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Enhanced flushing with cyclodextrin for the remediation of creosote contaminated soil

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ENHANCED FLUSHING WITH CYCLODEXTRIN FOR THE REMEDIATION OF
CREOSOTE CONTAMINATED SOIL

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
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requirements for the degree of
Master of Science

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by
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ABSTRACT

Past practices of applying creosote and coal tar preservatives to wood, such as unlined pits and trenches, have resulted in contamination of the surface and ground water at thousand of sites. The low aqueous solubility, volatility and bioavailability of many these constituents limit their degradation by natural attenuation and standard remediation techniques such as ground water flushing, soil vapor extraction, and bioremediation. While research has shown that cyclodextrin solutions have the ability to enhance the solubility of some of the components of creosote, additional work is needed to evaluate its potential as a remedial agent for these sites.

Equilibrium batch studies were conducted to determine the solubility enhancement of eight different PAHs commonly present in creosote in aqueous solutions of three different types of cyclodextrin. Three highly soluble cyclodextrins were tested which vary in their internal cavity size (smallest to largest: hydroxypropyl- α -cyclodextrin (HP α CD), hydroxypropyl- β -cyclodextrin (HP β CD), and hydroxypropyl- γ -cyclodextrin (HP γ CD)).

The results showed that all three types of cyclodextrin enhanced the apparent solubility of the tested PAHs. The degree of solubility enhancement ranged from 19.6 for naphthalene to 4136 for benzo (k) fluoranthene. Because previous research has shown that hydroxypropyl substitution does not favor forming complexes with low-polarity compounds, it is concluded that cyclodextrin with larger cavities slightly enhance the degree of PAH partitioning into their cavities and hence PAH apparent solubility. Comparison of the results also showed that the logarithm of the PAH solubility enhancement factor in the cyclodextrin solutions is inversely related to the logarithm of PAHs aqueous solubility, directly related to the mass of the PAHs, and directly related to the logarithm of the PAH hydrophobicity. Additional direct correlations were found between the logarithm of the ratio of molar concentration of the PAH to that of the

cyclodextrins with the logarithm of PAHs aqueous solubility. These strong correlations enable the ability to project the enhancement of other PAHs present in creosote and coal tar. Additional research has to be performed, but cyclodextrin shows promise as a remedial agent for creosote and coal tar sites.

CHAPTER 1: INTRODUCTION

Historically creosote and coal tar has been employed for preservation of utility poles, railroad ties and other wood products that are exposed to the environment. Past practices of applying creosote and coal tar to wood often involved immersion of the wood in unlined pits and ditches containing creosote and coal tar. Sites varying between less than acre to tens of acre containing these pits are located throughout the United States.

Creosote is a collective term used for three types of products; coal tar creosote, beechwood creosote and creosote bush resin. Coal tar creosote results from high temperature treatment of coal, beechwood creosote results from high temperature treatment of beech and wood and creosote bush resin is produced by high temperature treatment of creosote bush (Choudhary et al., 2002).

Creosote is a complex mixture of different chemicals such as poly aromatic hydrocarbons (PAH), phenols, and metals (Choudhary et al., 2002). Many of these organic compounds such as benzo [a] pyrene and naphthalene are known toxins (Mumtaz et al., 1996). They are released to the environment during their use in the wood preservation, asphalt and coke production.

Coal tar creosote entered the environment through past practices of gas manufacturing plant. The gas manufacturing plants in the past produced natural gas by burning coal. During this high temperature treatment of coal these industries produced vast amount of coal tar and commonly disposed this coal tar on the ground for decades.

From these near surface disposal sites coal tar and creosote spread through the environment in a limited fashion through dissolution in water, volatilization in air, and accumulation and degradation by the biosphere. But often, they remain as a separate non aqueous phase liquid. The more aqueous soluble components of creosote and coal tar are often lost to

water infiltrating through the vadose zone into ground water and into water flowing overland passing into surface waters. An additional mechanism for the loss of many of these same low molecular weight highly aqueous soluble components of creosote and coal tar occurs through volatilization into the atmosphere and soil gas. Of the remaining creosote and coal tar mixture, the more viscous versions may persist in surface soils. While, the less viscous versions may infiltrate into the vadose zone and if more dense than water the infiltrate into groundwater.

The vast majority of the components of creosote have low aqueous solubility. This limits the degree to which these components can dissolve in water and are hence available to the environmental microbial community (Reid et al., 2004). This is often termed bioavailability. As a result, when released into the environment, creosote does not readily dissolve in groundwater, but persists largely as a separate non-aqueous phase liquid (NAPL) in the subsurface. Due to the toxic nature of many of the creosote components, creosote contaminated sites should be remediated.

Limitations of Conventional Remediation Technologies

The limited solubility and persistent nature of creosote contamination inhibits the performance of the most common methods of groundwater remediation. The practice of flushing ground water through contaminated soils and aquifers, often referred to as the pump-and-treat method is most common method for restoring sites contaminated with NAPL (NRC, 2000). The pump-and-treat method involves pumping large amount of contaminated water from the subsurface through a series of wells, treating the water at the surface to remove contaminants and then either reinjecting the water underground through a second set of wells or disposing of the water offsite (NRC, 2000). However, this technique is often ineffective in restoring contaminated ground water to regulatory standards because the flushing action created by pump

and treat system is often insufficient to dislodge all of the contaminants from the subsurface (NRC, 1994; MacDonald and Kavanaugh, 1994). Diffusion of contaminants into the inaccessible subsurface region or entrapment of contaminant globules into the porous media prevents the adequate remediation through conventional techniques. Subsurface physical heterogeneity complicates delivery of the treatment fluids to the contaminated regions of the porous media. These factors limit the ability of the conventional technique to adequately remove contaminants from the subsurface. In a 1994 review of pump and treat systems at 77 sites, the NRC (National Research Council) found that clean up goals were achieved at eight of the sites and were highly unlikely to be achieved at 34 of sites (NRC, 1994).

Soil excavation is the conventional method for cleaning up contaminated soils. In this method, excavated soils are either treated to remove contaminants or are disposed of in specially designated sites. Often the treatment involves on-site incineration of soils, which increases the risk of releasing hazardous air pollutants (NRC, 1997). Excavation can temporarily increase the risk of human exposure to contamination especially for site workers and nearby residents. Excavation may also be destructive to native ecosystems.

Owing to several limitations of conventional remediation techniques, alternative techniques such as in-situ oxidation, soil vapor extraction, bioremediation, electrical heating and phytoremediation have been introduced (NRC, 2000). The technique of soil vapor extraction is primarily employed to remove volatile compounds from the soil gas (EPA, 1997a; Holbrook et al., 1998; Johnson et al., 1993). This technique involves inducing air flow through the vadose zone to remove the volatile contaminants. The soil vapor extraction technique is normally not applicable for treating creosote contaminated sites because of the low volatility of most of the creosote constituents.

The technique of in-situ oxidation involves injection of an oxidizing reagent into the contaminant source-zone and destruction of the contaminants by chemical reaction with the oxidizing agent. Permanganate from potassium and sodium salts and hydrogen peroxide are the most commonly used oxidizers. A limitation of this technique in the case of permanganate is its inability to easily react with chlorinated creosote compounds without double bonds (Pankow and Cherry, 1996). Also when permanganate reacts, manganese dioxide is produced and often precipitates. When permanganate is applied to heavily contaminated soils the amount of precipitation can result in coating the residual unreacted NAPLs and making subsequent remediation of the site more difficult. Additionally, strong oxidizers such as potassium permanganate and hydrogen peroxide react with all oxidizable compounds in the aquifer including the organic matter and microbes. This increases the amount of reagent required for the treating the subsurface and sterilizes the soil (Miller et al., 1996). Due to short half life and unstable nature of hydrogen peroxide, it is often only capable of treating a small volume of aquifer in the vicinity of the injection wells.

