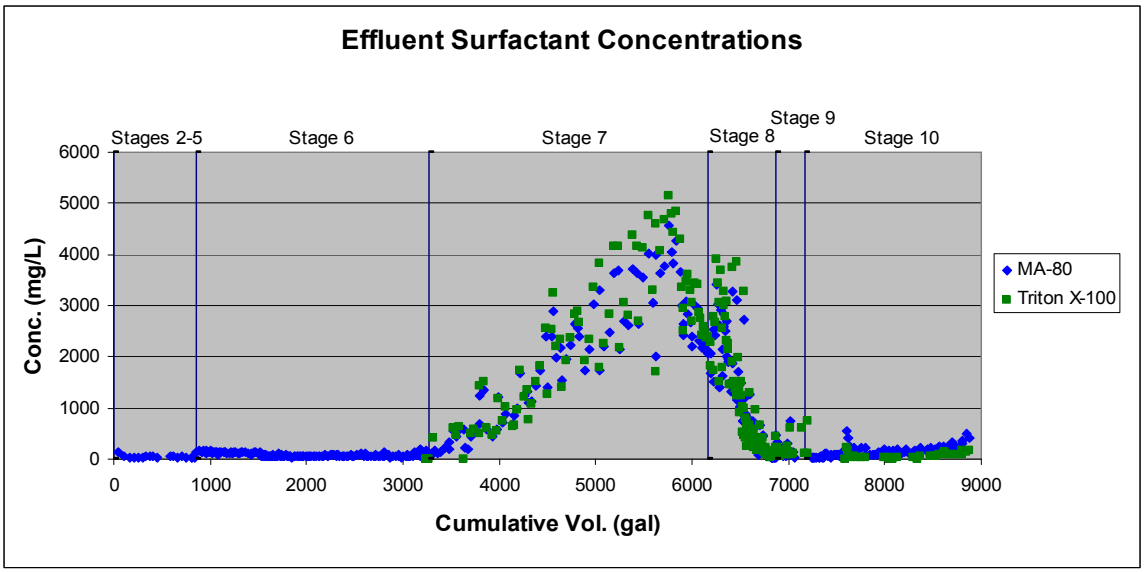


Figure 4.18: Effluent sample surfactant concentrations throughout the experiment.

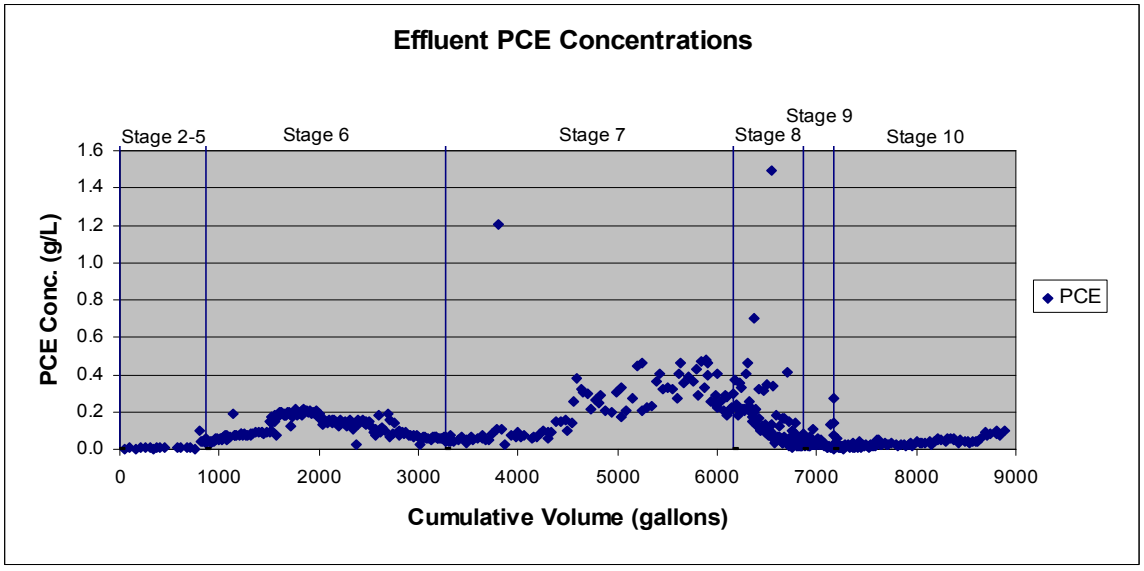


Figure 4.19: Effluent sample PCE concentrations throughout the experiment. Note the increase in PCE coinciding with increases in surfactant concentrations.

Viscosity and heterogeneity issues were evident during subsurface draining in Stage 8 in preparation for SVE. Aqueous phase residual after drainage was approximately 60%, which is extremely high for subsurface systems and likely indicated high residual of both contaminant and surfactants as well. Furthermore, such a high residual saturation was not an ideal situation for SVE implementation. If the high aqueous phase residual was due primarily to increased viscous forces, a much lower residual could eventually be attained though more time is required for drainage. However, since the duration of the experiment was limited, sufficient time could not be allotted to overcome increased viscous forces and in the process attain a lower aqueous phase residual saturation. Clearly, further drainage would have increased surfactant recovery as effluent surfactant concentrations rebounded late in Stage 10 (see Figure 4.18) when the water table was raised to the original depth. This as well as the fact that high surfactant concentrations were found in several MLS samples supports the notion that significant surfactant mass still existed in the residual aqueous phase at relatively shallow depths. The remaining issue hindering surfactant recovery was surfactant sorption to the solid phase. Sorptive behaviors between the two surfactants and Dover soils were examined in a supplementary set of experiments that will be discussed in a later section.

Profiles at several key points before, during, and after the surfactant flush were created from MLS data for both MA-80 and Triton X-100. The profile generated from MLS samples taken in Stage 6 before the surfactant solution was injected is shown in Figure 4.20. As expected, Triton X-100 did not appear in any MLS samples, and MA-80 was only found at low concentrations in the four MLS wells included in Figure 4.20. The MA-80 remaining in the cell from previous studies primarily resided at the lowest MLS depths around 12 m.

Again, this is not surprising as the MA-80 surfactant solution was injected at low depths and advected upwards in the prior study (Childs 2006).

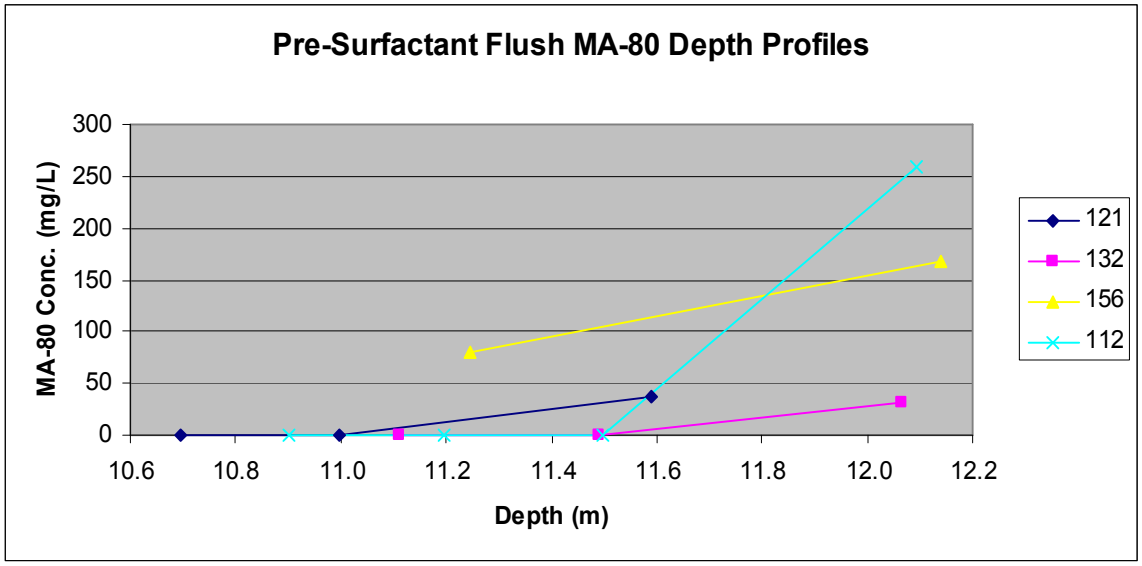


Figure 4.20: MLS depth profiles of MA-80 prior to surfactant flush.

MA-80 residual in the aqueous phase was determined to be low initially based on the relatively low MLS sample concentrations reported here.

Select MLS wells were sampled at several points during the surfactant injection from 2/17/2006 to 3/7/2006 to monitor subsurface surfactant transport. Surfactant breakthrough curves are shown for MLS wells 121, 145, and 161 at depths of 10.70, 10.77, and 10.70 m respectively in Figures 4.21, 4.22, and 4.23. As illustrated in the figures, surfactants appeared in each well at very similar times with MA-80 breakthrough occurring first in well 161 on 2/24/2006 followed shortly in wells 121 and 145 on 2/26/2006. All breakthrough curves exhibited similar shapes early on when data existed for all wells. However, the plots for each well were missing data points, making complete breakthrough curve shapes difficult to resolve. Whereas well 121 is well resolved during the actual flush, data does not exist for the period immediately following surfactant injection where increased surfactant concentrations

were likely as surfactants continued to migrate downward through the cell. The opposite is true in wells 145 and 161 as they possessed insufficient data to completely resolve the sharp increases seen in well 121 at the end of surfactant injection.

