An Investigation of Cosolvent Flushing for the Remediation of PAH's from Former Manufactured Gas Plant Sites

Arne P. Newman

A thesis submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Environmental Science and Engineering, School of Public Health

Chapel Hill
2008

Approved by:

Advisor: Dr. Cass T. Miller

Reader: Dr. Gregory W. Characklis

Reader: Dr. Michael D. Aitken

Abstract

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Manufactured gas plant (MGP) operations across the United States during the late 19th and early 20th centuries resulted in the release of polycyclic aromatic hydrocarbons (PAH's) into soil and groundwater systems, leading to degradation of groundwater quality and creating public health risks. Former MGP sites require appropriate cleanup methods; this study uses PAH-contaminated field soil to examine the potential for cosolvent flushing as an efficient remediation technology. Batch experiments examined the desorption and solubilization of PAH's with cosolvent solutions; a log-linear relationship between cosolvent volume fraction (f_c) and equilibrium partitioning coefficient K_p was observed. A linear relationship between f_c and the percentage of PAH's removed from the field soil was also noted. Cosolvent effects on individual PAH's increased with solute hydrophobicity, represented by log K_{ow}. Column experiments studying the transport of PAH's with flow observed more efficient contaminant removal with an increase in solution f_c. A large-scale column experiment designed as a simple representation of PAH transport in a field setting found an estimated 93% removal of contaminants after 13.6 pore volumes (PV) of flushing with a 95% methanol solution.

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List of Abbreviations and Symbols

1N	One normal
$^3H_20$	Tritiated water
α	Cosolvent-sorbent interaction parameter
ACN	Acetonitrile
ACE	Acenapthene
ACY	Acenapthylene
ad-10	Anthracene d-10
BAA	Benzo[a]anthracene
BAP	Benzo[a]pyrene
BBF	Benzo[b]fluoranthene
β	Water-cosolvent interaction parameter
BKF	Benzo[k]fluoranthene
BGP	Benzo[g,h,i]perylene
BT1	Batch test: f_c range 0 to 1
BT2	Batch test: f_c range .7 to 1
^0C	Degrees Celsius
$CaCl_22H_20$	Calcium chloride dihydrate
C_E	Concentration extracted (mg/kg)
C_I	Initial concentration (mg/kg)
C_m	Concentration in mixed cosolvent phase (mg/L)

cm	Centimeter
CHR	Chrysene
D	Dispersion coefficient (cm^2/hr)
D/uL	Dimensionless dispersion coefficient
DBA	Dibenzo[a,h]anthracene
DCM	Methylene chloride
DI	Deionized
DNAPL	Dense non-aqueous phase liquid
Eq.	Equation
f_{ad}	Fraction ad-10 recovered
FLT	Fluoranthene
FLU	Fluorene
g	gram
H_2SO_4	Hydrogen sulfate
HOC	Hydrophobic organic compound
hr	Hours
KCl	Potassium chloride
kg	Kilogram
$K_{p,m}$	Equilibrium partitioning coefficient in mixed cosolvent (L/kg)
$K_{p,w}$	Aqueous equilibrium partitioning coefficient
K_{OW}	Octanol-water partitioning coefficient
L	Column bed length
L	Liter

LC	Large column
log	Logarithm, base 10
LNAPL	Light non-aqueous phase liquid
m	Meter
mg	Milligram
mL	Milliliter
M_I	Initial mass (mg)
min	Minute
M_m	Mass in mixed cosolvent phase (mg)
MGP	Manufactured gas plant
$MgSO_47H_20$	Magnesium sulfate
MRT	Mean residence time
MW	Molecular weight
Na_2SO4	Sodium sulfate, anhydrous
NAP	Naphthalene
NAPL	Non-aqueous phase liquid
NPL	National Priority List
O&M	Operation and maintenance
OM	Organic matter
PTFE	Polytetrafluoroethylene
PV	Pore volume
f_c	Cosolvent fraction
IND	Indeno[1,2,3-c,d]pyrene

NaHCO$_3$	Sodium bicarbonate
PAH	Polycyclic aromatic hydrocarbon
PAT	Pump-and-treat
PCE	Perchloroethylene
PHE	Phenanthrene
PPM	Parts per million (mg/kg)
PTFE	Polytetrafluoroethylene
PYR	Pyrene
R^2	Regression correlation coefficient
R$_m$	Retardation factor in mixed cosolvent
R$_w$	Retardation factor in aqueous solution
RP	Removal percentage (mg/mg)
RPD	Relative percent difference
SC1	Small column experiment with an f$_c$ of 0.9
SC2	Small column experiment with an f$_c$ of 0.95
σ	Cosolvency power
S$_m$	Solubility in mixed cosolvent
S$_w$	Aqueous solubility
u	Pore velocity
V$_f$	Volume flushed

1 Introduction

1.1 *Groundwater*

Groundwater is a vital source of fresh water, accounting for approximately 30% of the total global reserves and up to 98% when water tied up in glaciers and the polar ice caps is discounted (Foster and Chilton, 2003). It is estimated that 50% of global potable water supplies come from groundwater, and it is often a much more economical source than surface water. In the US, groundwater is used by 53% of citizens and accounts for approximately 20% of total water usage (Foster, 2006). While groundwater usage by humans dates back to early civilization, heavy exploitation did not begin until the 1950's with major advances in both scientific knowledge and extraction technology. This newfound ability to extract groundwater on a large scale, combined with aquifer degradation and contamination, has led to a stress on groundwater resources at the national and global levels and an increased focus on groundwater quality issues.

The National Groundwater Association estimates that approximately 3% of groundwater in the US is contaminated, but due to the wide variety of contaminants and very incomplete history of waste disposal, the true extent of the problem is uncertain. There are many different types of groundwater contaminants; the National Research Council lists the most common contaminant classes as volatile organic compounds (VOC's), toxic inorganic compounds, polycyclic aromatic hydrocarbons (PAH's), polychlorinated biphenyls (PCB's), pesticides, and phthalates (National Research

Council, 2004). Each of these contaminant classes can come from a variety of sources, resulting in degradation of water quality to varying degrees and requiring appropriate cleanup efforts (Hardesty and Ozdemiroglu, 2005).

1.2 Research Objective

One particularly prevalent source of groundwater contamination is former manufactured gas plant (MGP) sites, which release PAH's into soil and groundwater systems. Several PAH's are classified as carcinogenic, posing a threat to public health; they are recalcitrant compounds that may persist in the subsurface for centuries (Khodadoust et al., 2000). Convential cleanup methods for MGP sites have proven inadequate in achieving remediation goals within a desirable time frame.

The overall goal of this work is to evaluate the physicochemical remediation of natural solid materials from a former MGP that are contaminated with PAH's. The specific objectives are: (1) to characterize the PAH's in the field soil; (2) to advance a promising cleanup approach through detailed experiments to determine factors affecting remediation; and (3) to examine the effects of scale on remediation efficiency.

2 Background

2.1 Manufactured Gas Plant Sites

Manufactured gas was the nation's primary energy source during the late 18th and early 19th century, relying on a variety of processes to produce gas from various feedstocks. The estimate of total MGP's in operation in the US over time varies greatly by source, in part due to differences in the definition of an MGP site. Brown's Directory of American Gas Companies identified approximately 1,500 MGP sites operating between 1890 and 1950, but the study was limited due to voluntary reporting (Murphy et al., 2005). An EPA report in 2004 found that from 1800 to the mid 1900s approximately 36,000-55,000 MGP's were in operation in the US, and approximately 88% of these sites were suspected to have released contaminants (US EPA, 2004).

During the gas manufacturing process various byproducts were created, some reusable and others purely waste. Non-reusable residuals such as coal tar, iron filings, or contaminated wood chips were often disposed of on site or at nearby locations without an appropriate containment method. The size of these disposal sites ranges from less than an acre to approximately 200 acres, and they were often located near waterways or residential neighborhoods (Hatheway, 2002). The three major forms of manufactured gas are coal-gas, oil-gas, and carbureted water-gas; while the exact waste components at each site differ based on the type of gas created, residual tars are present at the majority of MGP sites and are typically the most important waste form at sites where risk is driven

by PAH's (Murphy et al., 2005). Tars are dense, non-aqueous phase liquids (DNAPLs) that contain significant concentrations of PAH's and are very difficult to remediate (Khodadoust et al., 2000). The high densities of DNAPLs often cause them to sink below the water table and collect in pools at impermeable layers where they are less accessible to cleanup actions. In other cases, in part due to high NAPL-water interfacial tensions, NAPLs may become entrapped within pore spaces by capillary forces and become resistant to mobilization (National Research Council, 2005). Contaminants tend to dissolve from the NAPL phase into bulk groundwater very slowly because of low aqueous solubilities; therefore, NAPLs generally persist in soil and groundwater for long time scales; the expected life span of a subsurface NAPL ranges from several decades to a few centuries depending on specific contaminants and local flow characteristics (CH2MHill, 1997).

Overall, it is estimated that over 11 billion gallons of by-product tars were released into the environment, impacting thousands of acres and millions of gallons of water. Cleanup costs at a single site have ranged from a few thousand dollars to over $86 million, with a cost range at a "typical" site from $3-10 million. Depending on the extent of contamination at sites not yet investigated, this could lead to a total cleanup cost for MGP sites of $26-128 billion (US EPA, 2004).

2.2 Polycyclic Aromatic Hydrocarbons

PAH's are a group of over 100 semi-volatile, hydrophobic organic compounds (HOC) existing throughout the environment in air, water, and soil. They are formed through incomplete combustion, often from the burning of coal, oil, wood, or other

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organic materials, and occur as complex mixtures in ambient settings (Agency for Toxic

Substances and Disease Registry, 1995). They range in molecular weight from 128 to 366

grams per mole, vary in structure from two to over six rings, and generally exist as

colorless solids in pure chemical form. The majority of PAH's come from synthetic

sources; the largest single source is wood burning in homes, followed by automobile and

truck emissions. High concentrations of PAH's can be found at hazardous waste sites

such as wood-treatment plants and MGP's; they are very common soil and groundwater

pollutants (Agency for Toxic Substances and Disease Registry, 1995). In groundwater

systems they are often found sorbed to soils or as part of a NAPL such as coal tar; they

display extremely low solubilities in water, causing them to be very recalcitrant in the

subsurface.

The EPA regulates 16 "priority" PAH's (Table 1) representing the most prevalent,

potentially harmful compounds found in the environment; benzo(a)pyrene is regarded as

the most toxic and is often used as a benchmark contaminant. While no federal

regulations are set for specific PAH's, the EPA has set a maximum contaminant level

(MCL) of 2 parts per billion (PPB) for total PAH concentrations in drinking water.

Documented health risks with significant exposure to PAH's include cancerous tumors

and possible harm to skin, bodily fluids, and the reproductive process. Exposure

pathways of particular concern for contaminated groundwater and soil systems include

dermal exposure (skin contact), ingestion through drinking water, and inhalation of

volatilized compounds (Agency for Toxic Substances and Disease Registry, 1995). The

EPA places particularly important hazardous waste sites on the National Priority List

(NPL) for expedited cleanup; as of April 7, 2008 there were a total of 1,641 current and

former NPL sites. PAH's were reported at over 600 of these sites, and this may even be
an underestimate as it is unknown how many NPL sites were not evaluated for their
presence (US EPA, 2007). It is notable that the 7 PAH's classified as carcinogenic by
ATSDR have the highest MWs (all at least 228.29 g/mol); therefore, high MW PAH's are
of particular importance in remedial considerations.

Table 1 Characterization of 16 EPA priority PAH's

PAH	Chemical Formula	Structure	Molecular Weight	Classified as Carcinogenic?
Acenapthene	$C_{12}H_{10}$		154.21	No
Acenaphthylene	$C_{12}H_8$		152.19	No
Anthracene	$C_{14}H_{10}$		178.23	No
Benzo[a]anthracene	$C_{18}H_{12}$		228.29	Yes
Benzo[a]pyrene	$C_{20}H_{12}$[b]		252.32	Yes
Benzo[b]fluoranthene	$C_{20}H_{12}$[b]		252.32	Yes
Benzo[k]fluoranthene	$C_{20}H_{12}$[b]		252.32	Yes
Benzo[g,h,i]perylene	$C_{22}H_{12}$[c]		276.34	No
Chrysene	$C_{18}H_{12}$[b]		228.29	Yes
Dibenzo[a,h]anthracene	$C_{22}H_{14}$[b]		276.34	Yes
Fluoranthene	$C_{16}H_{10}$		202.26	No
Fluorene	$C_{13}H_{10}$[b]		166.22	No
Naphthalene	$C_{10}H_8$		128.17	No
Indeno[1,2,3-c,d]pyrene	$C_{22}H_{12}$[b]		276.34	Yes
Phenanthrene	$C_{14}H_{10}$[b]		178.22	No
Pyrene	$C_{16}H_{10}$[b]		202.26	No

2.3 PAH Remediation at MGP Sites

There are several existing techniques for the removal of PAH contamination at
MGP sites including methods such as bioremediation, electrokinetic extraction, chemical

oxidation, air sparging, thermal treatment, and pump-and-treat (PAT) (US EPA, 2004). PAT is the most prevalent groundwater remedy used at Superfund sites, but due to a number of shortcomings the overall effectiveness and the efficiency of this strategy with respect to time and cost has historically been very low. In order for PAT methods to remain a viable option for site cleanup in the future, particularly at PAH-contaminated MGP sites, significant improvements must be made in the ability to remove contaminants in an efficient manner.

2.4 Pump-and-Treat

Pump-and-treat is the most common remediation method for contaminated groundwater systems, used either as a stand-alone treatment method or in combination with other methods at over 75% of NPL sites through 2007 (US EPA, 2007). The basis for PAT technology is the extraction of contaminated water from the subsurface and subsequent above-ground treatment. In a conventional PAT system, a set of underground injection wells pumps clean water into the soil and through the contaminated region, mobilizing the contaminated fluid toward a set of extraction wells (National Research Council, 1994). Once the contaminated water is removed through the extraction wells it is treated by one or more methods including adsorption, volatilization, precipitation, oxidation-reduction, or biotransformation (Bhandari et al., 2007). After treatment the water may be discharged to a local surface water body or in many cases reinjected underground; reinjecting treated water as a form of recycling the flushing solution source can improve process efficiency.

There are several significant limitations to PAT systems, largely dependent on contaminant characteristics and site hydrogeology. PAT effectiveness relies on the

dissolution of contaminants into the pumped solution, therefore contaminants that display low solubilities in water or preferentially sorb to soils present problems. NAPLs such as coal tar fall into this category; the inability to efficiently mobilize these contaminants towards extraction wells renders conventional PAT systems impractical because cleanup goals cannot be met in a reasonable time frame or at an acceptable cost (Kent and Mosquera, 2001). The hydrogeologic setting also plays an important role in determining the feasibility of PAT methods. Groundwater systems with low hydraulic conductivities (below 10^{-5} cm/s is considered poor, greater than 10^{-3} cm/s is ideal) can prevent flushing at desired rates (Bhandari et al., 2007). Subsurface heterogeneities can lead to preferential flow patterns, missing portions of the contaminated zone and allowing for collection of contamination in areas of low permeability. Due to natural heterogeneities in all soil and groundwater systems, complete information regarding these hydrogeologic properties is impossible to achieve; estimates must be made using optimized sampling procedures and current modeling techniques. Studies of PAT systems are indicative of the importance of these chemical and physical limitations; an EPA study found that of 39 PAT systems underway in 2001, only 7 were estimated to have progressed to at least 80% of the restoration goal (EPA, 2001).