Bioremediation technique involves the breakdown of organic contaminants by microbial processes. In bioremediation microbes or microbial communities capable of degrading the contaminants need to be present and the nutrients to support this degradation need to be present in the groundwater to support the reactions. When bioremediation is enhanced these nutrients (typically nitrogen and phosphorus source), air (oxygen source) or any additional carbon source (easily degradable organic compound) are added into the ground through wells. The additional carbon source can facilitate destruction of the contaminants through co-metabolic reactions. Because the vast majority of the components have low solubilities in water and hence have limited bioavailability the remediation technique of enhanced biodegradation is often not suitable

for creosote contaminated soils. But, it should be noted that many creosote contaminated sites are not intensively being remediated. This means that bioremediation is one of the processes that result in the slow decontamination of these sites. This is often termed natural attenuation and because of the costs associated with other more proactive techniques it is often employed.

The phytoremediation technique involves removal of contaminants from soil or groundwater through the usage of plants. Studies have confirmed that certain plant species can take up chlorinated solvents from the ground water in the root zone (Chappel, 1997; Schnoor, 1997). Once plant takes up the solvent, it can store the chemical in its body via covalent bonding with plant lignin (Schnoor, 1997). But this is a time consuming technique and is in the early stage of development.

In the technique of electrical heating contaminants are driven out of the source zone by a combination of volatilization and thermally induced vapor-phase transportation. Different types of heating methods like resistance heating, microwave heating, and radio frequency heating can be used for this purpose. In each case electrical energy is used directly on the soil. The main disadvantage of using this technique is that contaminants are not directly recovered, but only vaporized. Secondary vapor extraction is also needed at most sites. Because most of the creosote components have relatively low vapor pressure, electrical heating is not normally applicable for creosote contaminated sites.

The physical and chemical principles, advantages and limitations of these methods have been discussed in detail in the literature review section of this paper. However, none of these methods have been proved to be sufficiently effective for removing all the organic contaminant from the subsurface.

Remediation with Solubility Enhancing Agents

Remediation of creosote contaminated sites with solubility enhancement reagents is an innovative remediation technique. These techniques are based on the ability of agents to increase the solubility of hydrophobic organic compounds in the mobile phase. Different types of cosolvents (Augustijn et al. 1994; Rao et al. 1997; Falta, 1998) and surfactants (Sabatini et al. 1996.; Abdul et al., 1990) are proposed for solubility enhancing reagents. Surfactant-induced remediation is a combination of two processes, solubilization and mobilization. Critical concentration of surfactant molecules aggregate to form big surfactant globule known as CMC (Critical Micelle Concentration). CMCs have hydrophobic interior and hydrophilic exterior. Solubilization enhancement occurs due to partitioning of organic contaminant into the hydrophobic interior of the surfactant micelles. Hydrophilic exterior of the micelle makes the surfactant molecule water soluble.

Surfactants also decrease the interfacial tension between the aqueous phase and NAPL phase. With increasing solubility and decrease in interfacial tension the mobilization of organic contaminants increases dramatically (Sabatini et al. 1999). Numerous researchers (Rao et al, 1985, Peters and Luthy 1993; McCRAY and Falta, 1996) have demonstrated the ability of solvents such as short chain alcohols (methanol, ethanol, propanol) to increase the solubility of hydrophobic organic compounds in water.

Solvent-induced remediation occurs due to interfacial tension reduction between the aqueous phase and organic contaminant phase and solubility enhancement of organic contaminant in aqueous phase (Falta et al. 1996). In practice, surfactants and alcohols are injected at various concentrations through contaminant source zone to remove the contaminant by dissolution and / or mobilization. Field trials of solvent flooding have been performed at Hill

Air Force Base at Utah, by EPA and researchers from Clemson University. Contaminant recovery range was between 40- 93 percent (NCR 2000). However, both surfactants (e.g. TMAZ 20, TMAZ 28, TMAZ 60) and solvents (e.g. ethanol, methanol, propanol) have inherent disadvantages for field application. Alcohols solvents are generally less dense than water and therefore their densities are also less than ground water. This sometimes presents a problem in circulating these solutions uniformly (Falta, 1996). The solubilization effect of solvents (e.g. alcohol) is not usually significant until their volume-fraction concentrations are above 10% (Wang et al. 1993). Surfactants on the other hand have high solubilization power but their remediation performances are affected by precipitation or sorption in the contaminated zone (Jafvert 1991, Brusseau 1993, Palmer et al. 1992).

Cyclodextrin Characteristics

Cyclodextrin, (CD) another type of solubility enhancing reagent, has several potential characteristics that can be used for remediation of creosote-contaminated soils. Cyclodextrin a polycyclic oligosaccharide or glucose-based molecule formed from degradation of starch by bacteria (Bender and Komiyama 1978). Cyclodextrin is composed of several glucose ($C_6H_{12}O_6$) molecules arranged in a toroidal shape. Specifically, the base units are composed of a number of “chair-shaped” D (+)-glucopyranose units. Cyclodextrin molecules are designated by Greek letters to denote the number of glucose units in the toroid ($\alpha = 6$, $\beta = 7$ and $\gamma = 8$). In most application, varieties of β -cyclodextrin are most widely employed. The average cavity diameter of α CD, β CD and γ CD is 4.5Å, 7.0Å and 8.0 Å (Bender & Komiyama 1978).

Aqueous solubility of the base cyclodextrins ranges from 18 to 232 g/L (Bender and Komiyama 1978). Their solubilities can be increased by addition of polar functional groups (e.g. hydroxypropyl group). Hydroxypropyl- β -cyclodextrin (HP β CD) is a modified form of

cyclodextrin where the hydroxypropyl group has been incorporated into the top and bottom of the torroidal structure, increasing the aqueous solubility of the CD and the hydrophobic nature of the cavity. This process raises the aqueous solubility of HP β CD to 950 g/L (Blanford 2001).

Cyclodextrin has a non-polar cavity into which the hydrophobic organic contaminants partition to form inclusion complexes and a polar exterior that provides the molecule with a relatively high aqueous solubility (Bender and Komiyama 1978). This gives cyclodextrin the unique property of enhancing the apparent solubility of hydrophobic organic contaminants in aqueous solutions. For instance, HP β CD enhances the aqueous solubility of naphthalene, a creosote component, from 31 mg/L to 1659 mg/L. (McCray et al. 1999). In addition, the presence of cyclodextrin in water has negligible effect on pH and HPCD is resistant to precipitation (Wang and Brusseau, 1995). Thus, cyclodextrin flushing through the contaminated aquifers does not induce well screen clogging and aquifer permeability remains unchanged.

Cyclodextrin is resistant to biodegradation for a time period of at least for a few months (Wang et al. 1998). However, it has shown to be biodegradable over long periods of time. Cyclodextrin is non-toxic to human and microbial populations which minimizes the impact to the subsurface environment (Wang et al. 1998). The sorption of cyclodextrin onto the aquifer solids is very low (Brusseau et al., 1994) and can be easily removed from the subsurface either by extracting through extraction well or by natural biodegradation. The usage of cyclodextrin as a remediating agent also satisfies regulatory concern. Because cyclodextrin is non-toxic to organisms and easily biodegradable by the microbes. However, cyclodextrin may induce mobilization of the NAPLs in the subsurface if it is not removed from the subsurface for a long period of time after application. Mobilization of the NAPLs eventually may contaminate the ground water. Injection of bacteria for natural attenuation of cyclodextrin or additional

monitoring of the site for possible prevention of NAPL mobilization may be needed to satisfy the regulatory concern.

Cyclodextrin induced remediation technique is based on the ability of cyclodextrin to increase the solubility of hydrophobic organic compounds that are common compounds of creosote. The results of laboratory experiments show that cyclodextrin solutions can be used to enhance the desorption of organic contaminant from soil and thereby further enhance their removal from porous media (e.g. Brusseau et al., 1994). There is an indirect benefit of using cyclodextrin as a remediating agent because of its potential to enhance in-situ bioremediation. In-situ bioremediation shows high promise for the clean up of contaminated soil and groundwater. However, in-situ bioremediation is often restricted by proper oxygen supply and factors related to bioavailability such as solubility, dissolution and sorption rate (Wodzinski et al. 1974, Thomas et al. 1986, Weissenfels et al. 1992). Wang et al. (1998) reported that the presence of HP β CD enhances the apparent solubility of phenanthrene (a type of PAH). The increase in apparent solubility enhances the rate of bioremediation significantly. Thus cyclodextrin molecules may enhance in-situ bioremediation as well as solubilization. Some modified cyclodextrin molecules have been shown to complex with metals in the presence of organic contaminants and are useful in remediation of sites contaminated with mixture of metals and organic contaminants (Brusseau et al., 1997). The use of cyclodextrin as an agent for chemically enhanced in-situ flushing was introduced by Brusseau and colleagues (Wang and Brusseau 1993, Brusseau et al., 1994).