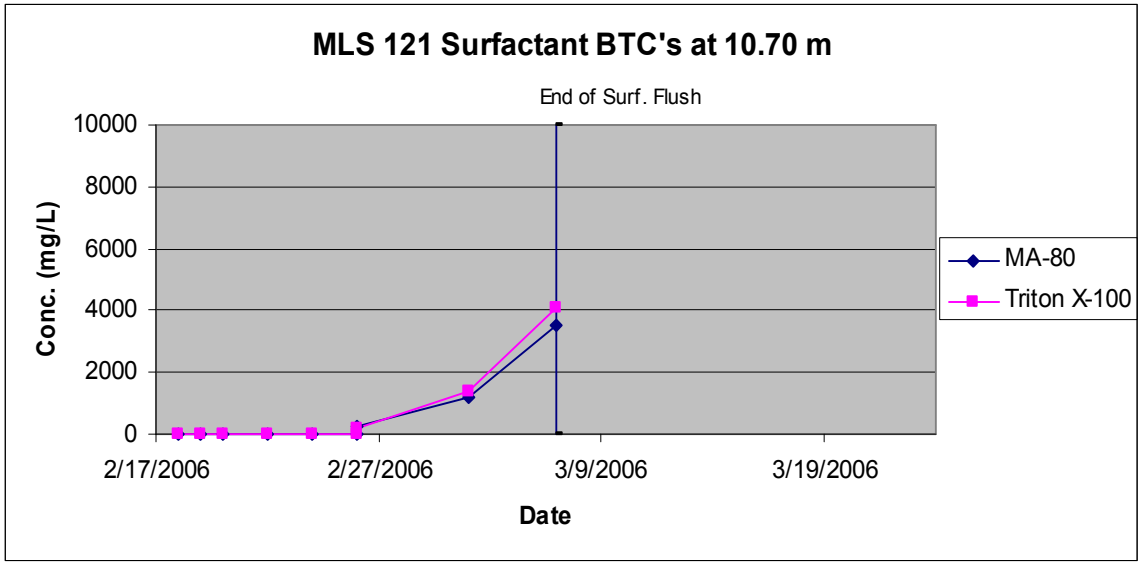


Figure 4.21: Surfactant breakthrough curves at MLS well 121 during surfactant flushing.

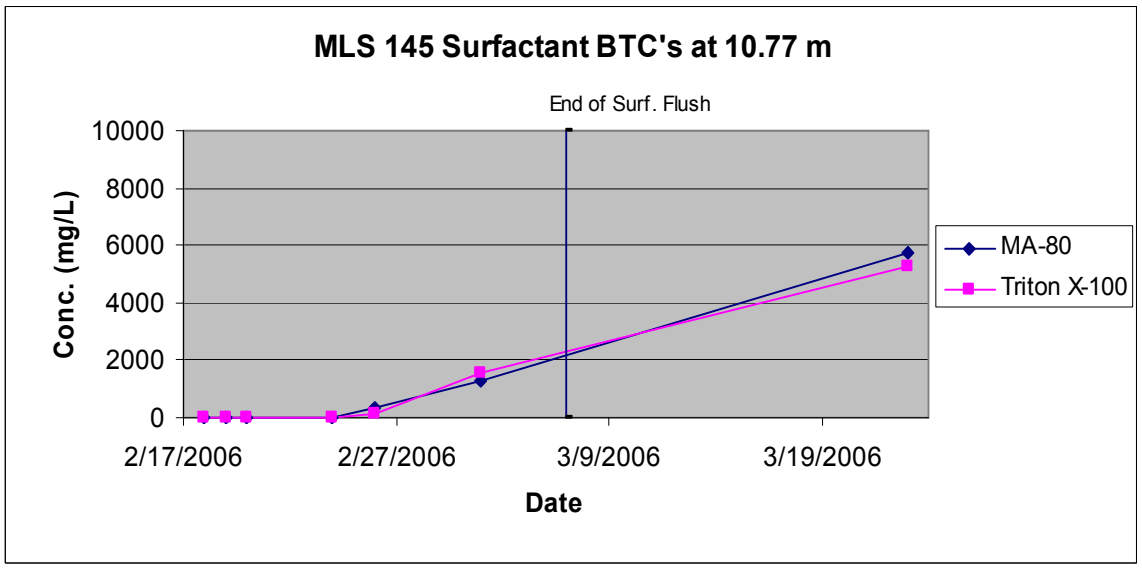


Figure 4.22: Breakthrough curves at MLS well 145 during surfactant flushing.

Concentrations of MA-80 and Triton X-100 were roughly in the same proportion as in the injected surfactant solution containing 1.425% MA-80 and 1.575% Triton X-100 by weight

with the exception of the final sampling point of well 161 where the Triton concentration was much lower in relation to the MA-80 concentration at the same point and time.

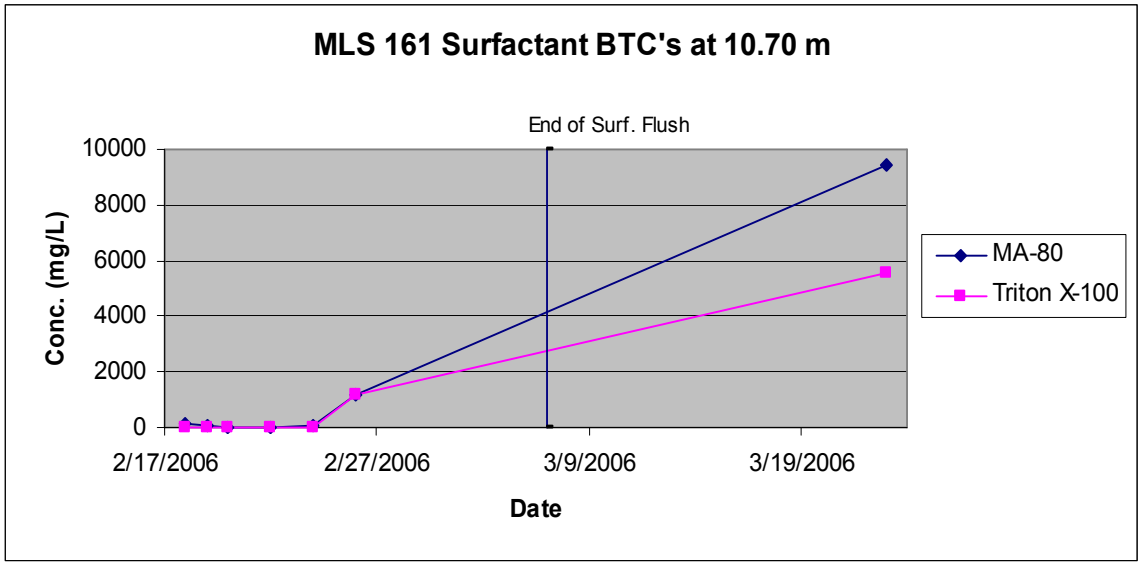


Figure 4.23: Breakthrough curves at MLS well 161 during surfactant flushing.

Influent surfactant concentrations were never approached at any well sampled. The final MA-80 concentration in well 161 was greatest at 0.66 times that of the influent concentration. The lack of complete breakthrough in the field was probably due to areas of low permeability as well as sorption to the solid surface and free-phase PCE partitioning that all resulted in transport retardation. Furthermore, the equivalent of only 1 PV of surfactant solution was injected into the system, and sorbing species in a heterogeneous system would not be expected to attain influent concentrations until the system has been flushed with several pore volumes.

Partitioning of Triton X-100 into free-phase PCE was likely a partial reason for relatively low aqueous Triton X-100 concentrations relative to MA-80 at late time points in MLS 161. Whereas PCE concentrations in wells 121 and 145 initially contained PCE concentrations of 306 mg/L and 0.46 mg/L respectively, well 161 displayed PCE

concentrations over 20,000 mg/L, signifying the presence of some free-phase PCE. Triton X-100 has been shown in past studies to dramatically partition into NAPL phase (John 2000, Atay 2002), and the PCE-water ($K_{PCE/W}$) coefficient was experimentally determined to be 12.5 (Sharmin 2006). Assuming that virtually all PCE present originally existed as free-phase, 20,000 mg/L translates to a PCE volume fraction of 0.0125. Therefore, based on the reported $K_{PCE/W}$ coefficient of 12.5, Triton X-100 lost to PCE partitioning is calculated at 13.7%, which yields a total Triton X-100 concentration of 6,400 mg/L. Though this is still somewhat lower than the MA-80 concentration of 9,500 mg/L, the presence of brine could enhance partitioning into PCE even further. In contrast, MA-80 hydrophobic tails will adsorb to the PCE surface, but do not appreciably solubilize into NAPL phase (Cho 2004). Thus, substantial amounts of MA-80 were not likely lost due to PCE partitioning.