The total cost of PAT systems is driven by the initial capital cost as well as operation and maintenance (O&M) costs; a 2001 EPA report of 79 large PAT systems found the mean and median annual O&M costs to be $570 million and $350 million, respectively. The large difference between the mean and median values can be attributed to several "megasites"; 13 of the 79 sites studied contributed approximately 50% of the total annual O&M costs. Over the course of a removal action these costs can become

prohibitive due to the longevity of PAT systems; a study of 67 PAT actions found that 52% lasted from 0-5 years, 42% from 5-10 years, and 6% for 10-15 years (Congressional Budget Office, 1994). In order to minimize these costs it is important to reduce PAT remediation time by increasing the efficiency of contaminant removal.

2.5 Improving PAT Methods: Introduction and Physical Processes

2.5.1 Decreasing PAT Time

In order to decrease the longevity of a PAT system, contaminants must be removed through extraction wells at a faster rate. Higher pumping velocities require more energy and are therefore more expensive; in many cases faster pumping is physically impossible due to the hydrogeologic setting. For highly contaminated areas, especially those containing hydrophobic organic contaminants (HOC's) such as PAH's, it has been estimated that up to tens of thousands of PV of water may be required to remediate to regulatory levels (Augustijn et al., 1994). This impractical strategy can be avoided by increasing the mass transfer of contaminant into the flushing solution and improving the mobility of NAPLs, thereby increasing the concentration of contamination in extracted fluid and reducing the total flushing volume (V_f) required. Increased mass transfer can be created by affecting two physical processes: the dissolution of contaminants into the flushing solution and the desorption of contaminants into the bulk fluid phase.

2.5.2 Solubilization

Equilibrium dissolution from complex wastes is often described by Raoult's law such that the concentration of component i (C_i) in contact with a complex solution (e.g. coal tar) can be determined by the simple relation

$$C_i = x_i S_i \qquad\qquad\qquad \text{(Eq. 1)}$$

where x_i is the mole fraction of component i in the waste mixture and S_i is the liquid solubility of the ith component; this does not hold for non-ideal fluids (Augustijn et al., 1997). Dissolution has a linear relationship with the difference between aqueous solubility and solubility in the secondary phase (e.g. NAPL); therefore, solubility enhancements will increase mass transfer in a predictable manner.

Solubility is inversely related with the hydrophobicity of a compound; one index for determining hydrophobicity is the octanol-water partitioning coefficient of a substance (K_{ow}), measuring the ratio of concentrations of a compound in octanol and water in a mixture of the two liquids. Hydrophobicity is positively correlated with MW such that PAH's of lower MW will solubilize into an aqueous solution more readily than the higher MW compounds. This effect makes high MW PAH's of particular concern for PAT methods; even in cases where the flushing solution is adequate for the removal of two and three ring PAH's, four, five and six ring PAH's may remain in the NAPL or solid phase.

2.5.3 Desorption

In order to design an effective enhanced soil flushing technology for PAH contaminated soils, it is important to understand the desorption process. Desorption is the reverse of sorption and is described as the release of contaminants from either a solid phase(sorbent) or liquid-solid interface into the adjacent fluid phase (Bhandari et al.,

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2007). Sorption includes two different processes, adsorption and absorption: adsorption is the attachment of contaminant to surfaces or interfaces, while absorption refers to the complete mixing of contaminant throughout the sorbent phase. PAH's can generally be absorbed into soils in two ways: entrapment in soil micropores and structures (also called intraparticle diffusion) and absorption into soil organic matter (OM) (Shore et al., 2003).

PAH desorption from soils occurs in two stages according to how the contaminant is sorbed to the soil. The first stage, known as the instant or fast stage, entails the relatively immediate release of contaminants either sorbed to the surface of or readily available within soil particles when exposed to a solvent, predominantly due to solubility increases. The second stage, known as the slow stage or nonequilibrium sorption, refers to the rate-limited process of PAH's diffusing through the OM and/or microporous structures of the soil. It has been hypothesized that in many soils, especially those with high OM content, PAH diffusion through OM is the dominant slow stage process (Shore et al., 2003). OM has been described as a three-dimensional polymeric structure perforated with voids, existing in a rigid, condensed state when in contact with an aqueous solution such as groundwater (Nkedi-kizza et al., 1989). Both the concentration and type of OM in soils affect this diffusive process; soils with high organic concentrations may experience greater nonequilibrium sorption . Since the fast desorption stage is relatively instantaneous, speeding up desorption during the flushing process may be best achieved by affecting the properties of the soil OM.

2.5.4 Mobilization

Increased NAPL mobilization is accomplished by reducing interfacial tension that creates pooling and entrapment (Okuda et al., 1996). With a large reduction in interfacial

tension, capillary forces holding the NAPL in place can be overtaken by pumping forces and moved toward extraction wells. Density-driven, gravitational and viscous forces may also come into play with reduced interfacial tensions, causing vertical mobilization of NAPLs. This is typically desirable with LNAPLs, as they float to the top of the water table and are more easily removed. In the case of DNAPLs such as coal tar, it may cause further contaminant migration towards an impermeable layer; this has been historically deemed problematic and hydraulic control of contaminants must be considered in remedial design (Augustijn et al. 1994). A recent technology designed to capture vertically mobilized DNAPLs, known as the Brine Barrier Remediation Technology (BBRT), may be a solution to this scenario. In this technology, a layer of dense brine is emplaced by injection above the impermeable layer; any vertically displaced DNAPLs will pool on top of the brine due to density differences and may be removed at that point (Hill et al., 2001).

2.6 Enhanced Soil Flushing

Injecting a flushing solution into the subsurface containing chemical additives can significantly improve the overall effectiveness, cost and time efficiency of PAT systems. This is achieved by increasing the mass transfer of contaminants into the fluid phase through enhanced solubilization and desorption of HOC's created by the chemical additives. This method can be referred to as enhanced soil flushing; one well-studied form of enhanced soil flushing is solvent flushing.

2.6.1 Solvent Flushing

Basic Principles

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Enhanced soil flushing utilizing water-miscible organic solvents as chemical additives is typically referred to as in-situ solvent washing or solvent flushing; since the solvents are generally mixed with water they are often called cosolvents. The theoretical basis for this method is the well studied enhancement of solubility and desorption of HOC's in aqueous solutions by cosolvents. Low-molecular-weight alcohols such as ethanol and methanol are the most common solvents of choice for in situ treatment methods; they are fully miscible in water, relatively biodegradable in the environment, and can increase the solubility of HOC's by several orders of magnitude (Augustijn et al., 1994).

Physical Description

Adding an organic solvent to water decreases the polarity of the solvent mixture, increasing the solubility of nonpolar organic compounds (Augustijn et al., 1997). It is well established that the solubility of nonpolar contaminants such as PAH's increases in a log-linear manner with increasing cosolvent volume fraction (f_c) such that

$$\log S_m = \log S_w + \beta\sigma f_c \qquad\qquad (Eq.\ 2)$$

where S_m is the solubility of a compound in the mixed cosolvent solution, $\log S_w$ is the solubility of a compound in aqueous solution, β is an empirical coefficient for water-cosolvent interactions, and σ represents cosolvency power (Morris et al., 1988). Through the linear relationship between solubility and dissolution of complex wastes expressed earlier, it can be seen that the dissolution of each coal tar waste component (e.g. individual PAH's) will increase in a log-linear manner with an increase in f_c.

Solubility and sorption of HOC's are inversely related; therefore, fast stage PAH desorption is expected to increase in a log-linear manner with the addition of cosolvent. The equilibrium partitioning constant K_p (L/kg), representing the ratio of the concentration of sorbed contaminant (mg/kg) over the concentration of contaminant in solution (mg/L), has a relationship with f_c such that

$$\log K_{p,m} = \log K_{p,w} - \alpha\beta\sigma f_c \qquad\qquad \text{(Eq. 3)}$$

where $K_{p,m}$ and $K_{p,w}$ are the equilibrium partitioning constant for the mixed cosolvent and aqueous phases, respectively (Brussea et al., 1991). The parameter α is an empirical constant representing the deviation of the K_p-f_c relationship from solubility dependence; a practical description for α is a quantification of the soil-cosolvent interactions. Cosolvent-sorbent interactions may cause positive ($\alpha > 1$) or negative deviations ($\alpha < 1$), depending on the system studied. The parameter σ is known as cosolvency power, a hypothetical partitioning coefficient for HOC's between a cosolvent and water expressed as

$$\sigma = \log(S_c/S_w) \qquad\qquad \text{(Eq. 4)}$$

where S_c and S_w represent the solubilities of the HOC in pure cosolvent and water, respectively (Rao et al., 1990). Cosolvency power has been described as the most important parameter in cosolvency theory as it quantitatively describes the relationship between a solute, cosolvent, and aqueous phase that drives increased solubilization (Augustijn et al., 1994).

Equilibrium sorption in transport problems is often evaluated in terms of a retardation factor (R) that represents the residence time of a contaminant in PV. R has a log-linear relationship with f_c derived from Eq. 3 such that

$$\log(R_m - 1) = \log(R_w - 1) + \alpha\beta\sigma f_c \qquad\qquad \text{(Eq. 5)}$$

where R_m and R_w represent the retardation factor in the mixed cosolvent and aqueous solutions, respectively (Nkedi-Rizza et al., 1987). Thus, contaminants should elute more efficiently with respect to relative V_f with increasing f_c in column experiments and field applications.

A principal effect of cosolvent on soils is through interaction with soil OM; as the aqueous phase is mixed or replaced with a solvent the reduction in polarity causes the rigid, condensed polymeric structure of the OM to expand or "swell" and become more flexible. This process has been called the cosolvent effect and allows for the release of previously entrapped contaminants. Cosolvent effects are reversible; OM will recondense when the mixed cosolvent is replaced with an aqueous phase. Octanol is an organic solvent that is used as a surrogate for OM in partitioning behavior; therefore, the hydrophobicity index K_{ow} can aid in the understanding of HOC sorption to soils containing OM. Cosolvency power has been shown to correlate positively with K_{ow} such that

$$\sigma = A \log K_{ow} + B \qquad\qquad\qquad \text{(Eq. 6)}$$

where both A and B are empirical constants applying to a specific compound (Chen and Delfino, 1997). This relationship signifies that cosolvent effects are greater on solutes that more readily partition into OM in aqueous solutions such as higher MW, more hydrophobic PAH's.

Soil sorptive properties studied both before the introduction of a cosolvent and after its removal have shown no differences, implying that cosolvents do not have an effect on the long-term retention capacity of soils (Brusseau et al., 1991). The effect of

cosolvents on OM is a significant benefit of solvent flushing, especially in soils with high

OM concentrations capable of entrapping a significant percentage of resident PAH's.

Field Precedent

Several field tests of alcohol flushing have found relative success in groundwater

remediation of DNAPLs using alcohol flushing solutions; two examples focused on

removal of perchloroethylene (PCE). The first study flushed two PV of a 95% ethanol,

5% water mixture over three days with approximate removal of 62-65% of initial PCE

contamination (Jawitz et al., 2000). A second study performed in an isolated cell utilized

a solution of approximately 70% ethanol and 30% water for approximately 10 PV over a

40-day period, removing an estimated 64% of PCE (Brooks et al., 2004). This study was

able to successfully recycle flushing solution, with recycling accounting for over 50% of

the total fluid injected; this allows for major cost reductions and is promising for future

field applications.

Both studies concluded that continued flushing would have led to increased

removal, and that the primary constraint on higher removal during the flushing period

was due to flow characteristics; subsurface heterogeneities and the resulting preferential

flow paths resulted in pockets of remaining PCE. This is best demonstrated by the second

study, which found 91% PCE removal in areas accessible by tracer tests. Each study

claims to support the use of cosolvent flushing under appropriate conditions, as removal

efficiencies based on both time and volume flushed were several orders of magnitude

higher than estimates for conventional pump-and-treat strategies. Improved performance

monitoring and adaptive management of pumping rates and locations have the potential to significantly improve removal rates.

Cosolvent Choice

Methanol and ethanol are the two primary candidates for solvent flushing application and display very similar partitioning coefficients for PAH's; therefore, it is very likely that their effectiveness in solubilizing and desorbing PAH's is similar (Augustijn et al., 1994). An ex-situ solvent washing process using ethanol was tested on PAH-contaminated soil from a former MGP site and found total PAH removal of greater than 93% compared to Soxhlet extraction including a calculated 100.1% removal for the two-ring and three-ring compounds. A set of small column experiments testing the cosolvent effects of ethanol and methanol on MGP field soil contaminated with PAHs found comparable removal rates for the two alcohols at a flushing solution volume fraction of 0.85 (Chen et al., 2005).

Methanol has received greater attention in the literature with respect to HOC desorption parameters, allowing for more direct comparison with experimental findings. A set of batch and column experiments found that methanol-water-soil systems spiked with PAH's displayed strong solubility and desorption enhancements and supported the hypothesis that nonequilibrium sorption is dependent on diffusion through OM (Bouchard, 1998). Column experiments performed utilizing different methanol volume fractions and PAH-spiked soil found that at lower volume fractions, contaminant elution was separated by molecular weight, essentially a chromatographic effect. As methanol

fraction increased to at or above 70% this effect became relatively negligible and PAH's began to quickly coelute; this is desirable for solvent flushing as it signifies a need for a reduced total V_f (Augustijn et al., 1994). The results of these experiments indicate that methanol may be able to remove PAH's from field soils effectively; this work furthers knowledge by (1) observing differences in the removal of a range of PAH's from an aged field soil as a factor of varying cosolvent f_c and (2) examining a large-scale solid material system, more representative of field site characteristics than small columns can achieve, to examine the effects of scale on the enhanced mass transfer of contaminants into flushing solution.

3 Materials and Methods

3.1 Materials

3.1.1 Soil Properties

The soil used in all experiments comes from a one-hectare former MGP site in Salisbury, NC. Samples were taken at a depth of approximately 1.2 m; soil was placed in plastic bags which were stored in 7 sealed buckets. The buckets were kept in a 4 ^{0}C walk-in refrigerator for the duration of this research to minimize PAH losses due to volatilization.

Analysis performed by Stephen Richardson determined that pure soil hydraulic conductivities were too low for column experiments; through experimentation it was determined that a 1:1 (g/g) mixture of field soil and 40/50 grain Accusand would provide the needed increase in conductivity. This mixture was used in several batch experiments and all column experiments. To create this blend, the field soil and Accusand were mixed together using a mortar and pestle. Properties of the soil/sand mix as found by the lab group of Dr. Aitken are listed in Table 2.