Background

Solubility Enhancement Laboratory Studies

Several laboratory studies have been performed with HP β CD to determine the apparent solubility enhancement factors for several organic compounds found in creosote contaminated soil. The term “apparent solubility” is well accepted terminology used by different researchers (e.g. Wang & Brusseau 1993, McCray et al. 2000, Boving et al.). The term “apparent solubility” means the enhanced solubility of the organic contaminants generated by the cyclodextrin solutions.

Wang et al. (1993) investigated the potential use of HP β CD to increase the apparent solubility of trichloroethene, chlorobenzene, naphthalene, anthracene, and p,p'-DDT. They measured the apparent solubility enhancement of these compounds with solutions of HP β CD at concentrations ranging from 0 to 7% wt./vol. They observed that relative aqueous phase concentrations of these compounds increase linearly with increasing HP β CD concentrations and the solubilization power of HP β CD is dependent on the size and relative polarity of its cavity.

Bizzigotti et al. (1997) determined the HP β CD induced solubilization enhancement factor of another low polarity organic contaminant (tetrachloroethylene) in presence of iron. They observed that HP β CD enhances the solubility of tetrachloroethylene in water both in static and flowing systems. McCray et al. (2000) measured cyclodextrin enhanced solubilization for some organic contaminants. They followed the same experimental method as followed by Wang et al. (1993). They found that more hydrophobic compounds experience a relative larger solubility than less hydrophobic compounds. Boving et al. (1999) performed column studies to compare water and HP β CD flushing of Borden sand containing TCE and PCE (two chlorinated

solvents). They observed that solubilization and mass removal were increased substantially with the use of HP β CD solution.

Brusseau et al. (1995) evaluated the sorption tendency of HP β CD solution in two types of soil including one with high organic content ($f_{oc} = 12.6\%$). They observed that flow of HP β CD was essentially the same rate (retardation of 1.0) in soil column studies as pentafluorobenzoate, which is considered a conservative tracer whose flow is similar to water. They further evaluated how HP β CD affects the degree to which several common groundwater contaminants are retarded in their flow through these soils. They observed that a 10% wt. vol. solution of HP β CD reduced the retardation of naphthalene, anthracene, and pyrene from 1.1, 28.6, and 161.8 in the low organic content sandy soil to 1.0, 1.9, and 2.6 respectively. For the high organic content soil the relative retardation in the transport of naphthalene was reduced from 92.0 to 15.7. These results show that cyclodextrin not only enhanced the apparent solubility of PAHs, but also enhances the ability to extract these compounds from an aquifer.

Cyclodextrin has also been evaluated under different geochemical conditions. Wang and Brusseau (1995) evaluated the performance of another form of cyclodextrin, carboxymethyl- β -cyclodextrin (CM β CD), under different pHs and ionic strengths conditions. They evaluated the effect of different pH solutions (4-8) on the apparent solubility of anthracene. They also followed the same experimental approach as Wang et al. (1993). They found for a 5% wt./vol. CM β CD solutions that pH of 4 the solubility enhancement factor for anthracene was 7.5, but then decreased to 6.3 at pHs of 5, 6, and 7 and then decreased to 6.0 at a pH of 8. While the decrease in solubility enhancement is minimal from pH of 4 to 5, this change in pH is also in the vicinity the log equilibrium acidity constant (pKa) of CM β CD, which is slightly below 5 (Wang and Brusseau, 1995). The pKa of HP β CD is near 12 (Bender and Komiyama, 1978). While an

evaluation of the influence of pH on the apparent solubility enhancement of this form of cyclodextrin has not been in the literature, it is likely that pH has a minimal affect. Wang and Brusseau (1995) also evaluated the influence of ionic strength on the solubility enhancement of anthracene by CM β CD. They found for 5% wt./vol. CM β CD solutions that over a broad range in the concentration of calcium chloride (1 to 10,000 mg/L) that the apparent solubility enhancement factor for anthracene rose only slightly (6.2 to 7.0). As with pH, an evaluation of the influence of ionic strength on the performance of HP β CD has not been published, but it is also likely that ionic strength has minimal impact.

The laboratory experiments conducted by Nasongkla et al. (2003) show that the amount of hydroxypropyl functional groups substituted in the CD molecule do not influence the formation of inclusion complex. They showed that β CD, without any hydroxypropyl group forms more inclusion complex with β -Lap, a hydrophobic compound in comparison to HP β CD. They also demonstrated that β CD (cavity diameter 7.0Å) generate more solubility enhancement in β -Lap in comparison to α CD (cavity diameter 4.5 Å) and γ CD (cavity diameter 8.5 Å). This second observation implies that the size of the cavity may not influence the amount of inclusion complexes formed by different CD molecules.

Solubility Enhancement Field Studies

In recent years four pilot-scale field studies of cyclodextrin remediation of NAPL contaminated sites have been performed (McCray et al 1999, Blanford et al 2001, Tick et al.2003 and Boving et al 1999). The cyclodextrin solution significantly increases the apparent solubility and rate of dissolution of several targeted organic contaminants for all these studies. The estimated cleanup time for this NAPL (non aqueous phase liquid) contaminated site decreases significantly as a result of that. It was estimated that more than 70,000 pore volume of water

flushing would be required to remove the undecane mass (A type of Alkane common in creosote). The same volume of undecane mass was removed in the eight pore volume of cyclodextrin flush (McCray, et al., 1999). In another field experiment at Dover Air Force base, Delaware (Tick et al. 2003), the cyclodextrin solution has increased the aqueous concentration of Tetrachloroethylene (PCE) in the extraction well effluent twenty two times the concentration obtained during water flushing. The seven pore volume flushes of cyclodextrin solution removed 33L of PCE whereas the same pore volume of water flushing removed 2.7 L PCE (Tick et al., 2003).

In another field study at Naval Amphibious Base Little Creek, Virginia (Boving et al. year 1999; McCray, et al. Blanford, et al. 2001) the cyclodextrin flushed through DNAPL (dense non aqueous phase liquid) contaminated groundwater and removed 30 L of DNAPL from the contaminated subsurface. The TCE concentration decreased around 70%.) investigated air stripping of TCE from HPCD solution under field conditions as a part of a vertical circulation study conducted in Arizona. The TCE concentration decreased from 900 ppb in a 7% hydroxypropyl-beta-cyclodextrin (HP β CD) solution to below detection levels (0.3 ppb).

McCray et al.(1999) demonstrated the effect of Raoult's Law in the cyclodextrin generated apparent solubility enhancement of different NAPL at a pilot scale field experiment conducted at Hill Air Force Base, Utah. According to Raoult's Law ideal equilibrium dissolution of NAPL constituents may be represented by $C^w_i = X^N_i S^w_i$, where C^w_i is the equilibrium aqueous concentration of NAPL constituent i in water, X^N_i is the mole fraction of i in the NAPL phase, and S^w_i is the single component aqueous solubility of component i in water. McCray et al. (1999) proposed a modified Raoult's Law for the NAPLs treated with cyclodextrin solution.

$C_i^{A*} = X_i^N E_i S_i^W$, where C_i^{A*} is the equilibrium aqueous concentration of NAPL constituent i in a cyclodextrin solution, E is the enhancement parameter for particular NAPL generated by the cyclodextrin, X_i^N is the mole fraction of particular NAPL in cyclodextrin solution, S_i^W is the aqueous solubility of particular NAPL.