MA-80 and Triton X-100 profiles for all MLS wells where sufficient data was accumulated are shown in Figures 4.24 and 4.25 respectively. With the exception of MLS wells 145 and 123, the highest MA-80 concentrations were consistently found at shallower MLS depths, which is sensible due to the downward transport of surfactant solution. Similarly, Triton X-100 concentrations decreased with increasing depth excluding only well 145, which again reported the highest surfactant concentration at an intermediate depth. The high levels of MA-80 observed at 11.64 m in well 123 did not coincide with increased Triton X-100 concentrations, and thus it is thought to have been the result of residual MA-80. However, concentrations of greater than 10,000 mg/L were quantified for both surfactants at 11.07 m in well 145, which was over twice the total surfactant concentration found anywhere else in the cell in this sample collection. Perhaps the close proximity of well 145 to a well used for extraction during the surfactant flush was the source of this discrepancy.

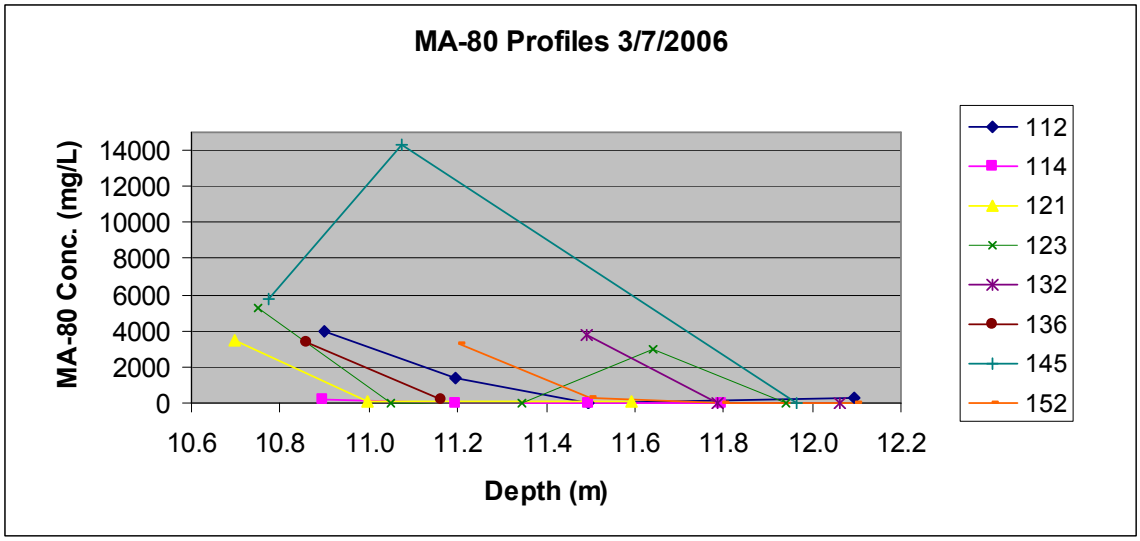


Figure 4.24: MLS depth profiles for MA-80 immediately following the surfactant flush on 3/7/2006.

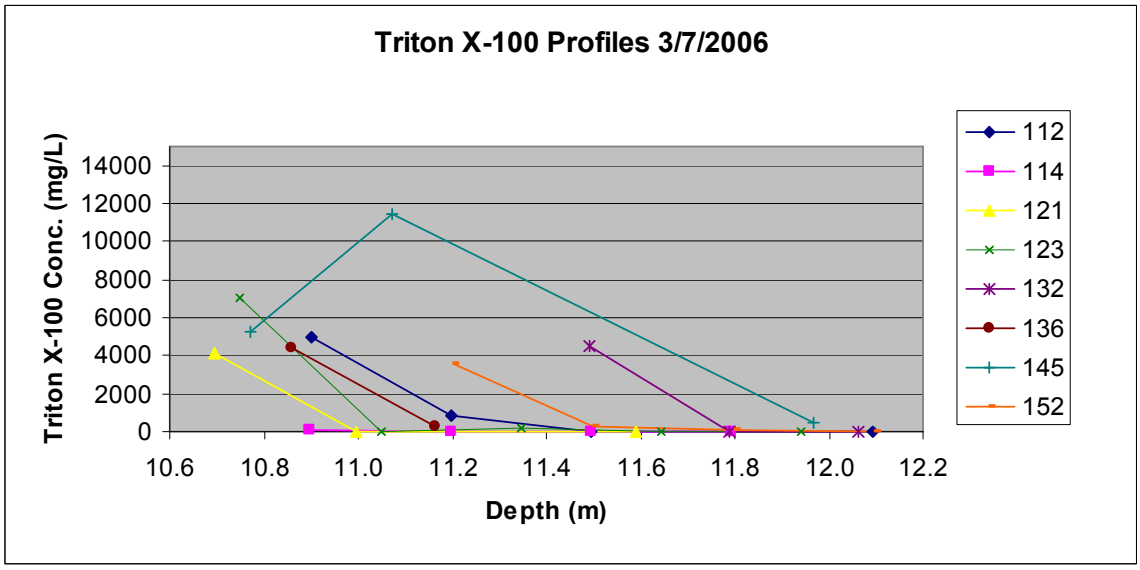


Figure 4.25: MLS depth profiles for Triton X-100 immediately following the surfactant flush on 3/7/2006.

MA-80 concentrations above those observed prior to surfactant flushing did not occur below 11.70 m, indicating that the surfactant front had not yet reached the bottom of the cell at this point. Triton X-100 showed slightly higher concentrations in cell locations below 11.70 m, which may have been due to the possibility that Triton X-100 may resist sorption to the Dover sand more than MA-80. As seen before in surfactant breakthrough curves, surfactant concentrations rarely approached levels of the injected surfactant solution. Once

again, the causes are thought to be a combination of solid phase sorption and soil heterogeneities that led to decreases in flushing efficiency of both surfactants. The presence of brine likely affected surfactant transport as well, but this interaction was outside the scope of this study.

Interesting trends appear in surfactant profiles in Figures 4.26 and 4.27 that were generated from MLS samples on 6/20/06 after completion of the experiment. A relatively low water table at this point prevented sample collection from more shallow MLS depths in many wells, and hence the profiles were incomplete for all wells shown. Considerable amounts of MA-80 were still present in wells 112, 121, and 132 at all depths sampled, though at concentrations approximately one order of magnitude less than those seen immediately following the surfactant flush. The remaining MLS samples analyzed exhibited MA-80 concentrations below 250 mg/L, which is less than 2% of the original surfactant solution concentration. Furthermore, MA-80 concentrations at this point were higher at depths below 11.70 m than in samples taken on 3/7/2006. Thus, small portions of MA-80 eventually migrated to the bottom of the cell in most locations though concentrations were relatively low. Although lower than MA-80 concentrations, the highest Triton X-100 levels occurred at the same well locations. In contrast to MA-80, Triton concentrations were under 200 mg/L for all samples collected below 11.50 m. Interestingly enough the wells showing high surfactant concentrations at the end of the experiment were all located in the southwest corner of the cell, which may not have been efficiently extracted using the flushing strategy implemented in the field.

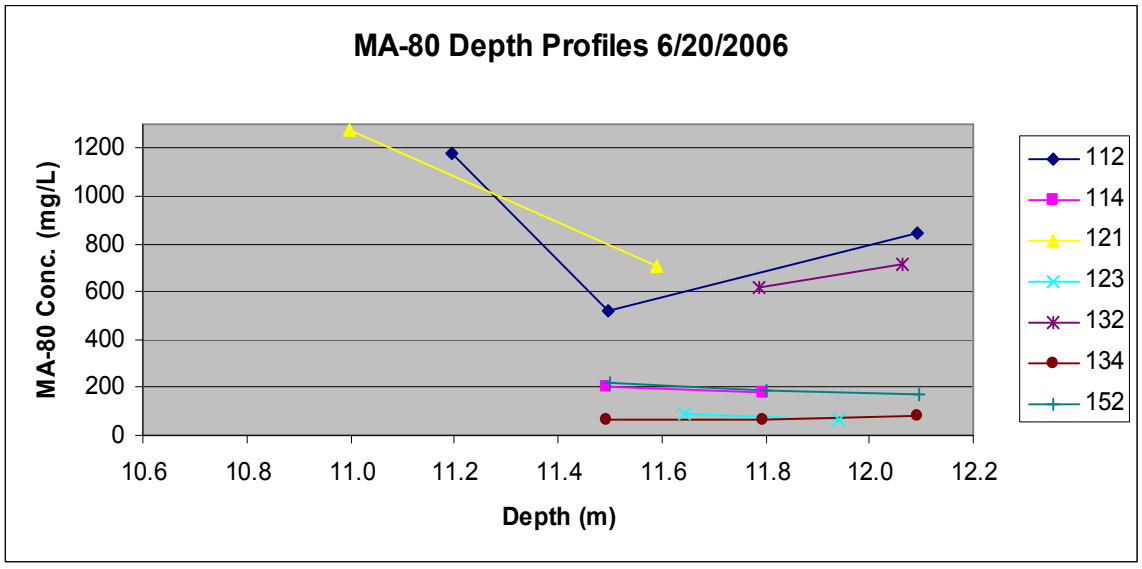


Figure 4.26: MLS depth profiles for MA-80 at the end of the study on 6/20/2006.