Table 2 Properties of soil/sand mix

Sand content	82.9%
Silt content	13.8%
Clay content	3.3%
Soil pH	7.6±0.1
Inorganic carbon	7.0±1.6 %
Organic matter	8.3±1.3%
Bulk density	2.6±0.1 g/cm^3
Avg. PAH Conc.	372± 57mg/kg

Initial analysis of the pure Salisbury soil found an average total PAH concentration of 863 PPM with a relative percent difference (RPD) of 18.84%, consistent with the findings of Dr. Aitken's group; soil PAH concentrations varied widely over experiments due to natural heterogeneity in field concentrations. No free phase coal tar was observed; the bulk of PAH mass existed sorbed to the soil. This is an important consideration for remediation as it indicates that mobilization through reduced interfacial tension would be negligible, causing solubilization and desorption of PAH's to be the primary processes of concern.

It is important to note that the soil OM content is high at $8.3\pm1.3\%$; it is likely that nonequilibrium sorption processes will exist and be dominated by diffusion through OM. Sorption kinetics of PAHs in the field soil are likely affected by aging as found in previous studies, making it more difficult to predict the desorbable fraction of contaminant and rate of release (Shor and Rockne 2003). It is important to test aged, contaminated soils in order to better reflect the processes that would occur at field sites; freshly spiked soils may behave in a more ideal manner, less applicable to field-scale implementation.

3.1.2 Soil Preparation

In batch and small column experiments even amounts of soil from each storage bucket were mixed prior to use for consistency. Batch experiments using pure soil utilized a soil slurry method to further standardize the material. The 7 bucket soil blend was poured into a glass beaker and DI water was added to form an approximate 4:1

(mL:g) water to soil mixture. The mixture was stirred for a 30-minute period; samples of the soil mixture were taken using volumetric pipettes and added to pre-weighed centrifuge vials. The vials were centrifuged and resulting supernatant poured off, leaving a layer of wet soil. Several vials were set aside for soil moisture content analysis, performed by fully drying the soil at approximately 100 ^{0}C overnight and determining the weight difference between wet and dry soil. The weight of wet soil in sample vials was then adjusted for moisture content (approximately 20% across experiments); all soil weights reported in this document are by dry weight.

The slurry method was not feasible for batch experiments using the soil/sand mixture due to separation of Accusand and field soil during stirring with water. Instead, the soil/sand mix was added directly to vials and a soil moisture content analysis performed; moisture content of the mixture was approximately 7% across experiments.

3.2 Analytical Methods

All PAH samples were analyzed by HPLC equipped with Waters 2475 Multi-Wavelength programmable fluorescence detector for quantification. A 10-cm LC-PAH column (Supelco 59134) was used with a mobile phase of an acetonitrile (ACN, Fisher Scientific A998-4) and water (Fisher Scientific W5-4) gradient . Flow and wavelength programs were modified from those used by Dr. Aitken's laboratory group. Of the 16 EPA priority PAH's, 14 were consistently quantifiable with good replication; acenapthylene (ACY) does not fluoresce appreciably, and acenapthene (ACE) was not able to be separated in chromatograms. This wide range of compounds allowed for

analysis of differences in behavior with variation of individual PAH characteristics, notably MW and hydrophobicity.

Calibration curves for the EPA priority compounds were performed using a 16 PAH standard solution (Supelco 4-8743). Calibration curves for anthracene d-10 (ad-10), an internal standard, were performed using solutions of solid phase ad-10 (Supelco 44-2456) in ACN.

3.3 Batch Experiment Methods

3.3.1 General Methods

Samples

Batch tests were designed to examine the ability of flushing solutions to desorb and solubilize PAH's from the Salisbury field soil. In each experiment, known amounts of soil and solution were added to 35-mL glass centrifuge vials with polytetrafluoroethylene (PTFE) septa screw caps along with several 5-mm glass beads to encourage mixing during equilibration. The vials were then sealed with Parafilm and allowed to equilibrate on a rotating tumbler for a set period of time. After the equilibration period, the vials were centrifuged at 3500 rpm for 20 minutes and the supernatant poured into glass volumetric flasks. The volumetrics were then filled to a known volume with ACN; subsequent dilutions were made to bring the PAH content into the range of the HPLC fluorescence detector. Finally, diluted samples were filtered using 0.22 µm pore-size PTFE syringe filters (Whatman 6879-1302 and Fisher Scientific

097207). During filtration, the first 1.5 mL was sent to waste to minimize the effects of sorption onto filters.

Extracts

PAH's were extracted from the remaining soil using a 2 round method developed by the lab group of Dr. Aitken. Before PAH extraction, a known amount of anthracene d-10 (ad-10) was added to each vial as an internal standard to control for sample loss, volatilization, instrument drift, or other sources sample error. The final PAH concentrations of each vial were adjusted based on the fraction of ad-10 recovered (f_{ad}) during extraction such that

$$C_{adjusted} = C_{analyzed} / f_{ad} \hspace{3cm} \text{(Eq. 7)}$$

Values of f_{ad} ranged from 0.65 to 1.13 over the course of experiments, with an average of 0.85±0.15.

Between 5 and 10 grams of Na_2SO4 (ACROS 1966 40025) was added to vials to remove residual water content (DCM is immiscible in water), then 10 mL each of acetone (Fisher Scientific A18-20) and methylene chloride (DCM, Fisher Scientific D150-4) were added. Samples were equilibrated for 24 hr, and then centrifuged at 3500 rpm for 20 min and the supernatant poured into volumetric flasks. Another 10 mL of DCM and acetone were added to vials and equilibrated for a second 24 hr period. Again the vials were centrifuged, and the supernatant from the second extraction round added to the corresponding first round volumetric flask. Each volumetric was then filled to a known volume with ACN, diluted and filtered for HPLC analysis.

Data Analysis

The initial total PAH mass in each vial was determined by a mass balance of PAH's removed to the fluid (mixed cosolvent) phase (M_m) and the PAH's extracted (M_e) such that

$$M_I = M_m + M_e \qquad \text{(Eq. 8)}$$

Where M_I represents the initial PAH mass in the vial soil. Concentrations were determined by dividing PAH mass by vial soil weight. Concentrations are reported as parts per million (PPM) by mass, calculated as mg PAH per kg of dry soil. With differing initial PAH concentrations in every vial due to inherent contaminant distribution heterogeneity in the field soil, directly comparing concentrations of PAH's in the cosolvent phase does not provide a good metric for comparison between samples; instead several other metrics are used.

PAH removal percentage (RP) is used as a practical metric representing the fraction of total PAH's removed from the soil into solution, determined by

$$RP = 100 \times (M_m / M_I) \qquad \text{(Eq. 9)}$$

RP was determined for each individual PAH; calculation of total PAH removal in the vial was performed by a summation of all individual PAH's removed to the mixed cosolvent phase, divided by the sum of all individual (*i*) PAH's remaining sorbed to the soil:

$$\text{Total PAH RP} = 100 \times \Sigma_i \ M_{im} / \Sigma \ M_{iI} \qquad \text{(Eq. 10)}$$

Equilibrium sorption partition coefficients $K_{p,m}$ (L/mg) are an important metric, determined by the ratio of the residual sorbed PAH concentration (C_E, mg/kg) to concentration of PAH's in mixed cosolvent phase (C_m, mg/L) such that

$$K_{p,m} = C_E/C_m \qquad \text{(Eq. 11)}$$

A plot of log $K_{p,m}$ versus f_c was used to test the relationship expressed in Eq. 3. The product $\alpha\beta\sigma$ was determined for each PAH, representative of the combination of cosolvency power, soil-cosolvent, and cosolvent-water interactions responsible for the fluctuation of $K_{p,m}$ with f_c. This was calculated by predicting a hypothetical $K_{p,w}$ value for each PAH based on the $K_{p,m}$ vs. f_c regression, and dividing the difference between log $K_{p,w}$ and log $K_{p,m}$ by f_c. Calculations were only performed for the range of f_c values that held to the f_c/log $K_{p,m}$ relationship; the average $\alpha\beta\sigma$ across all f_cs is reported.

3.3.2 Experimental Design

BT1: Methanol Batch Test of f_c Range 0 to 1

The first batch experiment studied methanol at f_c of 0, 0.2, 0.4, 0.6, 0.8, and 1 to test the RP and desorption of the aged field soil in cosolvent. Approximately 1.5 grams of pure field soil and 20 mL of cosolvent solution were added to each centrifuge vial for an equilibration period of 48 hr.

BT2: Methanol Batch Test of f_c Range 0.7 to 1

A second experiment was performed to examine RP and desorption kinetics of methanol in the soil/sand mixture at a f_c range of 0.7 to 1 by intervals of 0.05, representing potential flushing solutions. An f_c of 0.7 was chosen as the lowest point based on the results of the initial cosolvent test as well as literature findings that PAH's began to coelute (i.e. show no chromatographic effects during miscible displacement) in column experiments at a f_c of approximately 0.7 (Augustijn et al., 1994). Each f_c was

tested at equilibration periods of 24 and 48 hr to look for rate-dependent desorption differences. Approximately 4 grams of the soil/sand mixture and 20 mL of cosolvent solution were added to the vials.

BT3: Methanol Rate Release Batch Test

PAH removal with a methanol f_c of 0.9 was examined for the effects of rate limited desorption through a batch experiment with sample vials equilibrating for 1, 2, 4, 8, and 16, 24, 48, 72, and 96 hr. The extended time range was chosen to examine desorption over multiple time scales (days and hr); a methanol f_c of 0.9 was used to represent a viable field flushing solution based on methanol f_c experimental data and field precedent for an f_c of above 0.9 (Brooks et al., 2004; Jawitz et al., 2000). Approximately 4 grams of the soil/sand mixture and 20 mL of solution were added to each vial.

3.4 Small Column Experiment Methods

3.4.1 General Methods

Small column experiments were designed to study the ability of cosolvent solution to transport PAH's with flow based on solubility and desorption enhancements. High f_c values were chosen based on effectiveness in batch experiments, field precedent, and the goal of maximizing the effects of methanol cosolvency power.

Experiments were performed in a vertically oriented glass column with an inner diameter of 2.5 cm. A plastic insert with a metal end (facing the soil) was inserted into the bottom of the column to fill extra space and sealed by an O-ring; plastic tubing was

connected to the insert and led to a PHD 440 programmable syringe pump. A wet packing procedure was used to minimize air entrapment during setup; columns were packed with the soil/sand mixture. De-aired water was pumped upward through the base of the column, and an initial 30/40 grain Accusand bed was poured into the water from the column top in order to retain soil fines that may have otherwise clogged the effluent port. After leveling the sand bed, soil was slowly dropped into the water from the top of the column, always maintaining a water level of at least at least 2 cm above the soil; the column was gently agitated every few minutes to ensure air pockets were removed during soil addition. After the desired amount of soil was added, the column top was sealed with parafilm and allowed to settle overnight. The following day a plastic insert with a stainless steel end facing the soil was inserted downwards to fill extra space; this insert was also connected to the syringe pump by plastic tubing. The plastic tubing at the base of the column was disconnected from the pump, removed from the column base and replaced with stainless steel tubing to minimize effluent sorption. The column was allowed to equilibrate further with de-aired DI water pumped through slowly for 24 hr. Flushing solution was pumped from top to bottom, with effluent collected at the end of the stainless steel line; all column effluent was captured during experiments, enabling a PAH mass balance.

After the initial equilibration period, pumping solution was switched to the cosolvent mixture and pumping started. Effluent was captured in clear glass, 10-mL vials with PTFE screw caps containing a predetermined volume of acetonitrile to prevent sample volatilization or sorption to the glass. Samples were kept in a closed box in a 4 ^{0}C

refrigerator to prevent volatilization or photodegradation of PAH's, diluted to within optimal concentrations for HPLC analysis and filtered.

The post-flushing soil extraction procedure was the same as for the batch experiments, although different sampling methods for determining residual PAH distributions were used in each experiment.

3.4.2 Experimental Design

SC1: 0.9 Methanol f_c Flush

The column was packed with 159.75g of the sand/soil mix and a sand bed of 8.32 g at the base, with a total bed height of 20.5 cm.

A step tracer test was performed after the methanol flush for accurate measurement of column properties using tritiated water (^3H_2O), a non-reactive radioactive material. The column porosity, PV, mean residence time (MRT), and dispersion parameters were determined from tracer results.

After an initial equilibration period, a methanol solution with an f_c of 0.9 was flushed through the column at a pore velocity of 56.7 cm/day and flow rate of 5.334 mL/hr. Analysis of effluent PAH's was performed during flushing; once a period of extended tailing was reached, at 6.22 PV, de-aired DI water was pumped through the column to displace resident methanol. Total flushing time was approximately 62.3 hr.

All of the column soil was extracted post-flushing and separated into 9 segments based on bed depth to study residual contaminant distribution; soil remaining on the column was rinsed off and analyzed to complete the mass balance..

SC2:0.95 Methanol f_c Flush

The second column was packed with 172.19 g of soil/sand mix, with an Accusand bed at the base of 9.99 g, creating a total bed height of 22.2 cm. The column PV, porosity, and MRT were estimated to be 50.1 mL, 0.463, and 24 hr; due to high accuracy of initial estimates (within 0.05%) of PV and porosity for *SC1* and the time consuming nature of tracer tests, a tracer was not performed for *SC2*. After the initial equilibration period, a methanol solution with an f_c of 0.95 was pumped through the column at a pore velocity of 22 cm/day and flow rate of 2.041 mL/hr. This flow rate was chosen in order to create a MRT of approximately 24 hr, allowing desorption more time to reach near-equilibrium than in *SC1*.

A total of 8.01 PV of methanol solution was pumped through, followed by 68 mL of de-aired DI water to displace the methanol. A flow interruption was performed at 5.46 PV; the pump was shut down and the column closed off for a 48 hr period. The purpose of this interruption was to test for rate-limited desorption; this has been done successfully in past studies (Brusseau et al., 1997). When desorption is rate-limited, effluent concentrations will show a spike after the interruption; the size and shape of this spike can provide information about the magnitude of desorption nonequilibrium due to rate limitations.

The column was segmented into 4 soil sections and the sand bed for soil extraction. Triplicate samples were extracted and analyzed for each segment to increase data quality, but the entirety of the soil was not extracted as in the first experiment. This method was chosen to roughly match the method required for sampling of the large column.

3.5 Large-Scale Column Experiment Methods

The large column experiment was designed as a simplified, one-dimensional representation of solvent flushing for field application. The larger scale of the column allowed for improved simulation of inherent subsurface heterogeneities and variation in soil properties; sampling ports distributed over the length of the column enable study of contaminant spatial distribution. Efficient PAH removal from the large column may indicate the potential for success at the field scale.

The column was specially constructed by the UNC Environmental Science and Engineering shop; the body was made of stainless steel with a height of 110 cm and inner diameter of 10.2 cm; 3 soil sampling ports were built in at evenly spaced vertical intervals. The top of the column was sealed by a removable cap equipped with a pressure gauge and inlet port; PTFE tubing connected the inlet port to a peristaltic pump (Eldex Laboratories PN 1005 A-60-8). A switch valve at the base attached to two effluent lines: one made of stainless steel, for use during sampling to prevent sorption of PAH's to PTFE, and a second PTFE line for effluent sent to waste. Flushing solution was pumped from a sealed 20 L carboy. Discrete effluent samples were collected at set intervals in 40-mL glass vials, sealed with PTFE screw caps and pre-filled with 10 mL of ACN to decrease PAH volatilization and sorption to glass. Samples were stored in a closed box in a 4 ^{0}C refrigerator to prevent photodegradation and volatilization until prepared for HPLC analysis. Effluent flow rate and column pressure were measured at each sampling interval.