McCray et al. (1999) measured the enhancement factors of twelve NAPLs in the field study and projected the ideal concentrations (C_{ideal}) of these NAPLs in the cyclodextrin solution according to the Raoult's Law. However, the actual concentrations (C_M) of these NAPLs he measured in his field experiment is different from the ideal concentrations. The ratio of C_M/C_{ideal} is greater for the compounds with higher aqueous solubility (TCE ratio is 2.4) and lower for the compounds with low aqueous solubility (decane, ratio is 0.9). But according to Raoult's Law the equilibrium concentrations should be identical ($C_M = C_{ideal} = 1$) for all compounds. The difference from the ideal behavior can be attributed to the increase in rate limited dissolution of the NAPLs generated by the cyclodextrin solution. The apparent increase in the dissolution rate is attributed to the impact of cyclodextrin on the rate of mass transfer between the NAPL and aqueous phase. The mass transfer rate is greater for the NAPLs with higher aqueous solubility. As a result of that, the measured concentration (C_M) of the NAPL with high aqueous solubility is higher in cyclodextrin solution.

Cyclodextrin enhanced NAPL and DNAPL field remediation has been demonstrated by several researchers in the recent past (McCray et al 1999, Blanford et al 2001, Tick et al.2003 and Boving et al 1999) as discussed above. However, no research has been done on the potential use of cyclodextrin for remediating creosote-contaminated sites. The solubility enhancement factors of some common creosote components determined by McCray et al. (2000) are only with Hydroxypropyl beta cyclodextrin (HP β CD). These researchers did not determine the solubility

enhancement factors of other common creosote components with two other types of commercially available cyclodextrins (HP γ CD and HP α CD). No study has compared different amount of total PAH mass removed by different volumes of three types of cyclodextrin through a series of column studies.

Objectives

To evaluate the ability of cyclodextrin as remediation agent different forms of cyclodextrin need to be tested. This includes understanding how cyclodextrin complexes with more components of creosotes. This study assess the ability of three different types of cyclodextrin (HP α CD, HP β CD and HP γ CD) to raise the apparent solubility of the most common poly aromatic compounds found in creosote that have not been previously determined. This is then followed by an evaluation of the performance of these cyclodextrins to extract the most common 2, 3, 4, 5, and 6 ring PAHs from a soil from a creosote contaminated site. Specifically, the objectives are: (1) to determine the cyclodextrin-induced solubility enhancement factors of eight common creosote components (acenaphthene, fluorene, chrysene, fluoranthene, dibenzofuran, naphthalene, anthracene, and benzo(k) fluoranthene) through series of batch studies conducted with three different types of 30% cyclodextrin solution (2) evaluate and compare to water the PAH removal ability of three different types of cyclodextrin (HP α CD, HP β CD and HP γ CD) from creosote contaminated soil.

CHAPTER 2: LITERATURE REVIEW

Limitations of the conventional remediation techniques (such as Pump and Treat method and Soil excavation) gave rise to several alternative remediating techniques such as soil vapor extraction, Insitu oxidation, soil vapor extraction, bioremediation, electrical heating, phytoremediation, alcohol and surfactant flushing (NRC, 1997) have been adopted by different researchers. However, all of these techniques are not equally efficient for remediation purpose. Each technique has some advantages as well as some disadvantages. This section discusses about the physical and chemical principles, advantages and limitations of these alternative techniques.

Soil Vapor Extraction Technique

Description

Soil vapor extraction technique is mainly used to remove volatile compounds from the soil in the vapor phase (EPA, 1997a; Holbrook et al., 1998; Johnson et al., 1993;). This technique uses and induced flow of air through the vadose zone to remove the volatile contaminants. A blower or vacuum pump is connected to the well that is screened across the contaminated interval of the unsaturated zone. The reduced pressure within the well induces airflow toward the well from the surrounding soils. As the airflow through the contaminated soils, the volatile components present in the vapor phase flows toward the well and is removed through the well along with the extracted air. The volatile compounds associated with the soil will gradually be extracted with recovered air. The recovered air is treated and then discharged directly to the atmosphere (Johnson et al., 1994).

Bioventing is similar to soil vapor extraction except that the design emphasizes biodegradation rather than volatilization, with the intent to minimize physical removal (Dupont et al., 1998). Like soil vapor extraction system, bioventing systems also circulate air but require a

much smaller volume of air than soil vapor extraction system.. Sometimes the groundwater pumping may be used to lower the water table and thus increase the depth to which the soil vapor extraction technique may be applied. Heat may be used to increase the contaminant volatility.

Physical and Chemical Principles

Soil vapor extraction technique is based on the partitioning of compound among phases- dissolved in groundwater or air or adsorbed to soil, or present in a nonaqueous-phase liquid (Johnson et al., 1994; Wilson and Clarke, 1994). The concentration of a compound in the vapor phase in equilibrium with dissolved phase contamination can be calculated from a compound's Henry's Law constant. The partitioning between a NAPL and air can be calculated from a compound's vapor pressure. The vapor pressure of a compound is function of temperature. Increasing the temperature increases the vapor pressure and also the partitioning of a compound into vapor phase which increases the soil vapor extraction efficiency.

Soil vapor extraction is also function of the air movement through the soil because the contaminants are extracted in the vapor phase from the soil. The amount of contaminants can be extracted depends on the volume of airflow induced. The volume of air that can be induced is a function of the permeability and water saturation of the soil.

Performance

Soil vapor extraction technique has been most successful for treating volatile compounds in moderately to highly permeable soils. It is an in situ technology and thus causes minimum disruption of normal site activities. It can be installed beneath buildings and in the vicinity of other type of infrastructure. It will not cause further migration of contaminants (EPA 2000).

Limitations

Soil vapor extraction technique is not applicable for compounds with low volatility and Henry's Law constant unless the compounds are biodegradable under aerobic conditions. This technique is not useful for treating creosote contaminated soil because most of the creosote components have very low aqueous solubility. It also can not be used to treat wet, clayey soils and less permeable soil. Low vapor pressure of some compounds and soil heterogeneity also limits its applicability. Although these problems can be overcome to some extent by closely spacing wells, applying heat or increasing the operating time of the system. These alternatives, add to the cost of remediation.

In Situ Oxidation

Description

The in situ oxidation technique involves injection of an oxidizing reagent into the contaminated source zone and destruction of the contaminants by chemical reaction with the oxidizer. The excess oxidizer is extracted followed by flushing of water through the treatment zone. Potassium permanganate and hydrogen peroxide are most commonly used oxidizers.

Physical and Chemical Principles

This remediation technique is based on the oxidizing capacity of the reagents. Organic contaminants react strongly with the oxidizing reagents and can be oxidized to carbon dioxide and water under strongly oxidizing conditions.

Application

Potassium permanganate or Hydrogen peroxide injected in the source zone yields carbon dioxide, water and chloride or any other byproduct when organic contaminant oxidized by them. Persistent reagent like potassium permanganate is generally washed away from the treatment

zone by water flooding when oxidation is complete. Hydrogen peroxide spontaneously decomposes to water due to very short half life on the order of hours (Pardieck et al., 1992).

Performance

DOE conducted a field test of organic contamination remediation (mainly TCE rich) using potassium permanganate at Portsmouth, Ohio in 1997. A total of 780 m³ of potassium permanganate solution was injected in one well and recovered in other well. The result shows significant reduction of TCE in all localities reached by potassium permanganate. Concentrations of TCE were originally as high as several hundred thousand micrograms per liter, were reduced to nondetectable levels in numerous monitoring wells (NRC, 2000).

Limitations

There are several limitations of this technique. First of all, potassium permanganate is effective for oxidation of TCE and PCE but not for destruction of chlorinated compounds without double bond (Pankow and Cherry, 1996). Secondly, strong oxidizers like potassium permanganate; hydrogen peroxide oxidizes all oxidizable compounds in the system including the solid organic matter in the soil. That increases the reagent required for the treatment (Miller et al., 1996). Due to very short half life of hydrogen peroxide, it can treat only small volume of contaminant which can be reached within several hours. Apart from that hydrogen peroxide is capable of blocking the subsurface with gas and cause the ground surface to buckle, delivering a sufficient volume of reagent to large volume of contaminant may be difficult.