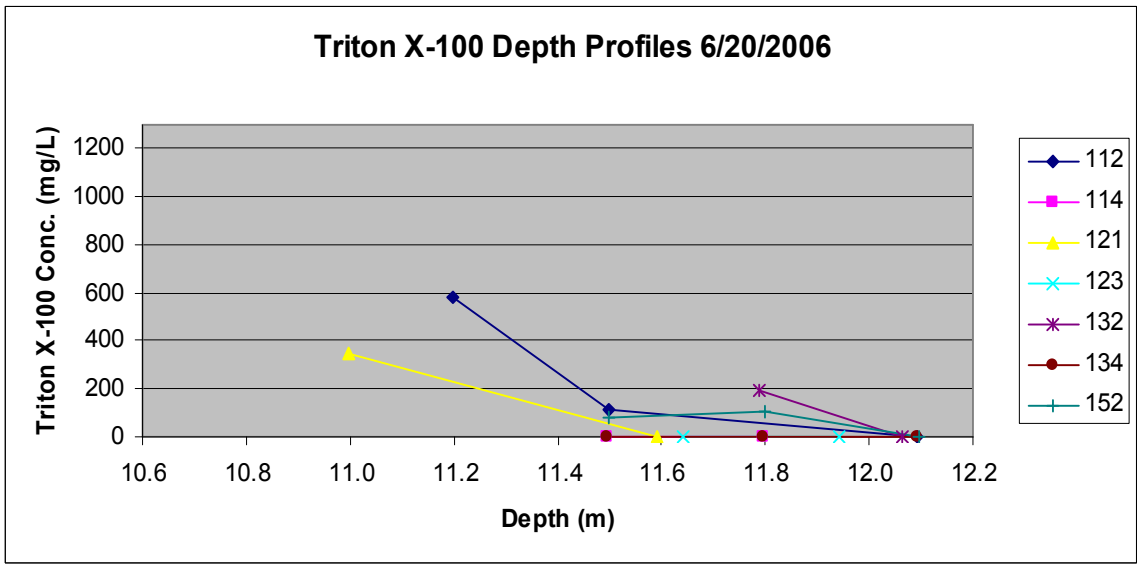


Figure 4.27: MLS depth profiles for Triton X-100 at the end of the study on 6/20/2006.

Contrarily, wells exhibiting low surfactant concentrations were located near the center of the cell, and thus were more efficiently accessed by flushing during Stage 10 when the water table was raised.

Absence of Triton X-100 near the bottom of the cell was again potentially due to free-phase PCE at low depths. Figure 4.16 conveys the occurrence of free-phase PCE from the

high PCE concentrations calculated near depths of 12.0 m. Any Triton X-100 originally present at this depth would have been subject to partitioning into the NAPL phase, and this may have resulted in Triton X-100 concentrations below detection limits at low depths. Sorption to the solid phase may also have played a significant role in the loss of Triton, but this would also have affected MA-80 recovery.

Though concentrations for both surfactants in MLS wells after the experiment finished showed high residuals in the lower reaches of the test cell, they still did not reflect the very large mass fractions of injected surfactant that were never recovered. As alluded to earlier, a portion of the unrecovered surfactant is believed to be trapped at depths above the current water table level along with the aqueous phase residual, and another portion is believed to have been lost to solid phase sorption and/or NAPL partitioning. However, it is unknown at this point which mechanism is more responsible for surfactant retention within the cell. For this reason, basic sorption experiments were performed in order to gauge the sorption behavior exhibited between the surfactant solution utilized and Dover soils. These studies were intended to elucidate the relative losses expected of each surfactant due to sorption, and in turn aid in resolving how much surfactant remains entrapped in the aqueous phase residual.

5. SURFACTANT SORPTION EXPERIMENTS

5.1 Introduction

In field experiments employing surfactants as remedial fluids, it is important to understand the sorption characteristics of the surfactants to be used for a number of reasons. Sorption to soils decreases the effective aqueous surfactant concentrations, and thus there is less surfactant available to solubilize and/or mobilize contaminant (West and Harwell 1992, Yuan 1997, Zheng 2002, Zhu 2003). When using nonionic surfactants such as Triton X-100, which exist as a series of oligomers rather than a pure compound, preferential sorption of certain oligomers shifts the overall makeup of the solution, and this can cause dramatic changes in surfactant behavior (Bao 2000). Also, depending upon the amount of surfactant present, surfactant sorption can further enhance the sorption of organic contaminants to soils (Lee 2000). Finally, sorption to the solid phase decreases the overall recovery of surfactant once injected into groundwater systems, and extremely long time periods may be required for complete removal of the sorbed surfactant through flushing (Adeel and Luthy 1995, Smith 1997). Most of these problems are not as limiting when using surfactant concentrations higher than CMC levels, which are typical in remedial techniques as sorption tends to decrease at high concentrations due to increased micellization (John 2000, Lee 2000, Cho 2004). However, higher surfactant residuals are likely to arise when large amounts of surfactant are added to the subsurface due to larger surfactant masses initially added to the system (Adeel and Luthy 1995). Additionally, as shown by the MLS surfactant profiles, a

wide range of surfactant concentrations were seen within the test cell, and hence vastly different surfactant behavior at different locations should be expected.

Due to its existence as a distribution of oligomers, Triton X-100 sorption patterns are very complex, and can change dramatically based upon concentration (Yuan 1997, Kibbey and Hayes 2000). At concentrations below CMC levels (130 mg/L), Triton X-100 sorption has been well characterized by a Freundlich sorption model (Deitsch 1995, Adeel and Luthy 1995, Zheng 2002) of the form:

$$q = K_F C_S{}^m \qquad \textbf{(5.1)}$$

Here, q is the surfactant sorbed to solid in units of mg/kg, C_S is the aqueous surfactant concentration (mg/L), and K_F and m are Freundlich coefficients. Contrarily, at concentrations above the CMC, sorbed Triton surfactant reaches a constant value and does not exhibit further sorption (Smith 1997, John 2000, Zhu 2003). However, sorption behavior of Triton X-100 is largely dependent upon the properties of the solid phase as well as every other component in solution (Kibbey and Hayes 2000). Thus, it is not surprising that Triton X-100 sorption measured on a variety of soil types does not follow a generalized sorption model (Yuan 1997, Zhu 2003).

Because of decreased polarity in comparison to other Triton oligomers, Triton oligomers with especially short ethoxy chains preferably sorb to soil organic matter (SOM) and NAPL if present, and these oligomers dominate sorption in soils with high organic content (Bao 2000). Linear relationships have been derived between Triton X-100 sorption and SOM at high concentrations. Therefore, in very organic soils, sorption beyond that predicted by Freundlich models is possible because of extensive partitioning of short ethoxy chain oligomers to SOM. In contrast, soils with low organic content such as Dover soils (f_{OC}

= 0.00025) often exhibit preferential sorption of long ethoxy chain oligomers, which is thought to be from solid surface adsorption through hydrogen bonding and metal ion bonding that interact more strongly with long ethoxy chain Triton oligomers (Yuan 1997, Bao 2000, Kibbey and Hayes 2000, Lee 2000). In fact, Triton X-100 sorption has been found to be more dependent upon factors such as clay minerals that promote hydrogen bonding over SOM yet organic matter obviously can play an important role in sorption behavior (Yeh and Lin 2003, Zhu 2003). Nonionic surfactant sorption is also enhanced by the presence of previously sorbed surfactant at relatively low concentrations, which results in a steep rise in sorption due to extensive surface aggregation of surfactant molecules in the form of hemimicelles or surface bilayers (West and Harwell 1992, Adeel and Luthy 1995, John 2000). As surfactant aggregations increase in size, they do not preferentially sorb Triton oligomers based on ethoxy chain length, and relative sorbed oligomer concentrations reflect the proportions seen in the original surfactant solution (John 2000, Kibbey and Hayes 2000). Still, sorption has not been shown to increase significantly from surfactant aggregation above CMC levels in soils with low organic content.

Sorption of MA-80 surfactant does not exhibit the complexities observed in Triton X-100 sorption. Aggregations that are common for nonionic surfactants do not occur extensively for MA-80 due to electrostatic repulsion between the head groups (Atay 2000). Furthermore, MA-80 is a single molecule with a uniform sorption affinity as opposed to a series of oligomers exhibiting a distribution of sorption behaviors. Consequently, MA-80 alone in solution has been shown to follow a linear sorption relationship for concentrations up to 91,000 mg/L (Franzetti 2006).

In typical soils, anionic surfactants undergo tail on or hydrophobic sorption because of repulsions between the negatively charged ions frequently found in soils and the surfactant head groups (Atay 2002). However, Dover sand, which is the primary component of Test Cell 3, includes high fractions of metal oxides, primarily iron (9800 mg/kg) and aluminum (4600 mg/kg) that provide positively charged sites for ion exchange with negatively charged surfactants (Cho 2004). Therefore, anionic surfactants such as MA-80 could potentially exhibit significant solid surface adsorption within Dover sand.

Despite the fact that substantial Triton X-100 partitioning and to a lesser extent MA-80 surface adsorption occur when free-phase PCE is present, significant surfactant losses to PCE were not expected in this study. This is due to the relatively low PCE saturation in the cell in comparison with past experimental studies with very high PCE residual (Hill 2001, Johnson 2004). The estimated 100 L of PCE originally present comprises a pore volume fraction of only 1.8×10^{-4} using a uniform porosity value of 0.32 (Ball 2002). This translates to a maximum of 0.22% Triton X-100 lost to free phase PCE, which is insignificant when attempting to account for the greater than 80% of Triton lost during the field experiment. Surfactant sorption in this situation probably involved primarily surface adsorption hydrogen bonding between polar groups of both surfactants along with ion exchange interactions between the negatively charged head groups of MA-80 and the high concentrations of metal ions found in Dover soil. Only minor surfactant losses should occur from Triton X-100 partitioning into organic matter due to the low overall organic content in the soil (Witt 2002).