The column was wet-packed using the same procedure as for the small column experiments with a total sand/soil mixture mass of 13.4 kg and bed height of 100 cm. An

802 g bed of Accusand was added at the base of the colum with a thickness of approximately 5 cm; there was a 5 cm aqueous layer between the top of the soil bed and the column top. After setup, the column was flushed with an aqueous solution designed to represent ambient groundwater; components of simulated groundwater were 1.83 g $CaCl_2 2H_2O$, 1.01g $MgSO_4 7H_2O$, 2.19g $NaHCO_3$, 1 mL of 8.77 g/L KCl solution, and 1g of 1N H_2SO_4 solution in 20 L DI water. The column experienced continuous flow with this mixture at a flow rate of 1.5 mL/min and pore velocity of 56.7 cm/day for a period of approximately 11 months before cosolvent flushing in order to equilibrate the system and test for mechanical issues (e.g. pump failure, leaks, etc.).

A pulse tracer test was performed with ^3H_2O before the cosolvent flush for accurate determination of the column porosity, PV and dispersion.

Cosolvent flushing was performed continuously using a methanol solution with an f_c of 0.95 for 13.56 PV over a period of 13 days, 14 hr and 23 min at a flow rate of 2.4 mL/min and corresponding pore velocity of 99 cm/day.

Soil samples were taken from the 3 ports and the top of the soil bed before and after flushing and analyzed for PAH content using the same extraction procedure as the batch and small column experiments.

After the 13.56 PV flush with clean cosolvent was completed and final soil samples taken, flushing was restarted using recycled effluent waste from the second half of the cosolvent flush, for a period of 16 days and 16 hr or approximately 16.6 PV. The flushing solution was then switched back to clean methanol with an f_c of 0.95 for approximately 1 day and 8 hr, an estimated 1.3 PV, with the effluent sent to waste. At this point the effluent line was placed into the clean cosolvent influent container for a

final recycling period of 4 days, 17 hr and 40 min, or approximately 4.7 PV. Finally, the

flushing solution was switched to DI water indefinitely and sent to waste. The recycling

period was designed to study continued slow rate desorption and attempt to maximize

PAH removal, under the assumption that the partitioning of contaminants into the solid

material as they reenter the column with recycled solution would be negligible. Data for

the recycling period was not yet analyzed at the time this document was completed.

4 Results and Discussion

4.1 Batch Experiments

4.1.1 Varying Cosolvent Fractions

Total PAH Concentrations

The average total PAH content per vial in *BT1* and *BT2* were 579 ± 205 PPM
(pure soil) and 546 ±439 PPM (sand/soil mix), respectively. Variation in contaminant
concentration between vials in *BT2* was driven by several samples with unusually high
PAH levels; removing these outliers results in an average total PAH concentration of
430±68 PPM for *BT2*. Due to analytical error, NAP and FLU are not included in the *BT1*
total and ANT is not included in the *BT2* total. Comparing only compounds analyzed in
both experiments leads to average total PAH concentrations by difference (excluding
outliers) of 553 and 378 PPM for *BT1* and *BT2*, respectively. Noting that sand/soil
mixtures should theoretically contain PAH concentrations ½ that of pure soil mixtures,
the significant difference in average PPM is a reminder of the uneven distribution of
PAH's within the soil. While several vials contained highly concentrated pockets of
PAH's, a large difference in concentrations is still observed after the removal of outliers.

Removal Percentage

The RP at an f_c of 0.2 was statistically comparable to the RP of water; at an f_c of
0.4 significant PAH removal was evident and continually increasing up to pure solvent

(Figure 1). Removal for an f_c of 0.8 does not appear to fit the increasing trend, largely

due to a single sample that recovered less than 10% of benzo[a]anthracene (BAA), which

accounted for close to 1/3 of the total vial PAH mass; the reason for this low recovery is

not clear. It is notable that BAA recovery was low across all values of f_c.
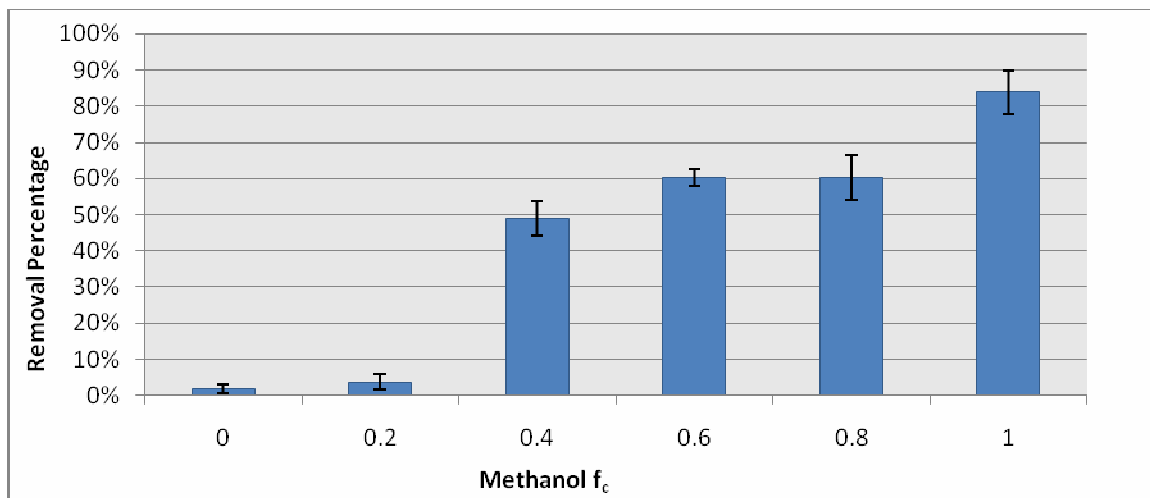
Figure 1 *BT1* **total PAH RP as a factor of f_c**

Observing removal of individual PAH's in Table 3shows that while f_c's of 0.4 and

0.6 showed differentiation in average RP between low and high MW compounds, similar

to a chromatographic effect, there was no distinct relationship between MW and RP for

samples at an f_c of 0.8 or 1. Linear regressions performed between RP and f_c for

individual PAH's over a range of 0.4 to 1 show high R^2 values. The linear relationship

did not hold over the full f_c range of 0 to 1, supporting previous findings that the fraction

of HOCs that desorb quickly may not increase until a threshold cosolvent concentration

in some soils (Brusseau et al., 1991).

Table 3: *BT1* RP values as a factor of f_c; regression statistics for f_c vs. RP

Compound	RP Values with f_c						Regression	
	0	0.2	0.4	0.6	0.8	1	Slope	R^2
PHE	5%	8%	65%	74%	82%	91%	0.441	0.999

ANT	1%	2%	37%	49%	61%	76%	0.643	0.994
FLT	1%	3%	54%	67%	81%	90%	0.617	0.994
PYR	2%	6%	78%	88%	94%	97%	0.313	0.936
BAA	1%	1%	9%	15%	9%	31%	0.300	0.569
CHR	0%	1%	16%	48%	71%	91%	1.252	0.988
BBF	6%	2%	52%	78%	93%	97%	0.755	0.901
BBK	0%	0%	6%	16%	40%	71%	1.093	0.955
BAP	1%	0%	15%	36%	64%	86%	1.204	0.997
DBA	2%	1%	21%	59%	84%	94%	1.225	0.940
BGP	7%	4%	35%	80%	94%	98%	1.010	0.819
IND	1%	1%	23%	60%	85%	94%	1.190	0.936

RP for PAH's generally increased with f_c from 0.7 to 1 in *BT2*, but linear regressions returned relatively low R^2 values, likely due to soil variation causing noise in the data; this was not as noticeable across the f_c range 0 to1, potentially because the ratio of noise to change in RP was much lower over f_c intervals of 0.2. The 48-hr samples averaged slightly higher (not statistically significant) RPs than the 24-hr samples at f_c's of 0.7, 0.75, 0.85, and 0.9; these differences were driven primarily by increased BGP removal for the 48 hr samples, suggesting that BGP removal experiences greater desorption rate effects than other PAH's.
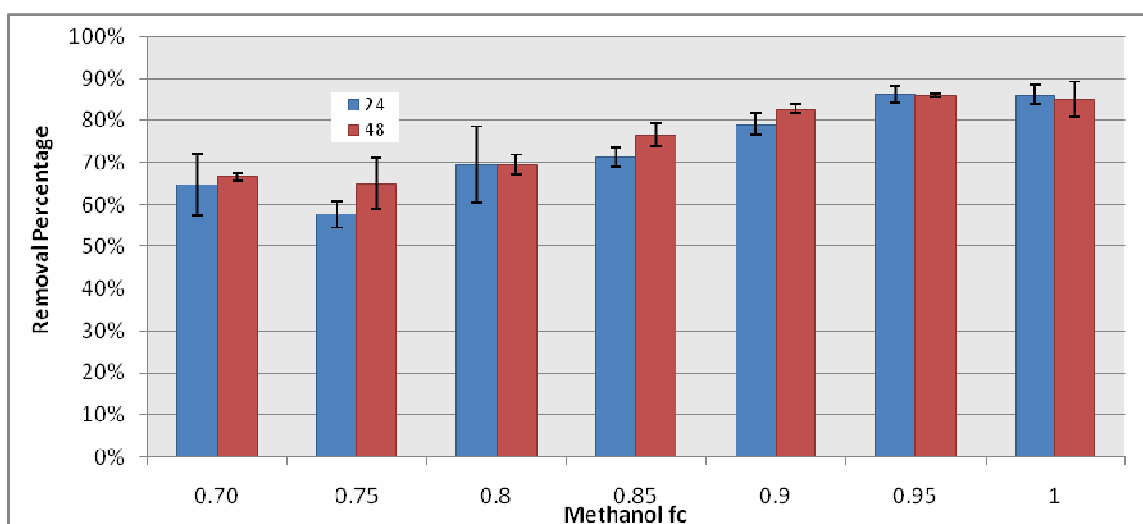
Figure 2 *BT2* **RP as a factor of f_c (24 and 48 hr samples)**

Increased removal between f_cs of 0.7 and 1 appeared to be driven primarily by improved desorption and solubilization of the higher MW PAH's. This is evident visually when looking at Figure 3, showing RP for individual PAH's versus f_c for the 48 hr samples (24 hr data was comparable). While lower MW compounds displayed relatively minor removal improvements with f_c increase from 0.7 to 1, the higher MW PAH's showed much more drastic improvements (PAH's in order of MW, increasing from left to right).
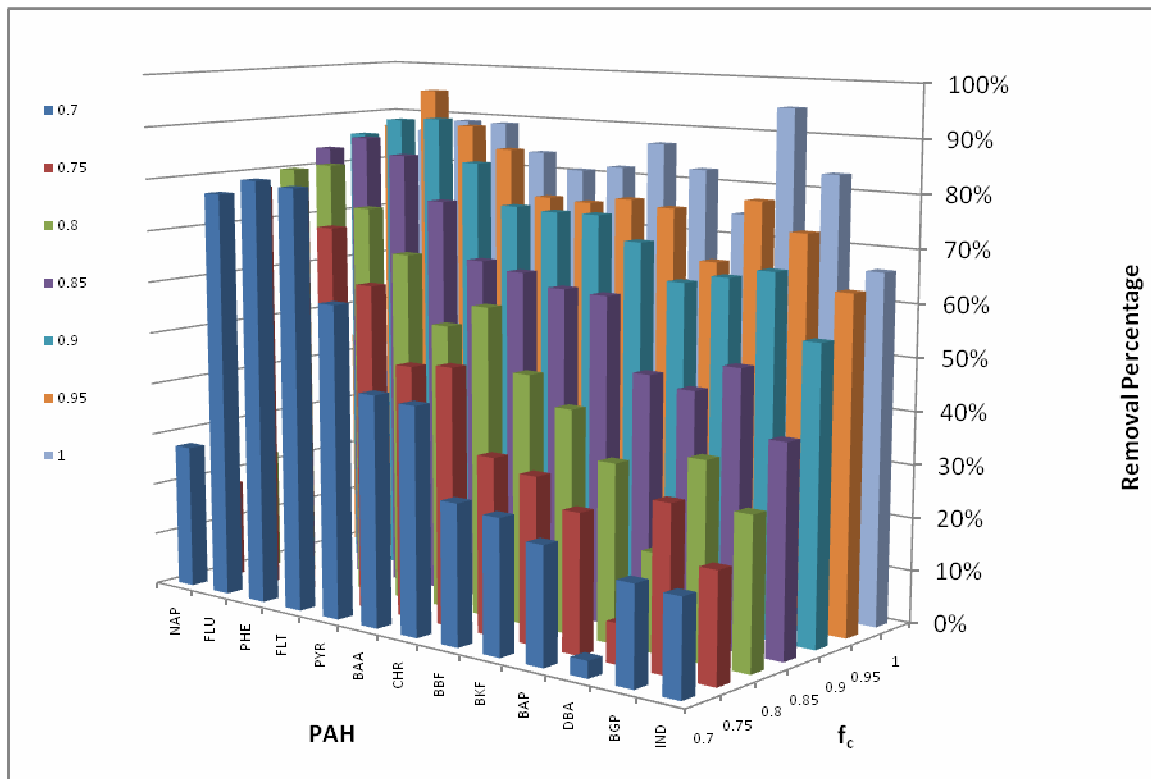
Figure 3 *BT2* **RP of individual PAH's as a factor of f_c (48 hr samples)**

Examining this trend quantitatively by performing linear regressions for individual PAH's of methanol f_c versus RP shows that higher MW PAH's (with higher K_{ow}) exhibit much higher slope and R^2 values (Table 4). This supports the hypothesis that σ is stronger for more hydrophobic compounds, making a case for the use of a high f_c during flushing

to coelute high and low MW PAH's. Each of the seven PAH's classified as carcinogenic show a correlation coefficient of greater than 0.96.

While total PAH removals were similar for both experiments at f_c's of 0.8 and 1, *BT2* showed lower RPs for the middle and high MW compounds than *BT1*, especially at f_c's of 0.7 to 0.85. The low recoveries of BAA in *BT1* balanced the generally lower RPs of the rest of the compounds in *BT2* to create similar total PAH RPs. There are several possible explanations for the lower RPs in *BT2*; potentially the OM properties of *BT2* soil were less amenable to the release of contaminants due to natural variability in the field soil. Another possibility is the difference in soil mass per vial between the experiments. The *BT2* vials have greater solid material surface area; therefore, if similar $K_{p,m}$ coefficients were seen in the two experiments *BT2* vials would have greater residual sorbed PAH concentrations. While PAH's may not attach to the Accusand, the pure soil mass in *BT2* vials is still greater than *BT1* vials by an average of approximately 0.5 g.