Air Sparging

Description

This technique involves injection of air or other gases directly into the groundwater to vaporize and recover the contaminants. Volatile components will vaporize and move upward to

atmosphere or to a vapor extraction system is installed in the vadose zone to extract the contaminated air. The injected air driven by the injected pressure moves laterally and upward due to buoyancy. As the injected air moves it comes in contact with the contaminants or water containing dissolved phase of the contaminants, the volatile contaminants partition into the air. Oxygen present in the air will dissolve in the water and promotes the insitu bio degradation of nonvolatile contaminants (EPA 2000).

Performance

An air sparging system was installed at Hill Air Force Base, Utah, to remediate dissolved phase TCE plume coming from an unknown source. After three months of operation, significant reduction in contaminant concentrations occurred at many monitoring points. However the system did not achieve drinking water standards at number of monitoring points. As a result the plume was not considered captured. A ground water pump and treat system was installed to ensure capture of the plume (EPA 2000).

Limitations

Achieving uniform flow of air through heterogeneous subsurface may be very difficult to remove all the contaminants form the subsurface. Even small changes in permeability will influence the pathways through which injected air flows. Apart from that injection of air below the contaminated zone is difficult at sites where contaminants occur at the bottom of the aquifer. Air sparging will not be effective in removing contaminants with low volatilities. In most cases, air sparging is used in conjunction with soil vapor extraction system to capture all contaminants.

Advantages

This remediation technique is very inexpensive because it involves only the introduction of air. It is shown to be an effective remediation technique under appropriate geologic condition.

Electrical Heating

Electrical heating method is used for volatilization and extraction of the contaminants. Different types of heating methods like resistance heating, microwave heating, and radio frequency heating can be used for this purpose. In each case electrical energy is used directly to the soil to produce heat. Contaminants are driven out of the source zone by a combination of volatilization and thermally induced vapor-phase transport. The electrical resistance heating method involves inserting electrodes in the ground and passing an alternating current through the water and soil between electrodes. The degree of heating depends on the current and the resistance of the unit. Rocks are generally nonconductive, so most current flows through the soil moisture and groundwater. The radio frequency heating uses an electrical field created by inserting antennas into treatment zone and heating the soil at appropriate frequencies (6.68-40.68 MHz). This technology has proven capable of heating low permeability soils to more than 150° C (Edelstein et al., 1994).

Physical and Chemical Principles

Electrical heating technology is based on increase in vapor pressure of the contaminants when adequate temperature is added in the soil. Most of the contaminants partition strongly into the vapor phase and can be extracted through vapor extraction.

Advantages

Each heating technology has the proven capability of heating fine grained soils to boiling or near boiling temperatures. At sufficiently high temperature volatile and semi volatile contaminants can be driven out of the system. Heating method also works well in fine grained soil, which is often difficult to treat by other method.

Limitations

The main disadvantage of using this technique is that, this technique does not recover the contaminants directly, it only vaporize the contaminants. This technique must be coupled with SVE for contaminant recovery. Heating technique is especially coupled with SVE technique when permeability of units to air is too low for SVE or the vapor pressure of the contaminant is too low.

In Situ Bioremediation

This technique involves the breakdown of organic contaminants by microbiologic reactions. often nutrients (typically nitrogen and phosphorus source), air (oxygen source) or any additional carbon source (easily degradable organic compound) are added into the ground through wells, that can serve as source of energy for indigenous microorganisms and allow the organisms to degrade the contaminating material where it is found. Organic contaminants can be degraded to carbon dioxide, water and their component ions. Biodegradation may not run to completion. Biodegradation reactions normally involve either oxidation or reduction of the organic contaminants and thus require either oxidizer (electron acceptor) or reducer (electron donor). The compounds serve as electron acceptor or electron donor is known as primary substrates. The organic contaminants usually serve as primary substrates and microorganisms use them as carbon source and obtain energy through their metabolism. Oxygen is the most common electron acceptor. Nitrate, sulfate, manganese and iron can also serves electron acceptor in absence of oxygen. Aerobic degradation is very effective for remediation of some chlorinated solvents and their metabolites but most DNAPL compounds including TCE and PCE degrade more readily under anaerobic condition (NRC, 1993). The organic contaminants usually serve as

primary substrates and microorganisms use them as carbon source and obtain energy through their metabolism.

The DNAPL plumes often composed of one or more chlorinated solvents. When the dissolved phase plume transports from the source zone, it often contain additional compounds that are metabolites of chlorinated solvents. Dichloroethenes and Vinyl chloride are two common metabolites of PCE and TCE. The presence of metabolites that were not typically present at the site is frequently taken as evidence that some biodegradation of organic contaminants has taken place.

Advantages

In situ bioremediation is most cost effective technique because it uses indigenous microorganisms to treat wide variety of soluble organic contaminants. Another advantage of this method is that the contaminants treated in situ are not transported to another medium. Treatment chemicals move with the plume which allows the treatment of sorbed contaminants.

Limitations

Biodegradation only occur in aqueous phase and not suitable for remediation of free phase DNAPL sources. Another disadvantage of this technique is that the metabolites of chlorinated solvents produced by biodegradation are often more toxic than the original compound. Another potential problem associated with this technique is that the introduction of nutrients may degrade the quality of groundwater and growth of biomass may reduce the flow of water.

Phytoremediation

Description

This technique involves the removal of contaminants from soil or groundwater with the usage of plants. Studies have confirmed that certain plant species can take up chlorinated solvents from the ground water in the root zone (Chappel,1997; Schnoor, 1997). Once plant takes up the solvent, it store the chemical in its body via covalent bonding with plant lignin (Schnoor, 1997). The plant may metabolize the chemical to other compounds. Poplar tree transforms TCE to trichloroethano, trichloroacetic acid and dichloroacetic acid- products similar to those produces by enzymes in the human liver on exposure to TCE (Newman et al. 1997). Research has also indicated that the growth of plant roots can stimulate degradation of TCE by microorganisms in root zone via reductive dechlorination (Chappell,1997); the plants exude substances through their roots that can stimulate the growth of microbes required to carry out these reactions.

Advantages

Phytoremediation is low cost technique because it is solar driven and eliminates the need for excavation and ex situ treatment. This type of treatment does not generate secondary waste.

Limitations

Phytoremediation technique is applicable above the water table and in very shallow ground water. It is very time consuming technique. Phytoremediation for treatment of dissolved chlorinated solvents is in very early stage of development.

Surfactant, Alcohol or Cosolvent Flushing

Description

This remediation technique involves surfactant, alcohol or cosolvent pumping at various concentrations through contaminant source zone to remove contaminant by dissolution and / or mobilization. . Different types of alcohols (ethanol, methanol, propanol) and surfactants are commonly used solubility enhancing reagents.

Physical and Chemical Principles

Injection of surfactants alcohol or cosolvent rich water in the contaminated zone reduces the interfacial tension of hydrophobic organic compounds which accompanies the increased solubility of these compounds in the water. Numerous researchers have demonstrated the ability of solvents such as short chain alcohols (methanol, ethanol, propanol) to increase the solubility of hydrophobic organic compounds in water (Rao et al, 1985, Peters and Luthy 1993; McCRAY AND Falta, 1996). As the solubility of the hydrophobic organic compounds increases, the interfacial tension between the hydrophobic compounds and water decreases. Displacement as well as dissolution may occur as interfacial tension decreases.

Application

Surfactant, Alcohol or cosolvent flushing system consists of series of injection and extraction wells to provide and efficient flood of source zone. The effluent solution produced at the extraction wells contains water, solvent, and contaminants must be treated prior to disposal.

Performance

This remediation technique is based on the removal of contaminants by dissolution and /or mobilization. Three field trials of solvent flooding has been performed at Hill Air Force Base at Utah, by EPA and researchers from three different universities (University of Florida,

University of Arizona, and Clemson University). Recovery range was between 40- 93 percent. This technique is more effective for chlorinated solvents.

Advantages

Alcohols are effective solvents and are not sorbed significantly in the soil. Many surfactants are FDA food-grade compounds and are readily biodegradable. Surfactant or Alcohol flushing techniques use conventional pumping equipments, so operation costs are relatively low. Application of this technology does not involve lot of site disruption and potentially can be performed beneath the buildings.