5.2 Materials and Methods

5.2.1 Column Experiment 1

A 2.5-cm diameter glass column was attached to a PHD 4400 programmable syringe pump by plastic tubing and fitted with a plastic insert lined with rubber O-rings to take up unused column space and apply an air-tight fit to the column. Then, 4.95 g of 12:20 diameter Accusand was added on top of the bottom insert followed by the addition of 93.47 g of Dover sand (ρ_S = 2.65 kg/L). The sand was then gently agitated to form an even sand height throughout the column, and another 10.56 g of 12:20 Accusand was added on top of the Dover sand layer. The Accusand at either end of the column served to keep the Dover sand layer in place, and to avoid sand particle migration into influent or effluent tubing causing potential blockage. Another plastic insert lined with O-rings attached to plastic tubing was tightly fit on top of the top Accusand layer, and the column was de-aired with CO_2 at 5.0 mL/min for approximately 45 minutes. De-aired water was then pumped through the column at 3.0 mL/hr for 12 hours to remove any remaining air bubbles in the column at which point pumping was halted and the sand column was compressed as much as possible. This procedure was repeated twice more at 12 hour increments. The resultant Dover soil length was 11.8 cm with lengths of 0.4 cm and 1.1 cm of Accusand at the bottom and top respectively for a total column length of 13.3 cm.

A surfactant solution of 1.0% MA-80, 1.0% Triton X-100, 3.0% IPA, and 1.7% $CaCl_2$ by weight was prepared in DI water, and subsequently pumped through the soil column in a bottom to top fashion at 4.0 mL/hr using the same syringe pump. The first sample was taken in a 25 mL glass vial with Teflon lined caps after 5 hours of pumping. Successive effluent samples were collected in similar vials at 1 hour (4 mL) increments for approximately 34 hours with overnight interruptions after 10 and 22 hours when the pump was stopped. The

syringe was refilled with surfactant solution after each interruption before pumping was continued.

5.2.2 Column Experiment 2

The second column was prepared in the same 2.5 cm diameter glass column, but fritted plastic fittings were used at the top and bottom instead of 12:20 Accusand. The fritted fitting was connected to a PHD 4400 programmable syringe pump via plastic tubing, and attached to a column insert with O-rings that was placed securely in the bottom of the column, and 49.99 g of Dover sand (ρ_S = 2.65 kg/L) was added directly on top of the bottom fitting. A similar fritted fitting attached to plastic tubing and a plastic column insert were tightly fit on top of the Dover sand. Once constructed, the column was subsequently de-aired with CO_2 at 5.0 mL/min for approximately 2 hours. The attached syringe pump was then filled with de-aired water, which was pumped through the column for 36 hours at 2.0 mL/hr to saturate the column and remove any air bubbles. After 36 hours, the pump was stopped and the soil column was compressed, and de-aired water was pumped through the column for an additional 36 hours. The resultant Dover sand column length was 6.0 cm.

A surfactant solution of 1.425% MA-80, 1.575% Triton X-100, 3.0% IPA, and 1.55% $CaCl_2$ by weight was prepared in DI water and pumped through the column at a rate of 4.0 mL/hr from bottom to top using the same syringe pump. Samples were collected in 25 mL scintillation vials with aluminum insert screw caps at 0.5-1 hour (2-4 mL) increments for approximately 24.2 hours when complete surfactant breakthrough had been attained in the effluent for several samples. Overnight interruptions occurred after approximately 12.4 and 21.7 hours. Once again, the syringe was refilled with surfactant solution after each interruption before continued pumping.

After complete breakthrough of the surfactant solution was apparent in effluent samples, the syringe pump was rinsed and refilled with DI water, which was then injected onto the column at a similar rate of 4.0 mL/hr. DI water was pumped through the column for an additional 43.0 hours with samples collected in a similar fashion. Overnight interruptions occurred in this phase of the experiment after 8.0, 17.0, 25.1, and 34.1 hours at which points the syringe pump was refilled with DI water.

5.2.3 Batch Sorption Experiment

Samples were prepared by first adding 30.0 g of Dover sand to twelve separate 35 mL glass centrifuge tubes with Teflon lined screw caps. Each sample was wetted with 5 mL of a background solution containing 3.0% IPA and 1.55% $CaCl_2$ by weight, and allowed to equilibrate for 12 hours. Meanwhile, a surfactant solution comprised of 2.85% MA-80, 3.15% Triton X-100, 3.0% IPA, and 1.55% $CaCl_2$ by weight was prepared in DI water in order to capture the entire range of surfactant concentrations seen in the field. This solution was subsequently diluted with the background solution to form six surfactant solutions containing between 600 mg/L and 60,000 mg/L total surfactant each with identical concentrations of IPA and $CaCl_2$. Then, 20 mL of each dilution was added to the centrifuge tubes containing pre-wetted Dover sand in duplicate.

Once prepared, samples were sealed and tumbled at approximately 5 rpm in the dark at room temperature. After 96 hours of agitation, samples were centrifuged at 1000 rpm for 30 minutes. Approximately 5 mL of each sample was then collected with 5 mL Luer-Loc syringes and passed through a PTFE filter tip prior to analysis.

5.2.4 Sample Analysis

All aqueous samples collected from column and batch experiments were analyzed by the same HPLC method developed using a Waters HPLC system including a Waters 717 autosampler, 616 pump, 600S mobile phase controller, and a Waters 996 photodiode array detector. A 25 x 4.6 cm, 5 μm particle size Suppelco C18 column was used for the separation of MA-80 and Triton X-100 surfactants.

In this method, 10μL of sample was injected to the system at a constant flow rate of 1.0 mL/min. The initial mobile phase consisted of 30% acetonitrile, 70% 0.003 M NaCl, and stepped to 50:50 acetonitrile: 0.003 M NaCl after 2 minutes, which eluted the MA-80 from the column. Then, at 5 minutes, the mobile phase stepped again to 85% acetonitrile, 15% 0.003 M NaCl, which mobilized the Triton X-100 oligomers as a single peak. The mobile phase was returned to initial conditions after 12 minutes to equilibrate the column prior to the next injection.

Detection was performed for both surfactants at a wavelength of 220 nm, which was possible in this situation due to the absence of PCE. Quantification for both surfactants was accomplished by a six point linear calibration ($R^2 > 0.995$ for acceptance) with calibration standards ranging from 15,000 mg/L to 60 mg/L of each surfactant. The total run time was 15 minutes per sample with MA-80 eluting at 7.5 minutes followed by Triton X-100 at 13.8 minutes. The detection limits were similar to those given for the methods previously described.

5.3 Results

5.3.1 Column Experiment 1

The porosity of the Dover sand layer was 0.39, which gives a pore volume (PV) within the Dover sand of 22.65 mL based on the sand density. Surfactant breakthrough was

first observed after 0.57 PV of the influent surfactant solution had been injected, which is earlier than expected. Near complete breakthrough curves are shown for MA-80 and Triton X-100 in Figure 5.1.

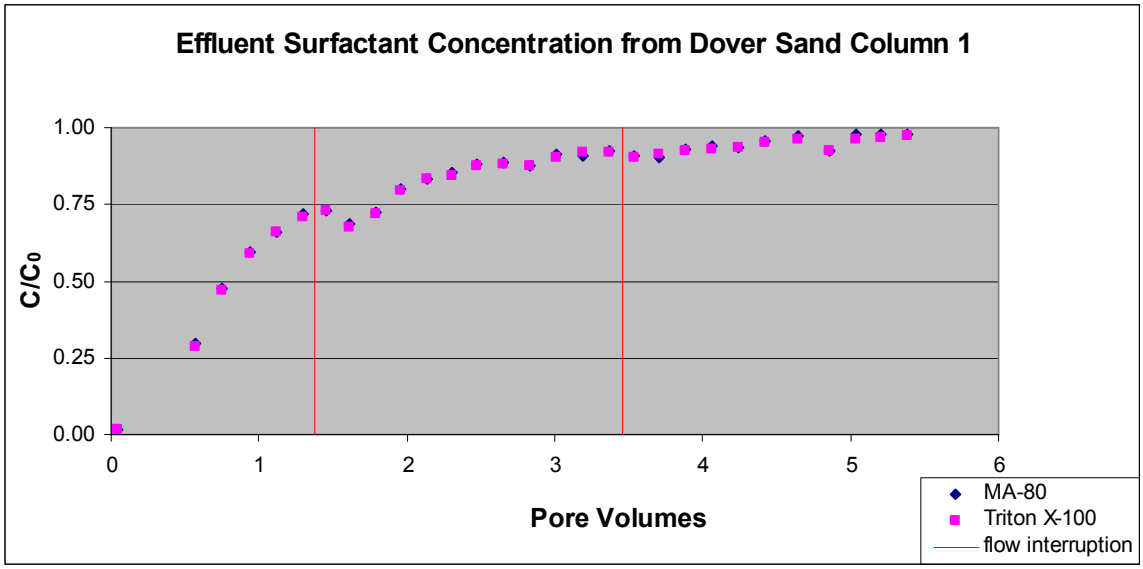


Figure 5.1: Breakthrough curves for 1.0% solution of MA-80 and Triton X-100 in Column Experiment 1.