Table 4 *BT2* RP values as a factor of fc; regression statistics for f_c vs. RP (48 hr samples)

Compound	RP values across f_c							Regression	
	0.7	0.75	0.8	0.85	0.9	0.95	1	Slope	R2
NAP	28%	19%	23%	23%	27%	44%	35%	0.545	0.487
FLU	78%	78%	81%	85%	87%	88%	87%	0.366	0.877
PHE	81%	79%	83%	87%	90%	95%	89%	0.466	0.726
FLT	80%	72%	75%	84%	91%	89%	89%	0.540	0.625
PYR	59%	62%	67%	76%	83%	85%	84%	0.957	0.920
BAA	44%	48%	54%	65%	75%	76%	81%	1.341	0.962
CHR	43%	49%	59%	64%	75%	76%	82%	1.327	0.976
BBF	27%	33%	47%	62%	75%	77%	87%	2.110	0.975
BKF	25%	31%	42%	62%	70%	76%	82%	2.062	0.968
BAP	22%	26%	33%	48%	64%	67%	75%	1.919	0.968
DBA	3%	8%	18%	46%	66%	79%	95%	3.314	0.975
BGP	19%	31%	37%	51%	67%	73%	83%	2.214	0.988
IND	18%	21%	28%	40%	56%	63%	66%	1.838	0.964

Equilibrium Sorption Partitioning Coefficients

$K_{p,m}$ values varied between the two experiments; log $K_{p,m}$ showed a strong linear relationship with f_c for most PAH's between an f_c of 0.04 and 1 in *BT1*. Yet in *BT2*, while f_c values of 0.75 to 1 showed a linear relationship with log $K_{p,m}$; the 0.7 f_c samples did not fit the regression. This may be consistent with previous literature findings that suggest some desorption relationships only hold up to an f_c of 0.7 (Brussea et al., 1991; Augustijn et al., 1994); it may also be the result of experimental error or variation in soil properties.

$K_{p,m}$ values at comparable f_c (0.8 and 1) were generally lower for *BT2*, indicating that for most compounds PAH's partitioned more readily into the cosolvent phase when in contact with the soil/sand mixture than pure soil. This is an intuitive observation because it is unlikely that a significant amount of PAHs sorbed to the OM-free sand while redistributing during the equilibration period; therefore, a large fraction of the solid surface area did not contain PAHs, decreasing C_E of the mixture.

Table 5 *BT1* log $K_{p,m}$ values with varying f_c ; regression statistics for f_c vs. $K_{p,m}$

Compound	Log $K_{p,m}$ Values across f_c						Regression	
	0.0	0.2	0.4	0.6	0.8	1.0	Slope	R^2
PHE	3.10	2.60	1.68	0.85	0.61	0.34	-2.95	0.953
ANT	3.55	3.14	2.24	1.39	1.14	0.85	-2.90	0.958
FLT	3.42	3.11	2.22	1.24	0.93	0.43	-3.21	0.973
PYR	2.82	2.54	1.66	0.62	0.31	-0.18	-3.24	0.969
BAA	3.43	3.47	3.20	2.21	1.86	1.35	-2.32	0.924
CHR	3.87	3.62	3.02	1.91	1.36	0.59	-3.47	0.976
BBF	3.02	2.81	2.53	1.34	0.72	-0.13	-3.32	0.950
BKF	4.45	4.04	3.73	2.66	2.03	1.17	-3.35	0.971
BAP	3.84	3.49	3.27	2.27	1.63	0.77	-3.14	0.960
DBA	3.71	2.98	3.04	2.44	1.19	0.24	-3.33	0.915
BGP	2.74	2.55	2.96	1.54	0.88	-0.18	-3.00	0.830
IND	3.27	3.20	3.18	2.06	1.31	0.33	-3.07	0.889

Table 6 *BT2* log $K_{p,m}$ values with varying f_c ; regression statistics for f_c vs. $K_{p,m}$ (24 hr samples)

Compound	Log $K_{p,m}$ values across f_c							Regression	
	0.7	0.75	0.8	0.85	0.9	0.95	1	Slope	R^2
NAP	1.75	1.47	1.16	1.22	1.28	0.83	0.88	-2.23	0.719
FLU	0.14	0.27	0.15	0.07	-0.06	-0.19	-0.20	-1.98	0.973
PHE	0.10	0.29	0.13	0.01	-0.19	-0.33	-0.31	-2.63	0.951

FLT	0.21	0.31	0.12	0.00	-0.18	-0.40	-0.38	-2.96	0.962
PYR	0.59	0.63	0.40	0.39	0.16	-0.04	-0.12	-3.03	0.968
BAA	0.82	0.85	0.69	0.55	0.32	0.13	0.04	-3.42	0.989
CHR	0.87	0.86	0.73	0.58	0.35	0.18	0.05	-3.36	0.992
BAP	1.05	1.14	0.98	0.72	0.31	0.18	-0.22	-5.48	0.982
BBF	1.05	0.91	0.83	0.75	0.35	0.14	-0.12	-4.35	0.951
BKF	1.15	1.18	1.03	0.89	0.58	0.36	0.21	-4.10	0.985
DBA	2.57	2.23	1.57	1.42	0.76	0.47	0.09	-8.40	0.980
BGP	1.04	1.43	1.09	0.92	0.56	0.29	0.09	-5.44	0.993
IND	1.39	1.40	1.13	1.01	0.72	0.50	0.31	-4.36	0.993

Values for $\alpha\beta\sigma$ were calculated for methanol over the range of f_c from 0.4 to 1 for *BT1* and 0.7 to 1 for *BT2*. Both sets of $\alpha\beta\sigma$ were lower than σ values presented in the literature for methanol-water-PAH systems, suggesting that $\alpha\beta<1$ for the aged field soil. An $\alpha\beta$ value of less than one indicates that the cosolvent-sorbent and cosolvent-water interactions led to a decreased overall effectiveness of cosolvent to remove PAH's to the fluid phase.

Table 7 Batch test $\alpha\beta\sigma$ values compared to literature σ values

Compound	*BT1* $\alpha\beta\sigma$	*BT2* $\alpha\beta\sigma$	Literature σ
NAP	-	2.23	3.72[a]
FLU	-	1.98	4.12[a]
PHE	1.27	2.63	4.61[a], 4.24[b]
ANT	1.22	-	4.67[a], 4.06[b]
FLT	1.54	2.96	5.31[a], 4.65[b]
PYR	1.70	3.03	5.19[a], 4.69[b]
BAA	-	3.42	5.74[a], 5.22[b]
CHR	3.03	3.36	5.68[a], 4.4[b]
BBF	2.58	5.48	6.44[a], 6.53[b]
BKF	2.64	4.36	6.51[a]
BAP	2.59	4.10	5.95[a], 4.05[b]
DBA	3.04	8.40	6.5[a]
BGP	3.27	5.44	6.9[a]
IND	2.94	4.36	6.66[a]

a - (Chen and Delfino, 1997), b - (Lane and Loehr, 1992)

Another possible explanation for this behavior is that sorption did not reach equilibrium during the 24 or 48 hr periods, and with a longer equilibration time $\alpha\beta\sigma$ values would increase; this would indicate a slow of rate desorption due to PAH

entrapment within OM. Using a common $K_{p,w}$ value in calculations, 12 of 14 PAH's in

48- hr samples did show marginally higher (only statistically significant for DBA and
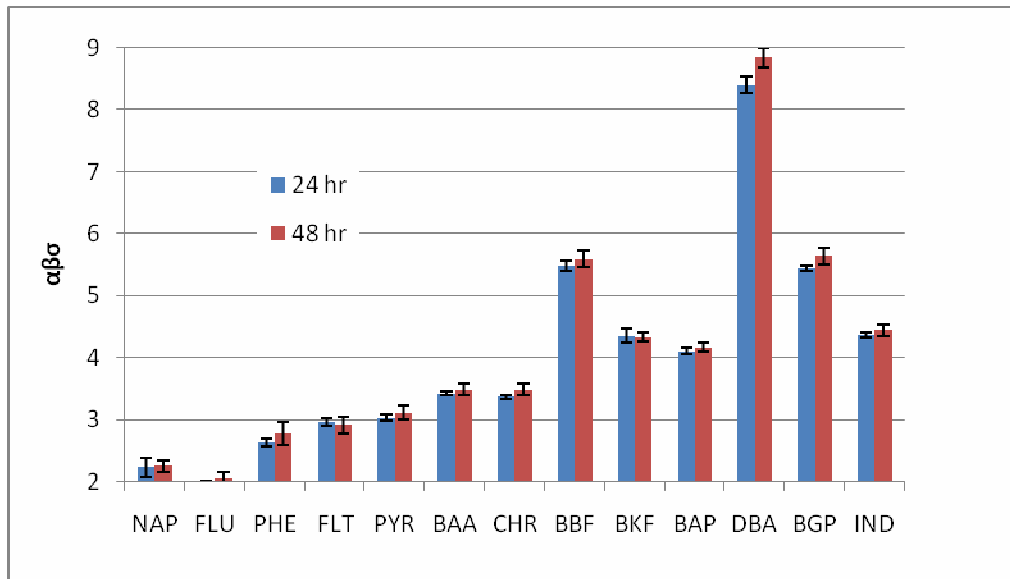
BGP) $\alpha\beta\sigma$ values than 24-hr samples.

Figure 4 *BT2* **values for αβσ (24 and 48 hr samples)**

A linear trend between log K_{ow} and $\alpha\beta\sigma$ was apparent for both experiments in

regressions as suggested in Eq. 6 ; literature linear regression analysis performed on a

range of cosolvents (Morris et al., 1988) found the slope of the coefficient A in

methanol-water systems to be 0.68, in between the slope values of .616 and .796 for *BT1*

and *BT2* (Figure 5). The same analysis found an R^2 value of 0.84, in comparison to R^2

values of 0.718 and 0.778 for batch experiments. Considering field soil variability, these
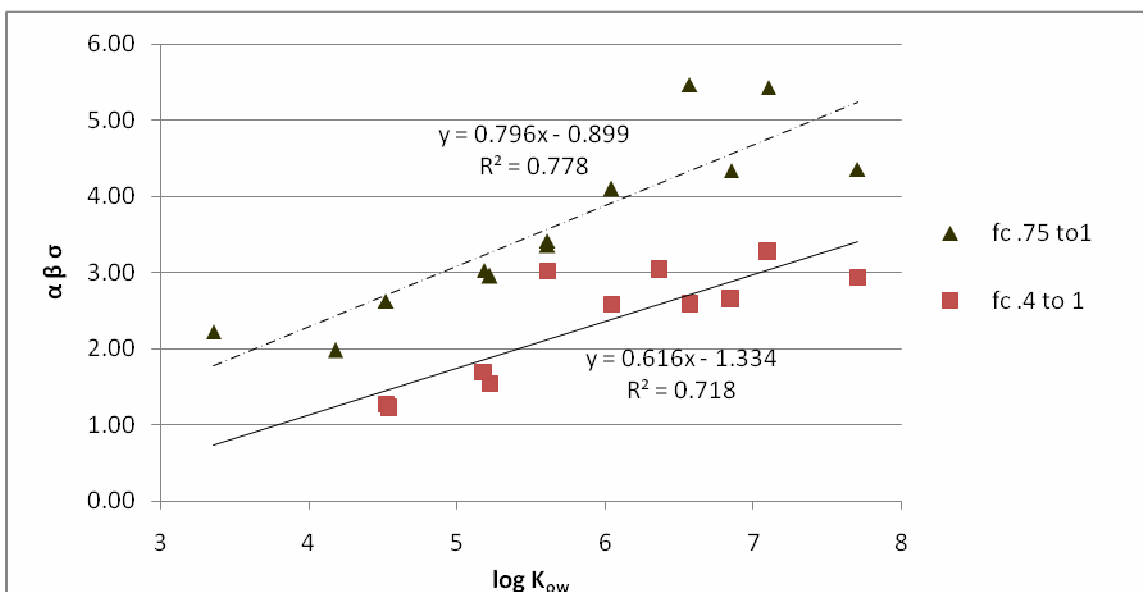
are relatively strong correlations.

Figure 5 αβσ from batch experiments as a factor of literature log K_{ow} coefficient

4.1.2 Methanol Rate Release Experiment

The average total PAH concentration per vial was 291 ±78 PPM. No relationship was evident between equilibration time and RP over the range of 1 to 96 hr; all time period averages were within a standard deviation (6%) of the total RP average at 81% (Figure 6).
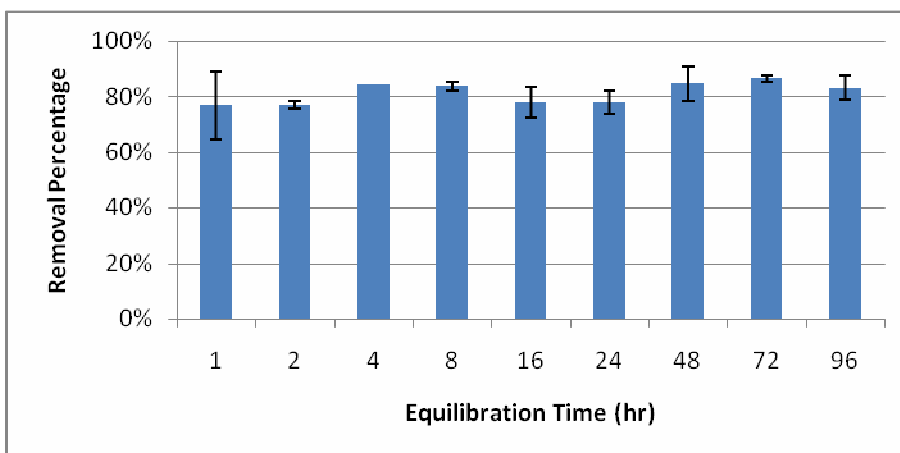

Figure 6 PAH RP with an f_c of 0.9 fc as a factor of equilibration time

A potential interpretation of this finding is that the swelling of OM caused by cosolvent is relatively immediate; at a high f_c this results in a quick release and solubilization of entrapped contaminants. The data does not match the proposed two-stage process for sorption or behavior suggested by *BT1* and *BT2* results; further slow stage desorption was expected after the initial immediate release, and it is concerning that average RP did not show gradual movement toward 100%. While the results are a promising indication that desorption equilibrium may be reached very quickly during flushing, they raise the possibility that a fraction of PAH's may be inaccessible to cosolvent. RP was consistent across samples, yet $K_{p,m}$ values for individual PAH's varied widely. $K_{p,m}$ did display a rough trend of decreasing over time for several PAH's based on individual vial data, indicating that greater partitioning was occurring into the cosolvent phase with longer equilibrations; regressions performed to quantitatively examine this trend returned very low correlation coefficients. The significant variation between individual samples caused averaged $K_{p,m}$ values to show no trend over time visually or quantitatively.

Column experiments were performed to provide further insight into whether sorption equilibration occurs at a fast rate when soil is exposed to flow, and whether continued introduction of fresh solution can bring PAH removal closer to 100%.

4.2 Small Column Experiments

4.2.1 Tracer Results

Calculations based on the results of the *SC1* tracer test found a PV of 46.3 mL, a porosity of 0.463, and an MRT of 8 hr and 41 min. The dispersion coefficient D (cm^2/hr) was 1.78. A dimensionless dispersion coefficient D/*uL* was determined to allow for comparison between *SC1* and the large column; *u* represents the pore velocity and *L* the column length. The value of D/*uL* for *SC1* was .037, very low for a field soil. The normalized ^3H_2O effluent concentration plot shows a relatively symmetrical profile, indicating low non-ideality conditions (Figure 7).