Limitations

The nonuniform distribution of contaminant in the subsurface aquifer may reduce the efficiency of this technique. To remove the contaminant from the soil, the entire contaminated volume of soil must be effectively flushed with alcohol or solvent. But due to heterogeneous pore volumes the circulation of the remediation solvent is limited and not sufficient for removing all contaminants. Subsurface heterogeneities also decrease the efficiency of the extraction technique. In heterogeneous subsurface some areas will be poorly swept by the flushing solution and therefore will require longer treatment times and larger treatment volumes than homogeneous subsurface. The decrease in interfacial tension created by this technique increases the risk of contaminant mobilization downward toward the previously clean impermeable layers depending upon the integrity of the aquitard. This risk must be evaluated for each site. Alcohols are generally less dense than water and therefore alcohol flooding solution will be less dense than ground water (EPA 2000). This sometimes presents a problem in circulating these solutions evenly.

CHAPTER 3: MATERIALS AND METHODS

The use of cyclodextrin as an agent for chemically enhanced in-situ flushing of contaminated aquifers was introduced by Brusseau and colleagues (e.g. Wang and Brusseau 1993, Brusseau et al., 1994). While there are over fifty derivatives of cyclodextrin commercially available, the laboratory evaluations of cyclodextrin (CD) as a remedial agent for volatile and semi-volatile organic contaminants has primarily focused on three commercially available types, hydroxypropyl - β -cyclodextrin (HP β CD) hydroxypropyl - α -cyclodextrin (HP α CD) and hydroxypropyl - γ -cyclodextrin (HP γ CD). The number of glucose units is 6,7 and 8 respectively for HP α , HP β and HP γ cyclodextrins. Figure 1 shows the basic structure of cyclodextrin molecule. The total volume of the hydrophobic interior of the HP α CD, HP β CD and HP γ CD molecule is reported to be 0.176, 0.346 and 0.561 nm³ respectively (Blyshak et al. 1986).

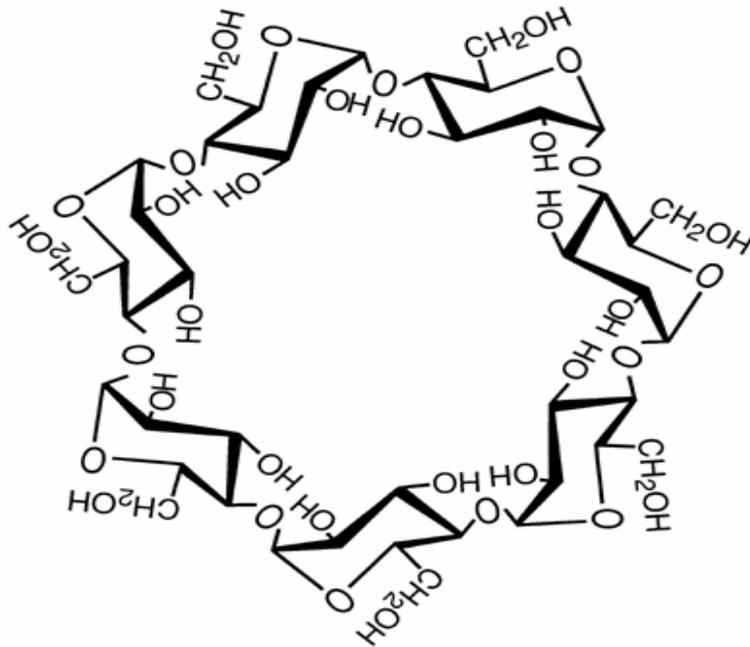


Figure 1. The Structure of Cyclodextrin Molecule

The hydroxypropyl functional groups give the molecule a high aqueous solubility and makes the inner cavity highly favorable for partitioning of low-polarity contaminants.

HP α CD, HP β CD and HP γ CD has been evaluated for the solubilization of eight common components of creosote (naphthalene, anthracene, fluorine, fluoranthene, benzo(k) fluoranthene, acenaphthene, chrysene, dibenzofuran.) through series of batch solubility experiments. These compounds comprise minor portions of the mixture of 2, 3, 4, 5 and larger ring sized PAHs commonly found in creosotes. In order for cyclodextrin to be evaluated for use as remedial agent for creosote contaminated sites the solubility enhancement of additional PAH components need to be evaluated. Further, to determine if the size of the inner cavity of the hydroxypropyl - cyclodextrin molecule markedly affects the remedial performance then each of the three HPCDs must be evaluated.

The eight poly aromatic hydrocarbons (naphthalene, anthracene, chrysene, fluorine, fluoranthene, chrysene, dibenzofuran, benzo (K) fluoranthene) selected for evaluation of the solubility enhancement are common PAHs found in coal tar creosote (Lorenz and Gjovik 1972). Most of these compounds have low aqueous solubility and high boiling points. These two characteristics contribute to the failure of conventional remediation techniques such as groundwater flushing. Table- 1 and 2 show aqueous solubility, molecular weight, boiling points, organic solubility and typical percentage of these PAHs found in creosotes (Montgomery, 2000; Lorenz et al. 1972). The Kow values of different PAHs reported in table 1 is the hydrophobicity of the compounds. The greater Kow values, the PAH compound is more hydrophobic.

The enhancement factor equation used here for data analysis has been adapted from McCray et al.(2000) to analyze our result ($S_a = ES_w = (1+K_{CW}C_H) S_w$, where S_a is apparent

enhanced solubility, E is the enhancement factor, S_w is aqueous solubility, K_{CW} is the Cyclodextrin/water partitioning coefficient and C_H is the Cyclodextrin concentration in wt./vol).

Table 1. PAH Characteristics

Polyaromatic Compound	Mol. Wt. ^a	logK _{ow} ^b	Aqueous Solubility ^c (mg/L)
Naphthalene	128.18	3.33	31
Acenaphthene	154.21	3.92	4.16
Fluorene	166.22	4.18	2.23
Dibenzofuran	168.2	4.31	4.22
Anthracene	178.24	4.68	0.048
Fluoranthene	202.26	5.23	0.177
Chrysene	228.3	5.78	0.0015
Benzo(k)fluoranthene	252.32	6.11	0.00109

a,b and c parameters from Montgomery (2000).

Table 2. General Characteristics of PAHs and Percent Present in the Coal Tar Creosote

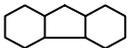
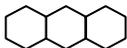
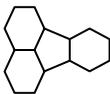
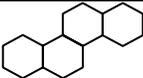
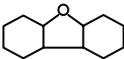
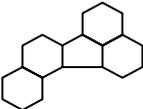
Polyaromatic Compound	Structure [^]	Aqueous solubility mg/L [^]	Organic solubility g/L [^]	Boiling point (° C) [^]	% present in the coal tar creosote*
Naphthalene		31 [^]	66.2(methanol) 95.2 (ethanol) 334 (propanol)	217.942 [^]	3*
Acenaphthene		4.16 [^]	17.9 (methanol) 32.3 (ethanol) 40.0(Propanol)	279 [^]	9*
Fluorene		2.23 [^]	Soluble in most solvents including acetic acid, chloroform	298 [^]	1.6*
Anthracene		0.048 [^]	14.6 (ethanol) 14.3 (methanol) 11.8 (Chloroform)	339.9 [^]	2*

Table 2 cont.

Fluoranthene		0.177 [^]	Soluble in acetic acid, ethanol, benzene, Chloroform	375 [^]	10*
Chrysene		0.0015 [^]	Soluble in acetone, benzene, ether	448 [^]	3*
Dibenzofuran		4.22 [^]	Soluble in acetic acid, acetone, ethanol and ether	287 [^]	5*
Benzo(k)Fluoranthene		0.001 [^]	Soluble in most solvents	480 [^]	
[^] Data adapted from Ground water chemicals desk references (Montgomery, 2000) * Data adapted from Lorenz and Gjovik (1972)					

Batch Studies

Analytical grade hydroxypropyl - α -cyclodextrin, hydroxypropyl - β -cyclodextrin, hydroxypropyl - γ -cyclodextrin were obtained from Wacker Biochemie (USA) all were at least 89% purity The target PAHs for this study are: naphthalene (99+% purity), acenaphthene (99% purity), anthracene (99% purity), chrysene (98% purity), fluoranthene (99% purity), fluorene (98% purity), dibenzofuran (99+% purity), benzo (k) fluoranthene (98% purity) were obtained from the Sigma Aldrich Chemical Co.