Drops in aqueous phase surfactant concentrations after each flow interruption, shown as red lines in 5.1, can be seen above. This was due to rate limited sorption, and hence further solid phase sorption occurred during the overnight interruptions. Surfactant injection continued for approximately 5.5 PV, but complete breakthrough was never attained for either surfactant. The highest relative concentrations (C/C_0) for effluent samples were 0.98 for MA-80 and 0.97 for Triton X-100 in the final sample collected.

Retardation factors (R_f) were calculated for both MA-80 and Triton X-100 by integrating the area above the breakthrough curves shown in Figure 5.1. The R_f for MA-80 was determined to be 1.32 and the Triton X-100 R_f was similar at 1.35. Then, using the following equation, a soil-water partition coefficient K_d was calculated for each surfactant within the Dover sand.

$$K_d = (R_f - 1)\frac{n}{(n-1)\rho_s} \qquad \textbf{(5.2)}$$

Here, n is the column porosity and ρ_S is the solid phase density. The K_d values calculated for MA-80 and Triton X-100 were 0.077 L/kg and 0.084 L/kg respectively in Column Experiment 1. Furthermore, of the unrecovered masses of MA-80 (389 mg) and Triton X-100 (398 mg), it was determined that 162 mg of MA-80 and 170 mg of Triton X-100 remained in the sorbed state. A desorption curve was not collected during this experiment.

5.3.2 Column Experiment 2

Porosity in the Dover sand layer was determined to be 0.35 for Column 2, which translates to a PV of 10.29 mL. Surfactant breakthrough was first observed at approximately 0.49 PV, which like the first column is premature. The complete breakthrough curve along with the subsequent desorption curve is portrayed in Figure 5.2.

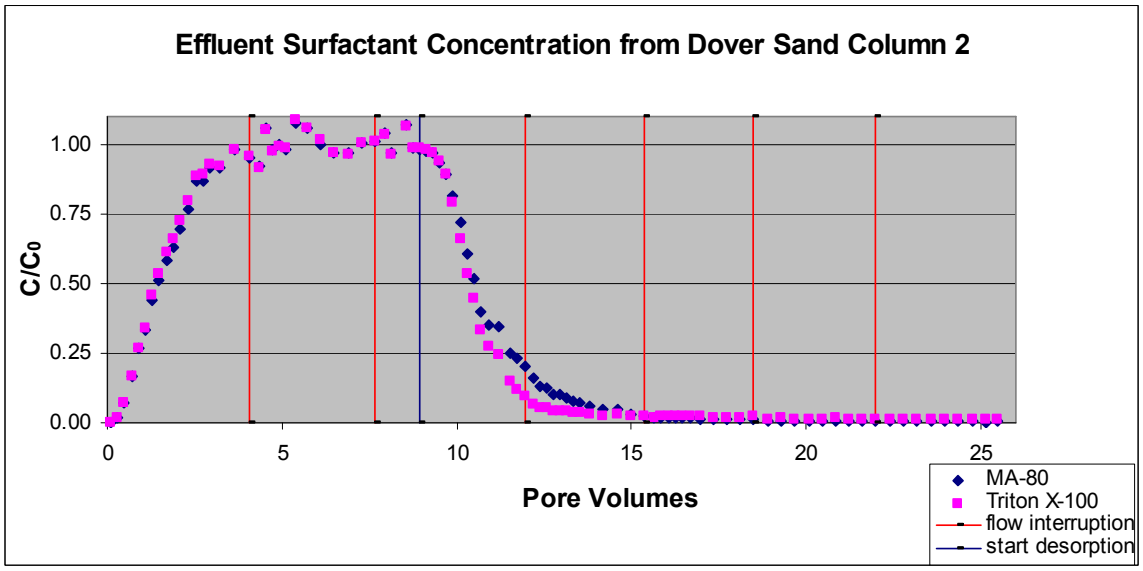


Figure 5.2: Breakthrough curves and desorption curves for solution of 1.425% MA-80 and 1.575% Triton X-100 in Column Experiment 2.

The column was flushed with surfactant solution for 8.9 PV, and complete breakthrough was first seen after approximately 5.4 PV. However, C/C_0 drops below 1.0 again due to flow

interruption at 7.6 PV. Additionally, HPLC analyses at very high surfactant concentrations displayed a lot of noise between samples, which is illustrated in Figure 5.2 between 5 and 10 PV. Surfactant injection was halted after 8.9 PV as C/C_0 values for both surfactants were very close to 1.0 for the final 1.5 PV of surfactant flush.

R_f values were calculated by a method similar to that described for Column Experiment 1. The R_f determined for MA-80 was 1.61 and 1.55 for Triton X-100 in Column 2, which are significantly higher values than those calculated for Column 1. Similarly, the K_d values for Column 2 were higher than the preceding experiment at 0.125 L/kg and 0.114 L/kg for MA-80 and Triton X-100 respectively. Masses of 318 mg MA-80 and 343 mg Triton X-100 remained in the column when surfactant injection ended, and it was estimated that 171 mg MA-80 and 181 mg Triton X-100 were sorbed onto the Dover sand.

The desorption phase of the experiment commenced immediately after surfactant injection ended at 8.9 PV, which is symbolized by the blue line in Figure 5.2. An additional 16.6 pore volumes of DI water were flushed through the system, but neither surfactant fell below detectable levels in effluent samples during this time. The final effluent sample collected contained 0.32% of the MA-80 concentration in the injected surfactant solution and 0.97% of the original Triton X-100 concentration. Furthermore, these levels were nearly constant for the final pore volume of DI water flushing as desorption curves tailed off at low surfactant concentrations. R_f values were calculated during desorption as well by integrating the area under the curve through this region of the plot. The R_f values calculated from desorption were 1.49 for MA-80 and 1.25 for Triton X-100, which are both significantly lower than R_f values calculated from sorption curves. Overall, 300 mg MA-80 and 293 mg Triton X-100 were recovered during desorption yielding final column residuals of 17.6 mg

MA-80 and 49.5 mg Triton X-100, which translates to 98.8% and 96.8% removal from the column for MA-80 and Triton X-100 respectively.

5.3.3 Batch Sorption Experiment

Sorbed surfactant concentrations were calculated by the difference in the initial surfactant concentration added to each sample and the sample C_s after equilibration with Dover sand was complete. The results are summarized as MA-80 and Triton X-100 sorption isotherms in Figure 5.3. This figure shows Triton X-100 is preferentially sorbed at low concentrations, and MA-80 sorption is slightly greater at high surfactant concentrations.

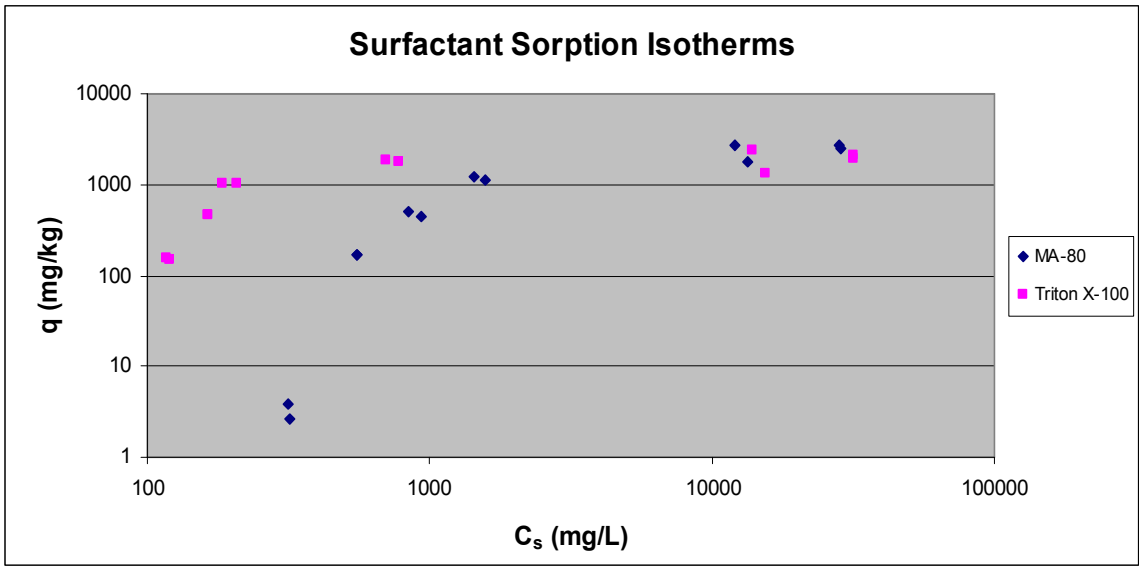


Figure 5.3: Sorption isotherms for MA-80 and Triton X-100 on a logarithmic scale.

The K_d calculated from Equation 5.3, in which q and C_s are sorbed and aqueous surfactant concentrations respectively, are plotted against C_s in Figure 5.4, which shows that the extent of sorption to Dover sand is largely dependent upon the influent surfactant concentration.

$$K_d = \frac{q}{C_s} \qquad \textbf{(5.3)}$$

Although no simple sorption model fits the sorption behavior exhibited by either MA-80 or Triton X-100 over the entire range of concentrations studied, both surfactant species fit

sorption models at relatively low concentrations. MA-80 obeys a linear sorption relationship to aqueous concentrations up to about 1600 mg/L (Figure 5.5) showing a correlation coefficient of 0.97 over this range.