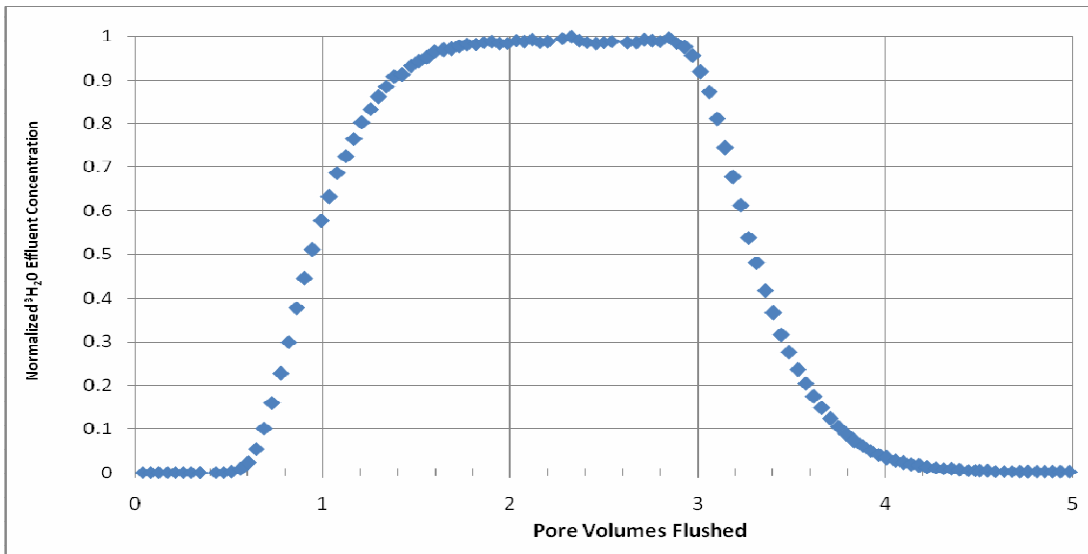**Figure 7 Effluent concentration profile of ^3H_2O step tracer**

4.2.2 Initial Concentration and Total Removal

Based on effluent concentrations and post-flushing soil extractions, *SC1* and *SC2* had estimated initial total PAH concentrations of 589 and 573 PPM, respectively. Total PAH's removed from the columns, calculated from a mass balance of all captured

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effluent, were 74.1g (*SC1*) and 87.6g (*SC2*), resulting in total PAH removal percentages over the duration of the flushing period at an estimated 78% and 89%.

4.2.3 Effluent Concentration and Total PAH Profiles

Effluent concentration profiles (Figure 8 and 9) showed behavior consistent with previous literature findings; the sharp increase in effluent PAH concentration at approximately 1 PV is assumed to correspond with methanol breakthrough (Augustijn et al., 1994). Dashed lines on effluent concentration figures represent the period of flow interruption for *SC2*.

SC2 displayed an increased maximum effluent PAH concentration, a more compressed, symmetrical peak and reduced tailing compared to *SC1*; the primary driver for this behavior is the increase in $K_{p,m}$ due to a higher f_c in *SC2*. These results are in agreement with column tests of methanol solutions with varying f_c's flushed through soils spiked with PAH's (Augustijn et al., 1994). The variation in MRT's (8 hr and 41 min versus approximately 24 hr), allowing for longer equilibration of desorption in *SC2* may have also played a role in creating these differences. The increased effluent concentrations and reduced tailing allow for much more efficient PAH removal with respect to volume flushed. It is apparent that PAH's favored desorption strongly enough in the 0.95 f_c solution that the majority of sorbed mass was released quickly and transported with flow.

The 48 hr flow interruption in *SC2* resulted in an increase in effluent concentration of less than 0.02 mg/mL, indicating that desorption rate effects existed but were minimal at that point for the majority of the contaminant mass.
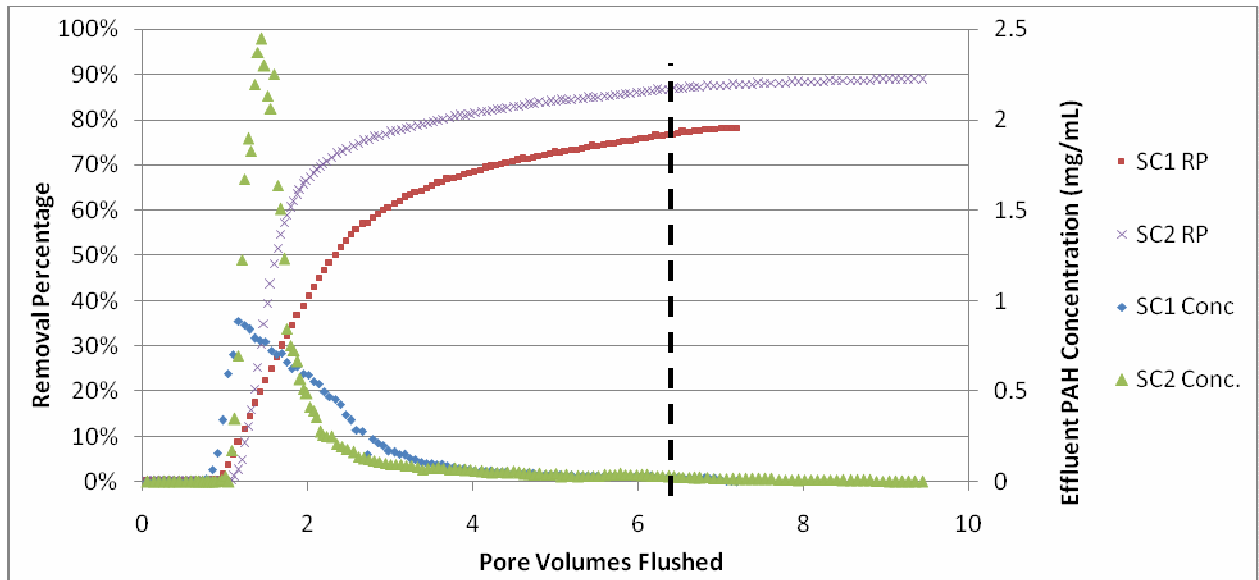
Figure 8 *SC1* **and** *SC2* **total PAH effluent concentrations and RP as a factor of relative flushing volume**

Even with a pore velocity close to 3 times that in *SC1*, the *SC2* column only lagged in removal over time by approximately 20 hr; in fact, after 60 hr the difference in removal percentage was only approximately 5% (Figure 9). This demonstrates that in a field-scale application, a higher f_c and slower pumping rate may be able to reduce total flushing volume needed, cutting cosolvent costs without sacrificing significant expense in added O&M.
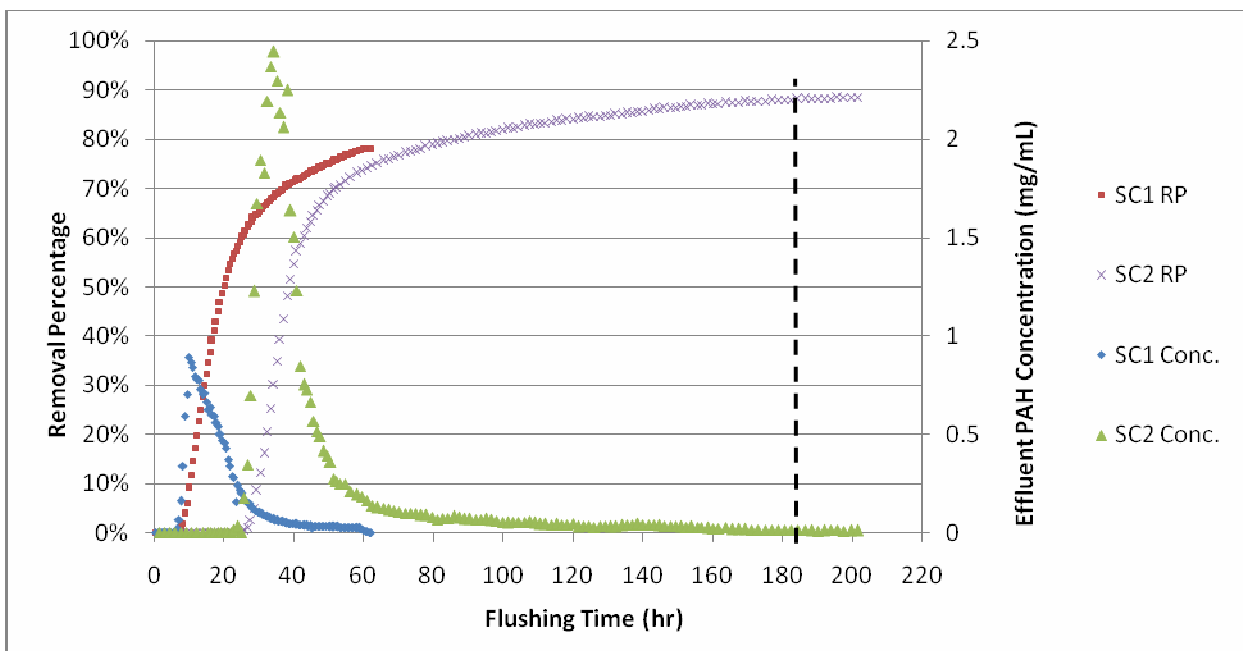
Figure 9 *SC1* and *SC2* **total PAH effluent concentration and RP as a factor of flushing time**

4.2.4 Individual PAH Profiles

Plots of individual PAH concentrations over the first 5 PV (Figure 10) show that differences in tailing behavior between columns are more pronounced for lower MW compounds; more hydrophobic, higher MW compounds experienced some tailing even in *SC2*. Coelution of all PAH's is desirable to minimize V_f needed; these graphs show that a chromatographic effect is occurring but reduced by an increase in f_c.
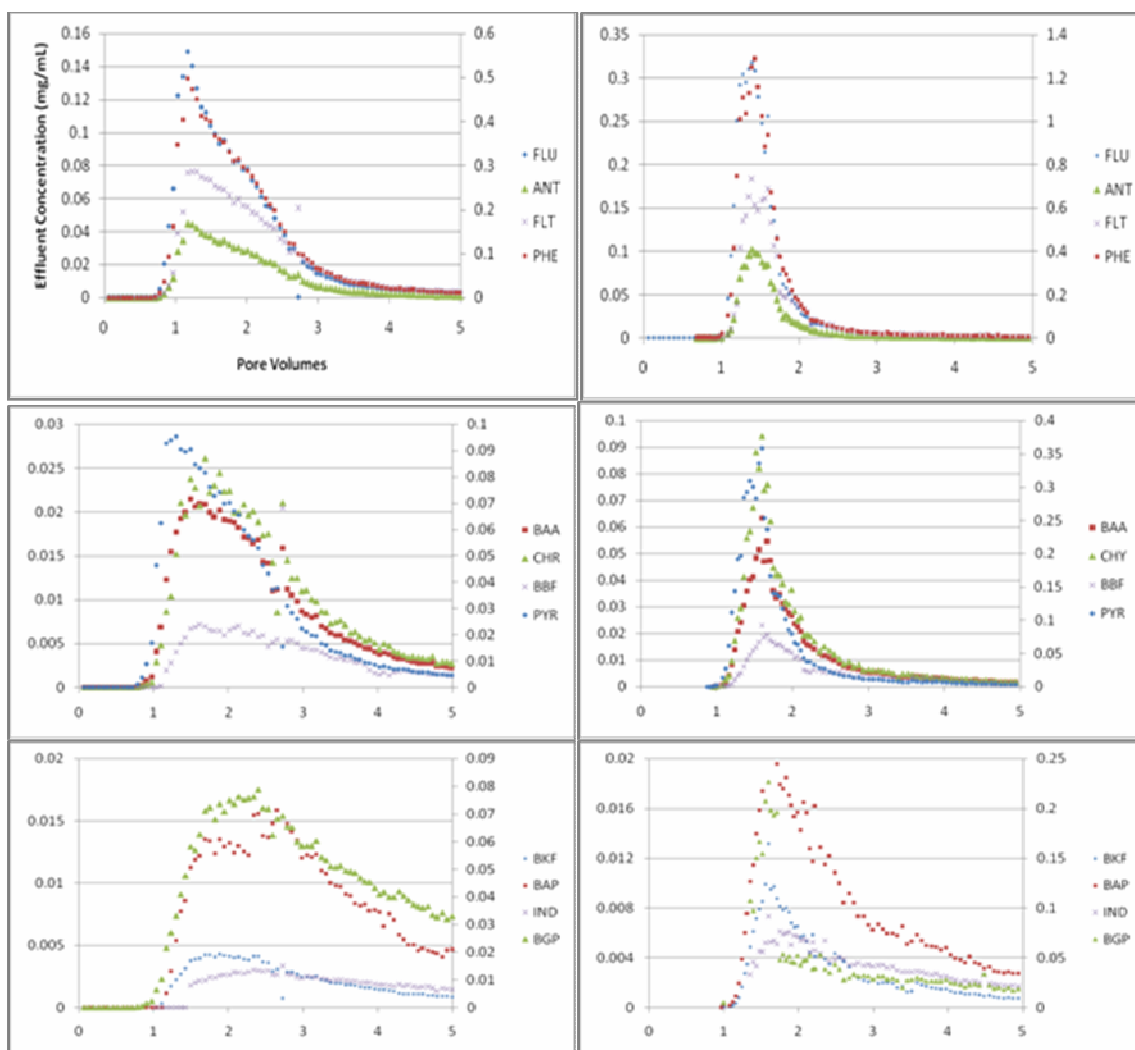
Figure 10. Effluent concentrations of small columns (*SC1* on left, *SC2* on right); PHE, PYR, and BGP on secondary vertical axes

4.2.5 Residual Concentrations

Post-flushing column soil extractions found average residual PAH concentrations of 125 and 64 PPM for *SC1* and *SC2*, respectively. For both columns BGP was the most persistent compound; this matches effluent data showing BGP at the highest concentration of all PAH's during tailing.
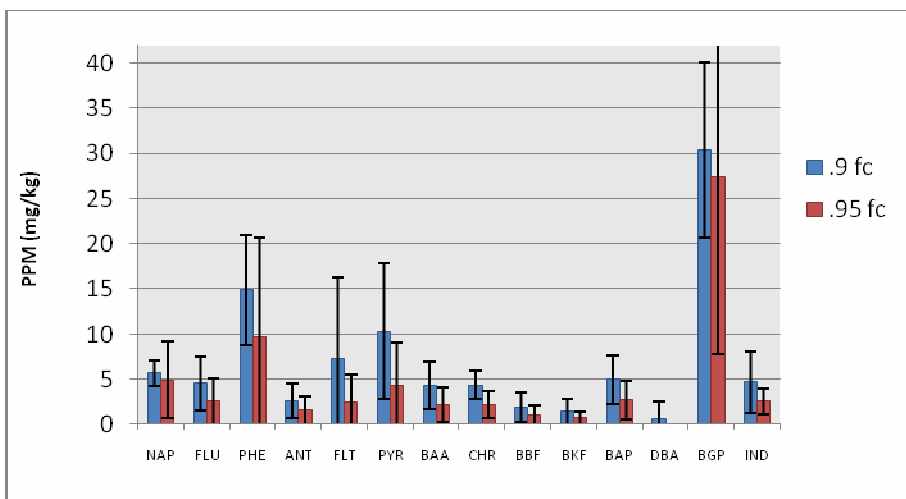
Figure 11 Residual concentrations of individual PAH's in *SC1* and *SC2*

Variation in PAH concentrations between post-flush samples was high for both columns; one possible explanation is that soil heterogeneities led to preferential flow paths that bypassed sections of the column, leading to pockets of remaining contamination. While *SC1* did not show a detectable relationship between residual PAH concentrations and depth in the soil bed, *SC2* showed higher concentrations toward the base of the column (Figure 12). This was the expected outcome, as some contaminants may have been mobilized downwards with flow but did not exit the column; no relationship was evident between individual PAH's and residual distribution.