Batch solubility measurements were performed to determine the apparent solubility enhancement of the target PAHs by the three selected cyclodextrins under equilibrium

conditions. The standard method for the solubility enhancement factors is with the use of a 10% wt./vol. solution of technical grade HP β CD solution (Wang et al. 1993; Bizzigotti et al. 1997; McCray et al. 2000). But, for this study we decided to perform the solubility enhancement tests with 30% wt./vol. solutions. This was done to raise the mass of the lowest solubility PAHs to be used in the batch tests well above the detection level (± 0.1 mg) of the analytical balance.

Preparation of the 30% wt./vol. cyclodextrin solutions consisted of measuring 30.00 grams of cyclodextrin powder in a 100 ml flask and dissolving it in high purity water (18 ohm). The flask was then placed on a magnetic stirrer (Telesystem make, Variomag model) for 30 minutes to create a uniform cyclodextrin solution.

To ensure that sufficient mass is available for each of the target PAH to reach equilibrium saturation in the cyclodextrin solutions excess amounts of PAHs were used. For these studies, amount of each PAH able to solubilized in 18ml of the 30% CD solution was projected from the relationship between octanol water partitioning coefficients vs. enhancement factor by McCray et al. (2000). This amount was then multiplied by four as a margin of error. The number four was chosen as margin of error. The batch experiment was then conducted by measuring the determined mass of PAH on analytical balance (Denver series APX 2000) and adding the PAH mass in the 18.0ml of the selected 30% cyclodextrin solution in a 20ml headspace vial (60827T-2375 autosampler vials, Ampolletas,S.A.). The experiments were done in triplicate and vials were placed on a shaker (Labline shaker) at 110 RPM for 36 days to ensure equilibration of the PAH in the cyclodextrin solutions. The headspace of the vial was not filled, but included a bubble to promote mixing. This was thought not to be problematic because the PAHs have low volatility and excess quantities were used. After 36 days aliquots of varying amounts (0.1-5.7 ml) were withdrawn from the 20 ml headspace vials for PAH analysis. The aliquots were poured

into 20 ml headspace vials and diluted with different amounts of 18 ohm water to produce different concentrations of the organic contaminants in the 20ml solution. This was done to reduce the concentration of the solution to fall within the range of calibration standard solutions.

Calibration standards are the solutions with known amount of PAH in it. The known PAH concentrations are measured using spectrofluorophotometer. The calibration curves are obtained by plotting PAH concentration along y axis and spectrofluorophotometer readings along x axis. The equation obtains with these two variables (PAH concentrations and readings) is used to determine the concentration of PAH in the cyclodextrin solution when spectrofluorophotometer produces particular reading for particular concentration of PAHs in cyclodextrin solution.

The concentrations of the organic compounds (PAHs) in cyclodextrin solutions were measured using fluorescence spectroscopy. Previously McCray, et al. (2000) used this technique for the measurement of the PAH (pyrene) concentration in 10%HP β CD solution .Schwarz and Wasik (1976) and Schwarz(1977) have also used fluorescence technique for the detection of PAHs in the aqueous solution. All fluorescence measurements were carried out with Shimadzu RF-5000 Spectrofluorophotometer equipped with a 150 W continuous high power xenon lamp, two monochromators (ion-blazed, halographic concave grating F/2.5) with wave length scale 200-1200nm and a high performance R452-01 photomultiplier detector.

Calibration standards were prepared to correlate the fluorescence readings to the known concentrations of PAHs. The standards were made with 30% wt./vol. of the same cyclodextrin as the batch solubility test. The 2 liter quantities of cyclodextrin solutions were made with the same method as discussed previously.

The most concentrated standard was created by adding 4mg of single target PAH in a 100ml 30% cyclodextrin solution in a 100 ml volumetric flask without any headspace. The flask

was then sealed with parafilm and placed on the magnetic stirrer machine for seven days to ensure dissolution of the organic compound into the cyclodextrin solution. The volume of CD solution within the bottle was determined through weighing and previously determined density analysis of the CD solution. To make the lower concentration PAH standard solutions, aliquots of varying amounts were then withdrawn from the 100 ml flask and added to 20 ml headspace vials. The headspace vials was then filled with 18 ohm water without any headspace for dilutions. Concentrations varying in amount from 0.1mg/L to 120mg/L for standard solutions were made for each PAH/cyclodextrin setup. The concentrations of the organic compounds were measured using the Shimadzu RF-5000 Spectrofluorophotometer.

Column Studies

Column studies were performed to simulate natural ground water conditions where CD solutions were flushed through soil contaminated with creosote. A series of soil column flush experiments were conducted to assess two aims: 1) comparison of PAH mass removal for the similar volumes and mass of the three different types of cyclodextrin and water and 2) an analysis of the volume of cyclodextrin solution flushed versus contaminant mass removal through a series of experiments. The bulk analysis of soil done by XRD shows that the soil contains 97.5% silica and 2% clay mineral (Table 3).

Table 3. Analysis of Soil by XRD

Mineral	% Present in the Soil
Quartz	97.5
Clay minerals	2.5

For the first experiments, a series of four column tests were performed to evaluate the mass extracted of eighteen different PAHs from 20 grams of creosote contaminated soil through flushing with 2L solutions of 10% wt./vol. solutions HPCD, HP β CD, HP γ CD and water. For the

second set of experiments, the PAH mass removal from the same mass of the same soil was compared for separate 0.5 L, 1L, 2L, 4 L and 7 L volume flush of 10% HP α CD and HP β CD solutions.

One HPLC pump (Accuflow series 1, Labline model), one HPLC (high pressure liquid chromatography) 316 grade stainless steel column (25 cm long, 2.25 cm wide; Alltech, Association Inc. IL, USA), Accusand (Unimin Corporation (USA) with 99.79% silicon dioxide), one three way switching valve and one 50 cc syringe, one stainless steel connecting tube(1/16" outer diameter, 16" length) between pump and column, and one 316 grade stainless steel connecting tube (1/8" outer diameter, 25" length, obtained from Swagelok Corporation) was used for column studies. Figure - 2 shows the basic experimental set ups for the column studies. The HPLC pump was connected to the column through a 316 grade stainless steel tube. The three way switching valve was placed in line with the column and the pump in order to facilitate switching between the syringe (used for sample collection) and the waste solution.

One L of heavily creosote contaminated soil obtained from Union Timber site, Homerville, Georgia. The HPLC column holds the creosote contaminated soil in stationary phase. To simulate natural ground water flow condition, a column was chosen with length of 250 mm and 22.5 mm inner diameter for the HPLC column. High purity (316 grade) stainless steel column with stainless steel wall was chosen over glass or teflon wall column to reduce surface sorbtion of the contaminant on the column wall and for withstanding high pressure exerted by the solution. One coarse grade frit (1" diam. X 0.125" thickness, 100micrometer grade 316 LSS (Mott Corp.) was used at the outbound end of the column and one fine grade frit (1" diam x 1.6 mm thickness 2 μ grade (Alltech) was used for the other end of the column. The 1/3 length of the column was packed first with creosote contaminated soil (~ 20.0g) and the

top portion of the soil was packed then with accusand (~115 g). Coarse grade frit, at the outbound end of the column acts as a filter between the accusand and the frit to prevent clogging created by the upward mobilization of fine clay particles of the soil during solution flushing. HPLC pump was used for this experiment to deliver consistent flow over wide range of pressure.

The creosote contaminated soil was first homogenized to ensure uniform conditions for each of the column tests. This was accomplished first by screening the soil through 3.35 mm sieve to remove rocks and other debris. The remaining 900 ml of soil was then repeatedly stirred to form a homogenous mixture of creosote contaminated soil.