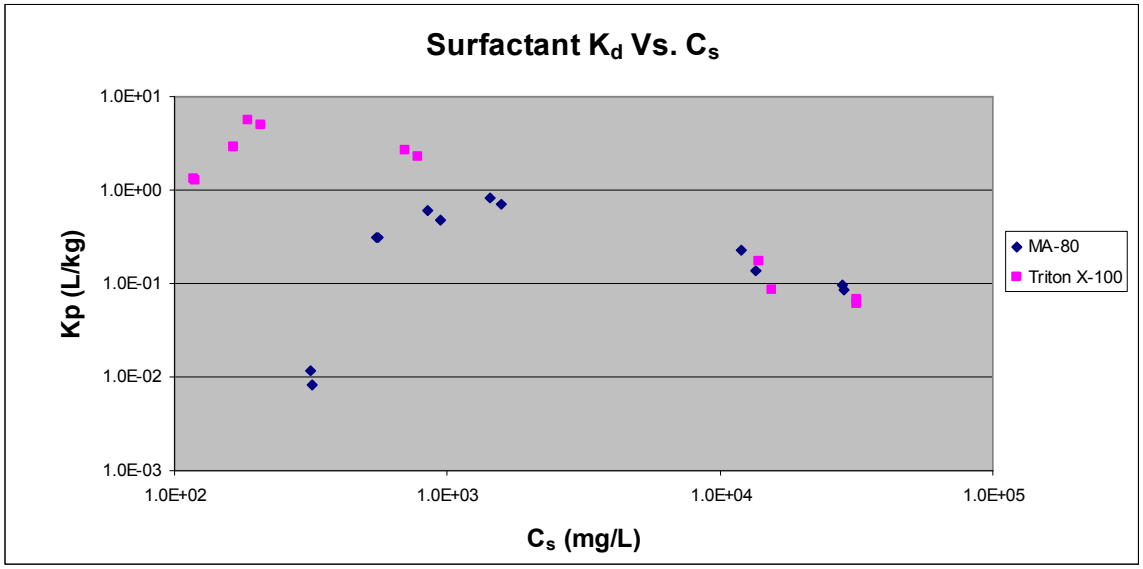


Figure 5.4: Sorption coefficients for MA-80 and Triton X-100 plotted against C_s.

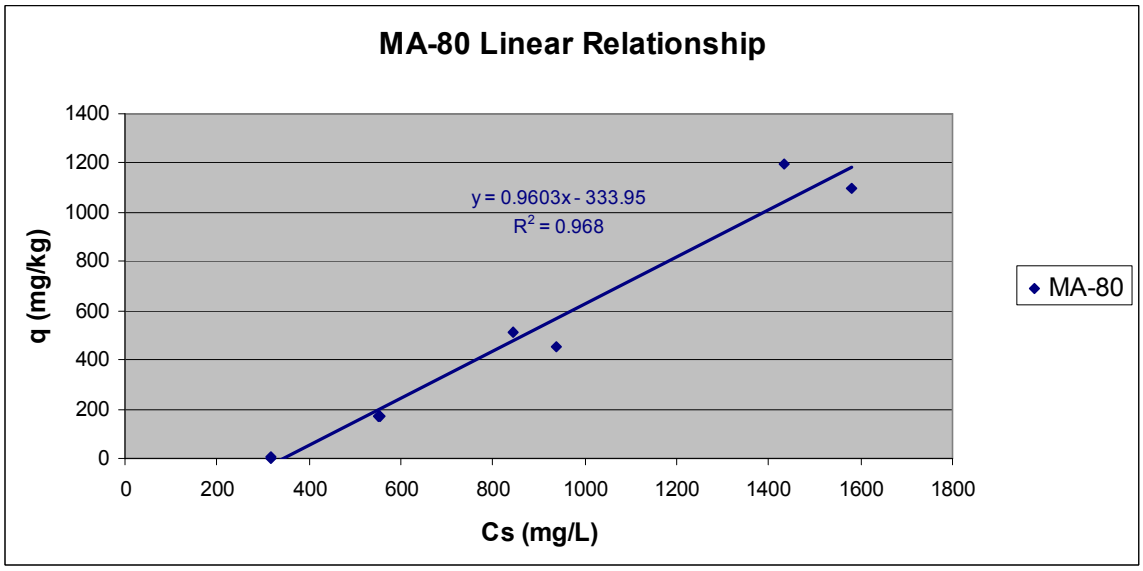


Figure 5.5: Linear relationship of MA-80 sorption at low concentrations.

However, MA-80 sorption approaches zero at approximately 300 mg/L, and thus K_d cannot be estimated from the relationship slope. Triton X-100 on the other hand closely resembles

Freundlich type sorption at low concentrations. Figure 5.6 shows a plot of ln(C_s) versus ln(q) below 200 mg/L Triton X-100 concentrations, which returns a correlation coefficient of 0.97. The Freundlich coefficients K_F and m from Equation 5.1 were determined from the experimental data to be 4.2 x 10^{-6} and 3.65 respectively. However, this regression was determined from a limited number of data points, and more Triton X-100 concentrations below CMC levels are needed to fully resolve the Freundlich relationship.

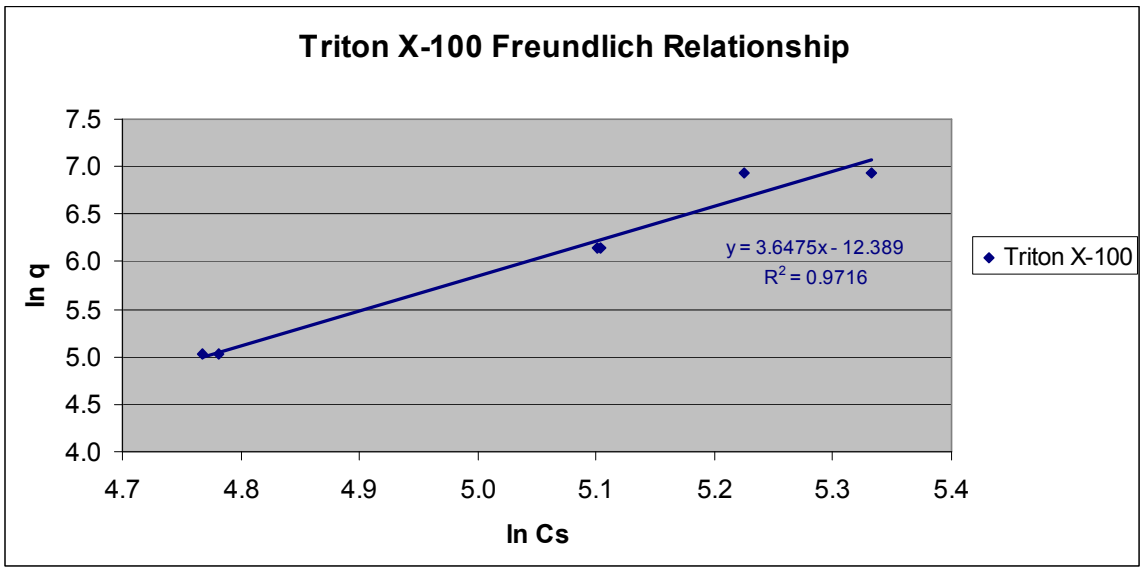


Figure 5.6: Freundlich relationship of Triton X-100 sorption at low concentrations.

5.4 Discussion

The K_d values calculated from retardation factors for MA-80 and Triton X-100 were 0.077 L/kg and 0.084 L/kg respectively in Column 1, while the K_d values at 1.0% MA-80 and Triton X-100 predicted from the batch study were significantly greater at 0.207 L/kg for MA-80 and 0.184 L/kg for Triton X-100. K_d values from Column 2 were 0.125 L/kg for MA-80 and 0.114 L/kg for Triton X-100, which are slightly less than the K_d values estimated for a solution containing 1.425% MA-80 and 1.575% Triton X-100 from the batch sorption experiment of 0.160 L/kg for MA-80 and 0.125 L/kg for Triton X-100. It is expected that

sorption coefficients predicted from column experiments should be somewhat lower than batch experiments due to kinetic and surface area limitations (Adeel and Luthy 1995). It should also be noted that due to the complex sorption behavior exhibited by both surfactants in these systems, the K_d values calculated from both column experiments may vary drastically for various influent surfactant concentrations.

However, the difference between Column 1 K_d values and batch sorption values were inconsistent as Column 1 sorption coefficients are lower than those calculated for Column 2 yet the batch experiment predicts higher sorption for the surfactant concentrations used in Column 1. The retardation factors calculated for Columns 1 and 2 were also surprising, for the degree of retardation should decrease for increasing surfactant concentrations (Adeel and Luthy 1995), and the opposite is seen here. There are a few possible explanations. First, initial breakthrough was earlier than expected in both columns, but it was earliest in Column 2. This possibly signifies more non-Fickian behavior exhibited in Column 2 that could lead to retention of surfactants beyond what was caused by sorption alone. In addition, the length of Column 2 was roughly half that of Column 1, which increased the likelihood of non-Fickian flow, and is likely a partial explanation for the increase in apparent retardation. Still, this does not appear to be the case in this situation as K_d values calculated from Column 2 more closely resemble those calculated in the batch study. Another major difference between the surfactant solutions used in Column 1 and 2 aside from the surfactant concentrations is that a higher amount of $CaCl_2$ was present in the surfactant solution injected into Column 1. Though it seems logical that an increase in salt concentration would shift K_d more towards solid phase sorption, it might also increase surfactant micellization, which would decrease the surfactant available for sorption. Also, surfactant breakthrough was not complete in

Column 1, and had the experiment been allowed to attain complete breakthrough, the K_d and R_f would increase. Thus, Column 1 K_d and R_f estimates were lower than the actual values.