Figure 12 *SC2* residual total PAH concentrations by segment

It is likely that with continued flushing PAH's would experience extended tailing, increasing removal but doing so in a relatively inefficient manner with respect to V_f and time.
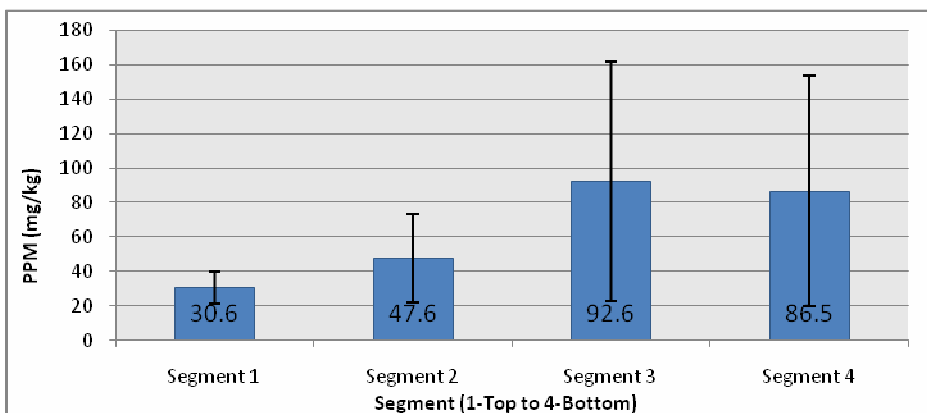
4.3 Large Column Experiment

4.3.1 Tracer Results

The ^3H_2O pulse tracer test resulted in a calculated porosity of 0.416 and a PV of 3470 mL. The dispersion coefficient D was calculated at 20.8 cm^2/hr, with a dimensionless dispersion coefficient D/uL of 0.395. Note that D/uL is over 10 times the D/uL value from *SC1* and represents a large deviation from ideal flow, likely created by greater heterogeneity due to the scale of the large column. The non-ideal flow conditions of the large column are more representative of field site conditions than those seen in the small columns; this is visually apparent in the asymmetry of the ^3H_2O effluent concentration profile (Figure 13).
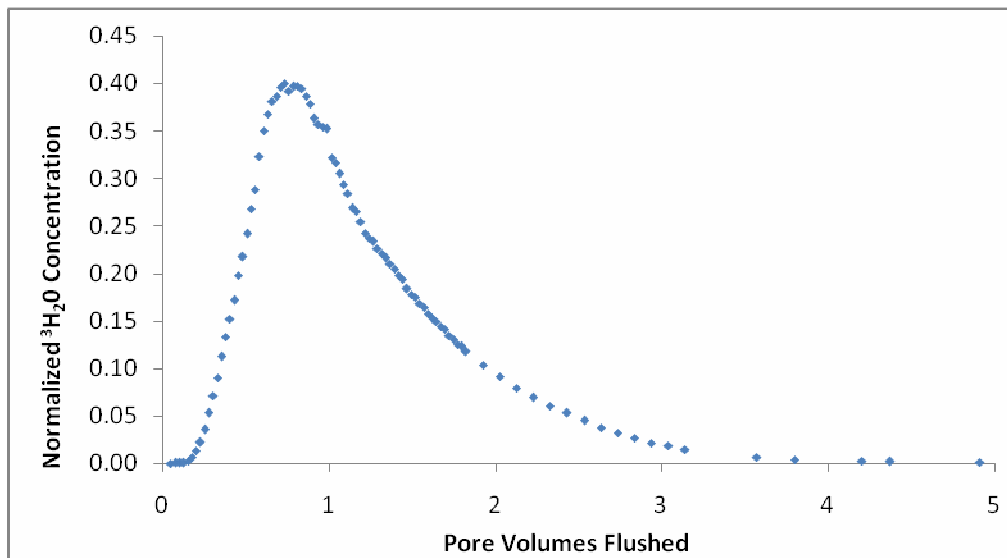

Figure 13 Effluent concentration profile of ^3H_2O pulse as a factor of relative flushing volume

4.3.2 Initial Concentrations

Initial soil samples showed an average total PAH concentration of 523 ±104 PPM; the three ports evenly distributed over the column vertically did not display a trend in contaminant distribution. The top of the column had significantly lower concentrations than the other ports, due primarily to decreased levels of the lower MW PAH's (with the exception of naphthalene (NAP)). This trend was expected because simulated groundwater had been flowing through the column for an extended period of time; therefore, PAH's with higher aqueous solubilities were more likely to be transported downward with flow and either removed from the column or deposited further towards the base. The PAH's at the top of the column were also more susceptible to aerobic degradation, because the simulated groundwater contained dissolved oxygen at a concentration corresponding to saturation with air. Phenanthrene (PHE) was present at the highest concentration at all sampling points, with ACE, fluorene (FLU), pyrene (PYR), and benzo[g,h,i] perylene (BGP) also prominent.

Table 8 Large column initial concentrations by location

Compound	Average Initial Concentration (PPM)				
	Column Top	Top Port	Middle Port	Bottom Port	Total Mean
NAP	12.0	8.4	8.1	10.3	9.7
FLU	22.7	43.9	60.2	67.9	48.7
PHE	110.8	230.3	213.7	244.3	199.8
ANT	12.0	23.7	21.4	25.6	20.7
FLT	31.3	49.0	39.0	43.0	40.6
PYR	61.5	74.2	63.5	70.0	67.3
BAA	17.0	19.2	16.1	17.3	17.4
CHR	19.6	19.0	16.8	19.1	18.6
BBF	11.1	7.9	6.1	7.0	8.0
BKF	7.5	5.7	4.4	4.9	5.6
BAP	18.7	13.8	11.9	13.0	14.4
DBA	0.2	0.1	0.0	0.1	0.1
BGP	92.6	52.7	50.3	56.9	63.1
IND	12.7	8.8	8.0	8.0	9.4
Total	429.4	556.6	519.7	587.5	523.4

4.3.3 Effluent Concentration and Total PAH Profile

The large column effluent profile (Figure 14) shows peak PAH concentrations at approximately 1/5 of those seen in *SC2* and tailing to an even greater extent than in *SC1*. With an estimated MRT of 29 hr allowing for greater equilibration time than in the small column experiments, these results indicate that the hydrodynamic characteristics of the large column significantly affected removal. Greater heterogeneity and non-ideal flow patterns observed in the large column tracer test may be the primary cause of tailing, as preferential flow paths dictated dissolution rates in areas of low permeability. This hypothesis is supported by the variability in the effluent concentration profile compared to *SC1* and *SC2*, implying that different portions of the soil mass were being exposed to cosolvent over time with shifting flow patterns, appearing to release PAHs sporadically.

A second factor to consider is that the difference in flushing pore velocity affected removal. A previous study observed general increases in desorption rates of HOC's with higher pore velocities; therefore, it is unlikely that the higher pore velocity of the large column adversely affected desorption rate (Brusseau et al., 1992).

Total PAH removal was calculated by using the trapezoid rule to integrate effluent concentrations over V_f, giving a total mass removed of 6380 g, or 472 PPM averaged over column soil mass. This is consistent with initial and final soil extraction calculations showing removal at 486 ±58 PPM.
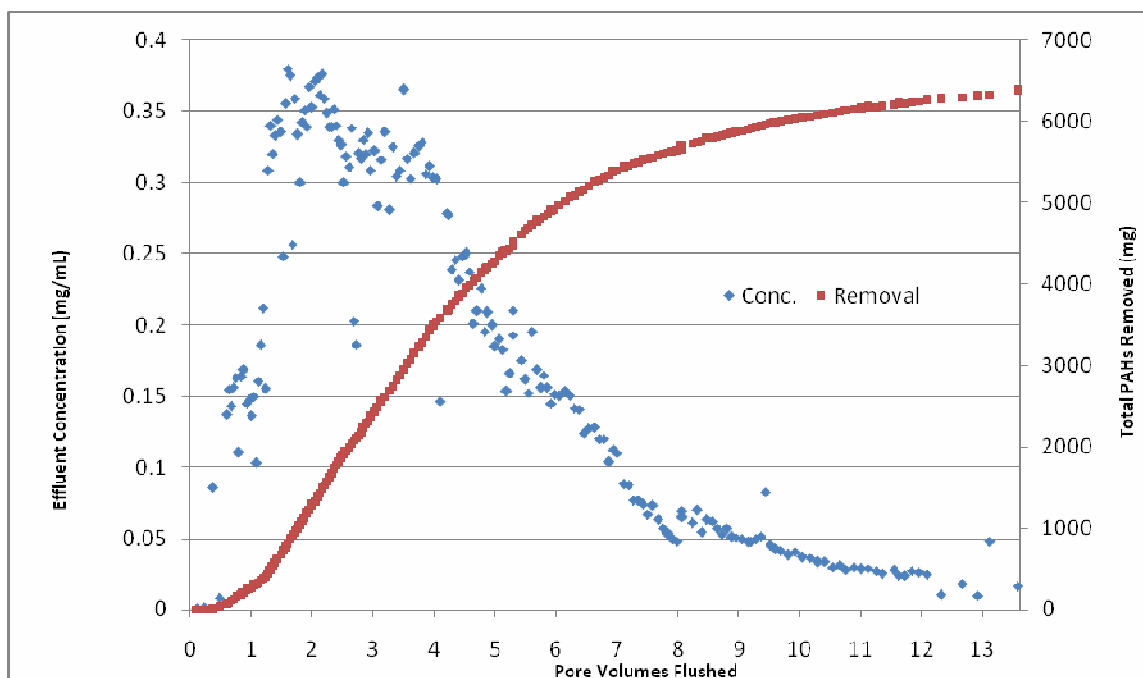
Figure 14 Total PAH effluent concentrations and total mass removed as a factor of relative flushing volume

4.3.4 Individual PAH Profiles

Examining individual PAH effluent profiles shows the expected trend of greater tailing of higher MW compounds. In fact, BGP and IND were still at over ½ of their peak effluent concentrations after the full 13.56 PV flush. A spike in effluent concentration is apparent around 7 PV; no flow interruption was performed, and an explanation is not evident. NAP did not follow the predicted behavior; it did not show any significant peak, instead appeared to be steadily desorbing over time.

Figure 15 Large column effluent concentrations; PHE, BGP on secondary vertical axes (right side)

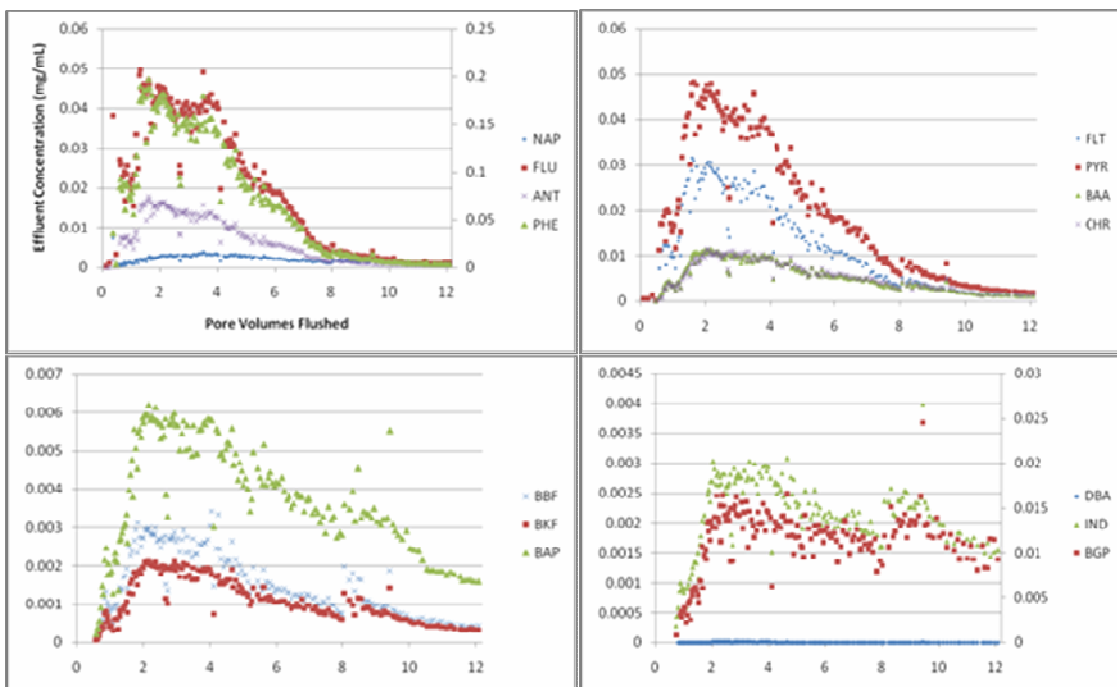Comparing maximum effluent concentrations for individual PAH's across all column experiments shows that no single compound or set of compounds was primarily responsible for the decreased total PAH effluent concentrations in the large column; 10 of the 14 analyzed PAH's had maximum concentrations in the large column experiment between 11% and 18% of that in *SC2* .