Retardation factors calculated from desorption in Column 2 were lower than the values derived from sorption, which is again slightly misleading because relatively large amounts of MA-80 and Triton X-100 remained on the column at the end of the experiment. Therefore, R_f values estimated from desorption are too low. The retention of surfactant could be partially due to non-Fickian behavior, but the fact that 3 times more Triton X-100 than MA-80 is retained leads to the belief that sorption plays a major role in these extensive retention times. Although the relative oligomer concentrations of Triton X-100 were not monitored, it is possible that partitioning of hydrophobic, short ethoxy chain Triton oligomers into organic matter may be the cause of Triton X-100 recalcitrance during the desorption phase. Such interactions are more strongly binding than hydrogen bonds and Van der Waals interactions, which are the primary factors governing MA-80 and long ethoxy chain Triton sorption (Yeh and Lin 2003). Long retention times have been reported for Triton X-100 in past studies also (Adeel and Luthy 1995, Smith 1997, Yeh and Lin 2003).

In batch study samples, MA-80 sorption consistently increased with concentration, but began tailing off dramatically around 1,500 mg/L. This was in excess of its CMC of 890 mg/L (Franzetti 2006) where maximum MA-80 sorption has previously been determined (Cho 2004). Also, it did not appear that significant MA-80 sorption occurs below 300 mg/L. This finding does not agree with sorption isotherms produced in another study (Franzetti 2006) yet the K_d of 0.17 L/kg given in the same study is very similar to the K_d calculated at high concentrations from batch samples. However, all prior studies examined MA-80 sorption characteristics in the absence of Triton X-100 and other solution components. It

appears that Triton X-100 sorption was strongly preferred over MA-80 at low concentrations, but due to the presence of large amounts of metal oxides, MA-80 sorption persisted even at very high concentrations (Cho 2004). In addition, MA-80 sorption at low concentrations could have been slowed by the existence of previously sorbed MA-80 from past studies.

The discovery that Triton X-100 sorption followed the Freundlich model near CMC levels is well supported in previous studies (Smith 1997, John 2000, Zhang 2002). Furthermore, Triton X-100 sorption has formerly exhibited a plateau in sorbed concentrations at about 200 mg/L (Zhu 2003), which is similar to what was observed in the batch experiment. Although individual oligomers were not quantified throughout the field study, the distribution of Triton oligomer distribution seen in effluent samples shifted towards the more hydrophobic, short ethoxy chain oligomers when compared to the distribution observed in the original surfactant solution. This shift is realized by comparing the oligomer distribution of the injected surfactant in Figure 5.7 to the distribution in a typical effluent sample in Figure 5.8. Notice here that the more hydrophobic oligomers increase in relative concentration in the effluent sample. Therefore, the dominant sorption mechanisms within the field experiment were likely hydrogen bonding and Van der Waals interactions, which primarily affected the sorption of Triton oligomers with long ethoxy chains.

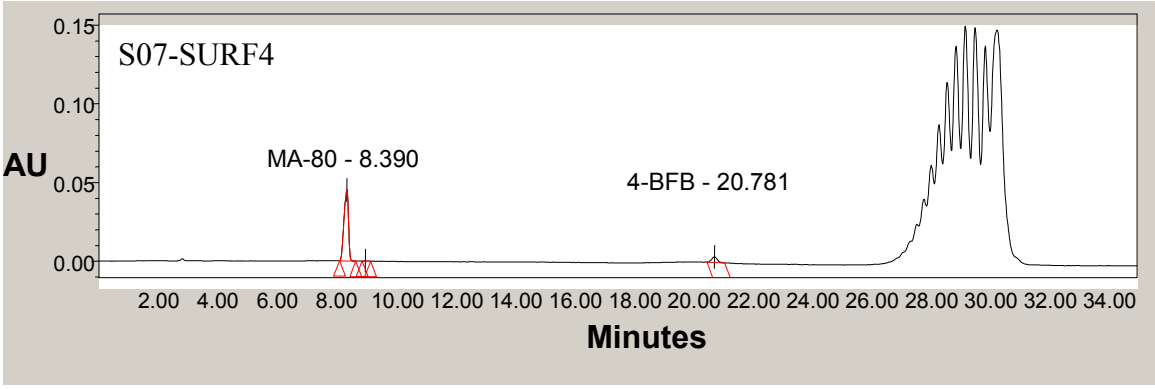


Figure 5.7: Triton Oligomer Distribution in Surfactant Solution Prior to Injection.

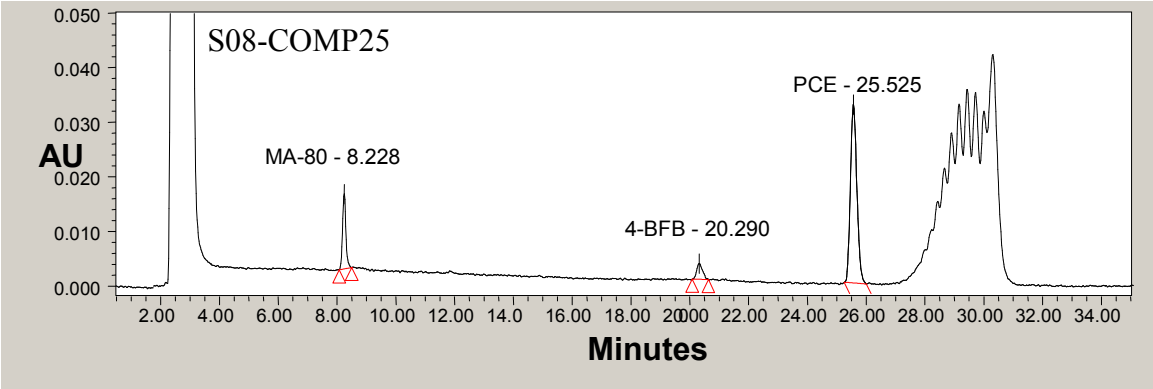


Figure 5.8: Triton Oligomer Distribution in a Typical Effluent Sample.

6. SUMMARY AND CONCLUSIONS

This research included several experimental objectives all aimed at measuring the efficiency of the Brine Barrier Remediation Technique as a remedial strategy for removing DNAPL contaminants and in particular PCE. The first objective was to develop analytical methods capable of quantifying PCE, chlorinated daughter products, and surfactants MA-80 and Triton X-100 in a complex subsurface system. The methods developed were subsequently utilized to measure PCE, MA-80, and Triton X-100 recovery from a contaminated groundwater field setting. Finally, upon creating mass balances for PCE and both surfactants, further experimentation was conducted to determine the effect solid phase sorption had on limiting the recovery of MA-80 and Triton X-100 injected into the system.

The HPLC analytical methods developed provide a viable alternative for PCE quantification when classical GC techniques fail due to incompatibility with components of the experimental system, which is the case in this particular BBRT implementation. Furthermore, the developed methods provide a more universal analytical technique capable of quantifying the primary chlorinated solvents and both surfactants within two relatively short sample runs, which is especially important for high sample throughput, frequently required for field scale experiments. Though VOC recovery is an issue in the methods developed, the inclusion of a surrogate spike in each field sample to serve as a correction factor for the chlorinated solvents alleviated the majority of recovery issues due to sample preparation steps and analysis.

Though it appeared from MLS data that PCE concentrations dropped approximately 90% above 12.0 m in the cell during the study, which implied that some mobilization occurred, less than 10% of PCE initially present in the field was recovered during the field study. Therefore, if BBRT techniques are to be used for field-scale remediation in the future, it is imperative that more efficient removal techniques are developed to deal with PCE after it has been mobilized. Brine barrier techniques might also be employed with different surfactant solutions such as those aimed at greatly increasing PCE solubility, which drop in density due to the dramatic uptake of PCE. These solutions could potentially be more easily extracted from groundwater systems than free-phase PCE due to its high density and viscosity.

The lack of efficient MA-80 and Triton X-100 recovery in the field experiment is due to a combination of subsurface heterogeneities causing large aqueous phase residual in the unsaturated zone, and sorption to the solid phase. It was shown from column experiments that after surfactant flushing over 50% of both MA-80 and Triton X-100 residuals can exist in the sorbed state. Furthermore, although much of the sorbed surfactant can be removed with extensive water flushing, complete removal is not likely to be attained for long periods of time. Though MA-80 sorption appears to dominate in Dover soils at high concentrations typically seen in remedial systems, the sorptive forces binding MA-80 molecules to the surface are relatively weak when compared to the partitioning behavior responsible for retaining the more hydrophobic, short ethoxy chain oligomers that prefer organic matter to the aqueous phase. This results in surfactant residuals predominately high in Triton X-100 oligomers, which is especially problematic due to the potential toxicity and resistance to biodegradation exhibited by Triton X-100 oligomers.

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