Table 9 Maximum effluent concentrations for column experiments; ratios of maximum effluent concentrations between experiments

Compound	Max. Effluent Concentration			Max. Effluent Concentration Ratio	
	SC2	*SC1*	*LC*	*SC1/SC2*	*LC/SC2*
NAP	0.017	0.006	0.007	34%	42%
FLU	0.318	0.149	0.050	47%	16%
PHE	1.286	0.498	0.198	39%	15%
ANT	0.103	0.045	0.018	44%	17%
FLT	0.184	0.077	0.032	42%	17%
PYR	0.358	0.095	0.048	27%	13%
BAA	0.063	0.021	0.011	34%	18%
CHY	0.094	0.026	0.011	28%	12%
BBF	0.023	0.020	0.003	89%	15%
BKF	0.013	0.004	0.002	32%	16%
BAP	0.025	0.033	0.006	134%	25%
DBA	0.000	-	0.000	-	3%
BGP	0.227	0.079	0.025	35%	11%

4.3.5 Residual Concentrations

Soil extracted after cosolvent flushing showed almost complete PAH removal at the top of the column and varied removal at the three other sampling points, resulting in an average residual concentration of 37 PPM. Excluding the column top, averages show a trend towards lower residual concentrations in the bottom of the column, but high variation between samples resulted in large standard deviations; as an example, the top port variance is driven by one sample that showed a total PAH concentration of 124 PPM. A hypothesis for this variation in samples is that preferential flow paths, especially surrounding sampling ports that may have affected fluid dynamics, left pockets of PAH's inaccessible to cosolvent flow.
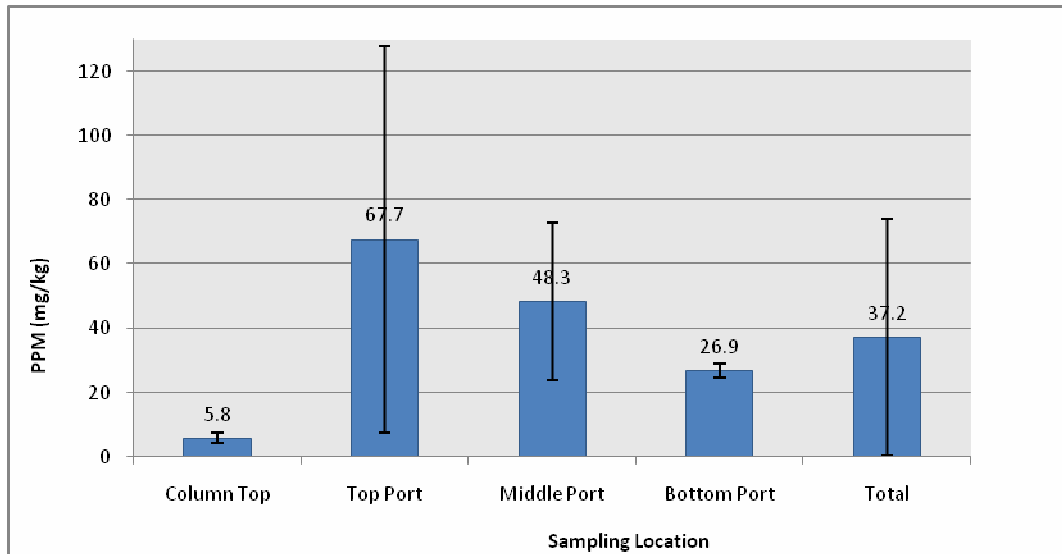

Figure 16 Large column total PAH concentration by sampling location

Examining residual concentrations of individual PAH's shows BGP and PHE to be the most persistent in the column, similar to the results of the small column experiments and

consistent with tailing in effluent concentration profiles; there is no apparent relationship

between MW and the distribution of residual concentrations across sampling points.

Table 10 Large column average residual concentrations by location

Compound	Average Residual Concentration (PPM)				
	Column Top	Top Port	Middle Port	Bottom Port	Total
NAP	1.7	2.5	3.1	2.8	2.5
FLU	0.4	4.7	2.6	1.0	2.2
PHE	1.3	23.6	10.6	3.8	9.8
ANT	0.3	2.7	1.6	0.8	1.3
FLT	0.2	3.0	2.6	1.0	1.7
PYR	0.3	7.1	4.7	1.7	3.4
BAA	0.2	1.8	1.5	1.0	1.1
CHR	0.1	2.8	1.0	0.7	1.2
BBF	0.0	0.7	0.8	0.6	0.5
BKF	0.0	0.3	0.5	0.4	0.3
BAP	0.2	1.3	1.8	1.5	1.2
DBA	0.0	0.0	0.0	0.0	0.0
BGP	1.0	16.2	15.2	9.2	10.4
IND	0.2	1.0	2.1	2.5	1.5
Total	5.8	67.7	48.3	26.9	37.2

4.3.6 Removal Percentage

Comparing initial and final PAH concentrations at each sampling point resulted in

RPs between 87.8% and 98.6%, with an average of 93%.

Table 11 Large column total PAH initial and residual concentrations and RP by location

Location	Total PAH Average Concentration (PPM)		RP
	Initial	Residual	
Column Top	429.4	5.8	98.6%
Top Port	556.6	67.7	87.8%
Middle Port	519.7	48.3	90.7%
Bottom Port	587.5	26.9	95.4%
Total	523.3	37.2	93%

Despite extended tailing, RP was greater for the large column than for either of the small

columns, in part due to increased cosolvent V_f. RPs for the large column and *SC2* at 8 PV

(the total *SC2* V_f) were estimated at 82% and 89%, respectively; the higher final removal

in the large column may be accounted for by the greater relative V_f. It is expected that

continued removal would occur from the large column with continued flushing, albeit at a greatly reduced efficiency with respect to V_f.

Average RPs were greater than 90% for 11 of 14 PAH's; while lower BGP and IND RPs were predictable due to their hydrophobicity, the low RP of NAP was unexpected and consistent with its flat effluent concentration profile.
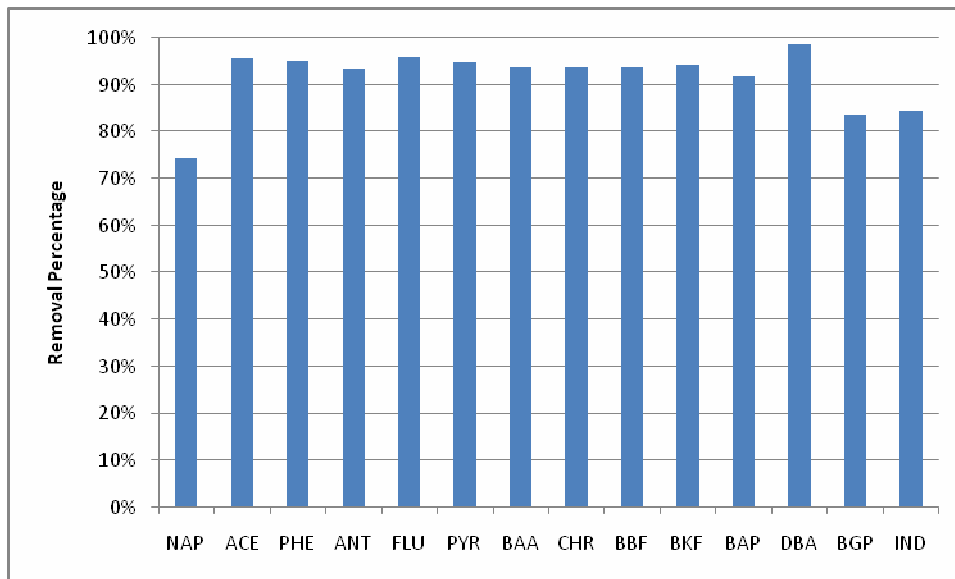

Figure 17 Large column individual PAH average RP

5 Summary and Conclusions

The potential for cosolvent flushing as a remediation technique for PAH's at former MGP sites was studied through a set of batch and column experiments performed on contaminated field soil. Batch experimental results found strong enhancements of PAH solubility and desorption with the introduction of methanol, consistent with literature cosolvency theory. The percentage of PAH's removed from soil and the partitioning coefficient log $K_{p,m}$ showed linear relationships with methanol f_c; individual PAH's behaved differently dependent on hydrophobicity, expressed as log K_{ow}. High MW, carcinogenic PAH's were more persistent in the field soil than the low MW compounds but were able to be removed with high f_c solutions. Study of nonequilibrium desorption in the batch tests was inconclusive; slow stage desorption was not found in a test for rate effects, but evidence for it was seen in other batch tests. Small column experiments showed expected differences in PAH transport dependent on the f_c of the flushing solution, removing 78% and 89% of PAH's over 6.22 and 8.01 PV flushed.

A large-scale column experiment designed as a simple representation of PAH transport with cosolvent for field application showed removal of over 93% of PAH's with a 13.56 PV flush; it is expected that continued removal would have occurred with further flushing. Extended tailing in the large column was hypothesized to be caused by non-ideal flow patterns seen in tracer tests, likely due to high soil heterogeneity. The scale of the large column was able to provide a more accurate simulation of the variation in subsurface properties that would occur at the field scale than small-scale column

experiments. The large column results indicate that small-scale column experiments may overestimate the removal efficiency of cosolvent flushing by presenting more ideal flow conditions than would be found in a field setting; yet, they still support potential implementation of cosolvent flushing at MGP sites considering the efficiency of contaminant removal with respect to time and flushing volume, especially when compared to conventional PAT systems that may require thousands of PV flushed.

Pilot tests and small field studies at MGP sites are needed to corroborate these results and address additional issues that may arise at the field scale. An important consideration for remedial design is the scale of the contaminated area; removal of PAH's with cosolvent flushing would be prohibitively expensive at large sites that necessitate a high volume of cosolvent to achieve the desired level of removal. Cosolvent flushing is a much more likely candidate for source zone removal actions than the cleanup of a contaminant plume; source zones would require a much smaller relative flushing volume per contaminant mass removed. The source zone at many MGP sites may characterized by higher concentrations of PAH's than the field soil used in this study and contain a significant NAPL presence, making mobilization an important process during removal. While this work does not provide insight into mobilization, it demonstrates the ability of cosolvents to remove the fraction of PAH's sorbed to the soil, including the more persistent, carcinogenic, high MW compounds.

6 Works Cited

Agency for Toxic Substances and Disease Registry. "Toxicological Profile for Polycyclic Aromatic Hydrocarbons." 1995.

Augustijn DCM, Jessup RE, Rao PSC, Wood AL. "Remediation of Contaminated Soils by Solvent Flushing." *Journal of Environmental Engineering*, 1994: 120(1),42-57.

Augustijn DCM, Lee LS, Jessup RE, Rao PSC, Annable MD, Wood AL. "Remediation of Soils and Aquifers Contaminated with Hydrophobic Organic Chemicals: Theoretical Basis for the Use of Cosolvents." In *Subsurface Restoration*, by Cherry JA, Scalf MR, Ward CH, 231-250. Chelsea, MI: Ann Arbor Press, 1997.

Bhandari A, Surampalli RY, Champagne P, Ong SK, Tyagi RD, Lo IMC. *Remediation Technologies for Soils and Groundwater.* Reston, VA: American Society of Civil Engineers, 2007.

Bouchard DC. "Sorption Kinetics of PAHs in methanol-water systems." *Journal of Contaminant Hydrology*, 1998: 34,107-120.

Brooks MC, Annable MD, Rao PSC, Hatfield K, Jawitz JW, Wise WR, Wood AL, Enfield CG. "Controlled release, blind test of DNAPL remediation by ethanol flushing." *Journal of Contaminant Hydrology*, 2004: 69,281-297.

Brussea ML, Wood AL, Rao PSC. "Influence of organic cosolvents on the kinetics of hydrophobic organic chemicals." *Environ. Sci. Technology*, 1991: 25,903-910.

Brusseau ML. "Nonequilibrium transport of organic chemicals: The impact of pore-water velocity." *Journal of Contaminant Hydrology*, 1992: 9,353-368.

Brusseau ML, Hu Q, Srivasta R. "Using flow interruption to identify factors causing nonideal contaminant transport." *Journal of Contaminant Hydrology*, 1997: 24,205-219.

CH2MHill. *Technology Practice Reviews for Surfactants and Cosolvents.* 1997.

Chen SC, Delfino JJ. "Cosolvent effects of oxygenated fuels on PAH Solubility." *Journal of Environmental Engineering*, 1997: 123(4),354-363.

Chen SC, Rao PSC, Delfino JJ. "Oxygenated fuel induced cosolvent effects on the dissolution of polynuclear aromatic hydrocarbons from contaminated soil." *Chemosphere*, 2005: 60,1572-1582.

Congressional Budget Office. "Analyzing the Duration of Cleanup at Sites on Superfund's National Priority List." DC, 1994.

Foster SSD, Chilton PJ. "Groundwater: the processes and global significance of aquifer degradation." *Phil. Trans. R. Soc. London*, 2003: 358,1957-1972.

Foster S. "Groundwater-sustainability issues and governance needs." *Episodes*, 2006: 29(4),238-243.

Hardesty PE, Ozdemiroglu E. *The Economics of Groundwater Remediation and Protection.* Boca Raton: CRC Press, 2005.

Hatheway A. "Geoenvironmental protocal for site and waste characterization of former manufactured gas plants; worldwide remediation challenge in semi-volatile organic wastes." *Engineering Geology*, 2002: 64,317-338.

Hill EH, Moutier M, Alfaro J, Miller CT. "Remediation of DNAPL Pools Using Dense Brine Barrier Strategies." *Environ. Sci. and Technol.*, 2001: 35,3031-3039.

Jawitz JW, Sillan RK, Annable MD, Rao PSC, Warner K. "In-Situ Alcohol Flushing of a DNAPL Source Zone at a Dry Cleaner Site." *Environ. Sci. Technol.*, 2000: 34(17),3722-3729.

Kent B, Mosquera GCB. "Remediation of NAPL-Contaminated Aquifers: Is the Cure Worth The Cost?" *J. Environ. Sci. Health*, 2001: A36(8),1559-1569.

Khodadoust AP, Bagchi R, Suidan MT, Brenner RC, Sellers NG. "Removal of PAHs from highly contaminated soils found at prior manufactured gas plant operations." *Journal of Hazardous Materials*, 2000: B80,159-174.

Lane WF, Loehr RC. "Estimating the equilibrium aqueous concentration of polynuclear aromatic hydrocarbons in complex mixtures." *Environ. Sci. Tech.*, 1992: 26(5),983-990.

Morris KL, Abramowitz R, Pinal R, Davis P, Yalkowsky SH. "Solubility of aromatic pollutants in mixed solvents." *Chemosphere*, 1988: 17,285-298.

Murphy BL, Sparacio T, Shields WJ. "Manufactured Gas Plants - Processes, Historical Development, and Key Issues in Insurance Coverage Disputes." *Environmental Forensics*, 2005: 6(2),161-173.

National Research Council. *Contaminants in the Subsurface.* Washington, DC: National Academies Press, 2005.

National Resource Council. *Alternatives for Ground Water Cleanup.* Washington, DC: National Academy Press, 1994.

Nkedi-kizza P, Brusseau ML, Rao PSC. "Nonequilibrium during displacement of hydrophobic chemicals and 45ca through soil columns with aqueous and mixed solvents." *Environ. Sci. Tech.*, 1989: 23,814-820.

Nkedi-Rizza P, Rao PSC, Hornsby AG. "Influence of organic cosolvents on leaching of hydrophobic organic chemicals through soils." *Environ. Sci. Technol.*, 1987: 21,1107-1111.

Okuda I, McBride JF, Gleyzer SN, Miller CT. "Physicochemical Transport Processes Affecting the Removal of Residual DNAPL by Nonionic Surfactant Solutions." *Environ. Sci. Technol.*, 1996: 30,1852-1860.

Rao PSC, Lee L, Pinal R. "Cosolvency and sorption of hydrophobic organic chemicals." *Environ. Sci. Technol.*, 1990: 24(5),647-653.

Shor LM, Rockne KJ, Taghon GL, Young LY, Kosson DS. "Desorption Kinetics for Field-Aged Polycyclic Aromatic Hydrocarbons from Sediments." *Environ. Sci. Technol.*, 2003: 37,1535-1544.

US EPA. *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends.* Cincinatti: US EPA/National Service Center for Environmental Publications, 2004.

US EPA. *Groundwater Pump and Treat Systems: Summary of Selected Cost and Performance Information at Superfund-financed Sites.* Cincinatti: US EPA National Service Center for Environmental Publications, 2001.

US EPA. *Treatment Technologies for Site Cleanup: Annual Status Report (Twelfth Edition).* Cincinatti: US EPA National Service Center for Environmental Publications, 2007.