Preliminary studies where the HPLC column was filled with only the creosote contaminated soil were unsuccessful because the filter of the outbound end of the column became clogged with debris suspended due to the water and CD solution flushing. To solve this issue it was decided to add a non-reactive accusand filter. The accusand is unlikely to act as strong reactive adsorbent because of its low organic matter content. The accusand was made more inert by washing it with alkaline and acidic solution. This addition had the added benefit of reducing the volumes of CD solution needed to evaluate the technology to more manageable levels. Before adding to the column, the accusand was washed with pH 12 solution of sodium hydroxide to remove any organic matter then repeatedly washed with ultra pure water until a pH of 7 was reached. Then to remove any metal oxide coating the soil was washed in a pH 2 solution of sulfuric acid and again with ultra pure water until a pH of 7 was obtained. The 10% cyclodextrin solutions or water flushed through the column through the HPLC pump were created in ultra pure water with 5g/L CaCl_2 to prevent any clay swelling. Because the creosote contaminated soil was unsaturated at the beginning, the column studies were performed with an upward flow (flow rate of 2.0 ml/min) to maintain a uniform one dimensional flow regime.

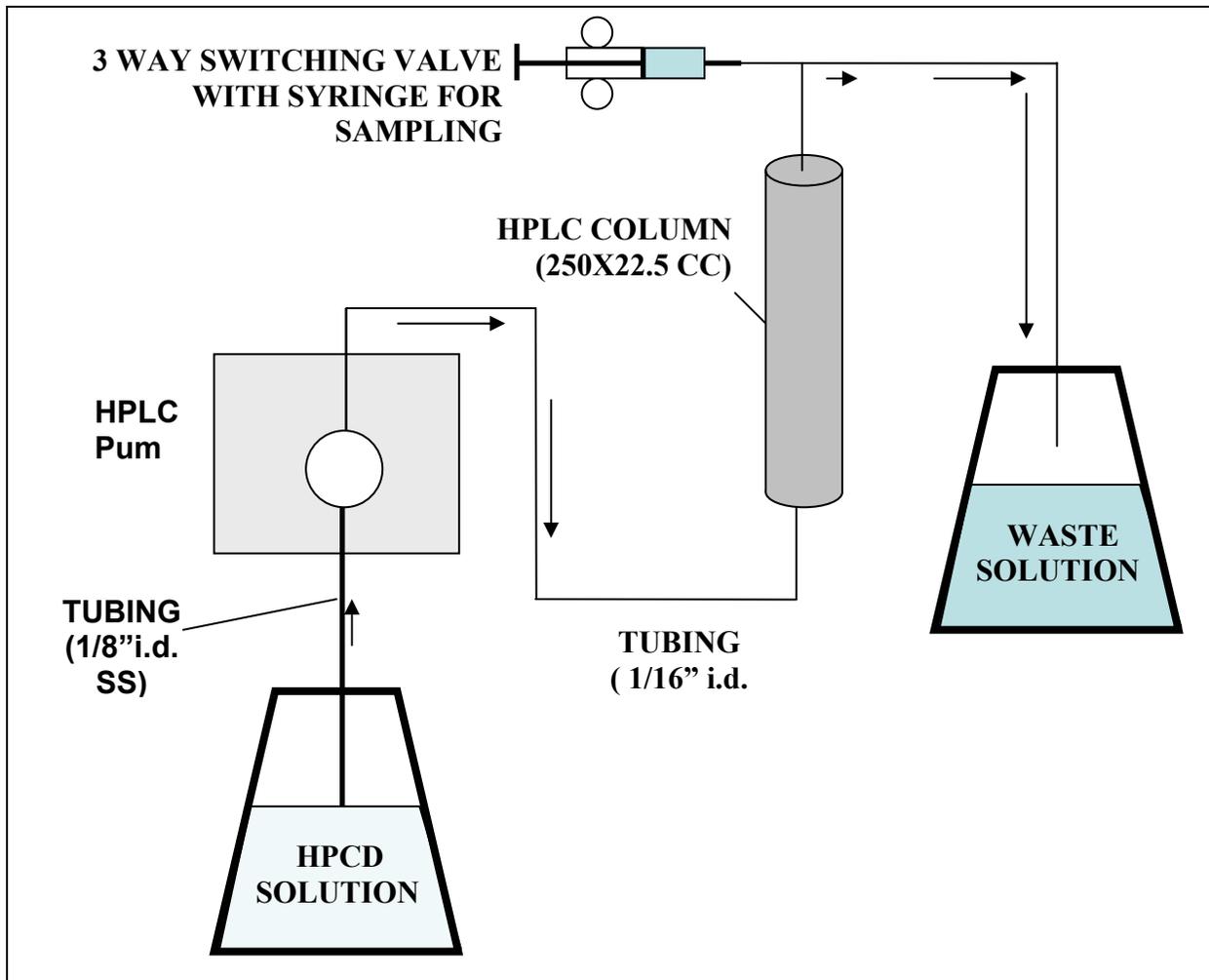


Figure 2. Experimental Setup for the Column Studies

After flushing the desired volume of 10% solution through the column the soil and the accusand were removed from the column and analyzed to determine the amount of contamination removed by solution flushing for all column studies.

The soil and accusand was extracted following ultrasonic soil extraction method (EPA 3510C method) and analyzed by gas chromatography (EPA 8270 method) determine the remaining organic contaminant mass.

EPA 3510C soil extraction method was performed to determine the amount of PAH mass removed by 10% cyclodextrin solution. Contaminated soil plus accusand (~130 g) were mixed

with adequate amount of sodium sulfate. Sodium sulfate acts as water absorbent to remove the moisture from the soil plus sand. Adequate amount of dichloromethane was poured into the soil plus sodium sulfate mixture to extract organic contaminants from the soil plus sand mixture. One ml of surrogate solution (Phenanthrene d/10 and Alphanthro 100µg/ml) was poured into the mixture. The mixture was then placed on a sonic vibrator (FS-14, Fisher Scientific) for 15 minutes to extract the maximum amount of organic contaminant from soil phase to dichloromethylene phase. After that the liquid portion of the mixture was filtered into a flat bottom flask using filter paper to remove any soil debris or rock particles. Again some dichloromethane was poured into the remaining mixture and placed the mixture on sonic vibrator for 15 minutes to extract organic contaminants from the soil plus sand mixture. After 15 minutes the liquid portion of the mixture was filtered into the flat bottom flask. This procedure was done one more time to ensure removal of 99% of the contaminant from the contaminated soil to dichloromethane solution. The contaminated liquid collected into the flat bottom flask was then placed into a rotovapor (R-114, Buchi Rotavapor) at 50°C for 10-45 minutes to vaporize the dichloromethane (the vapor pressure of the dichloromethane is lower than most of the nonpolar organic compounds) leaving behind the nonpolar organic contaminants for analysis with gas chromatography.

CHAPTER 4: RESULTS

Batch Studies

Enhancement Factor Analysis

Enhancement factors for the three types of cyclodextrins were compared to several parameters including aqueous solubility, molecular weight and hydrophobicity as measured by octanol/water partitioning coefficients. The primary objectives for these comparisons are:

- 1) Evaluate the trends in the apparent solubility enhancements for the different PAHs
- 2) Evaluate if the apparent solubility enhancement factors for the eight different types of PAHs are influenced by cavity sizes of the cyclodextrins
- 3) Evaluate the ability of the widely existing experimental data on the PAHs to project the apparent solubility enhancement factors for other different PAHs
- 4) Evaluate the linkage between the values of apparent solubility enhancement and the amount of cyclodextrin present

Enhancement factors determined in this experiment for eight selected PAHs with three different types of cyclodextrins are shown in Table- 4. Enhancement factors for all eight compounds are greatest for HP γ CD, in comparison to HP α CD and HP β CD. Table-5 shows HP γ CD works best for naphthalene (% enhancement factor difference between HP γ CD and HP β CD is 21.87%, between HP γ CD and HP α CD is 34.32%) and dibenzofuran (% enhancement factor difference between HP γ CD and HP β CD is 19.04%, between HP γ CD and HP α CD is 23.10%) in comparison to HP β CD and HP α CD. The HP γ CD genated enhancement performance in comparison to HP β CD and HP α CD for fluoranthene and benzo (k) fluoranthene is only 0.21% and 12.89% better than HP β CD and HP α CD for fluoranthene and 2.55% and 7.37% better than HP β CD and HP α CD for benzo (k) fluoranthene.

Table 4. HP α CD, HP β CD, HP γ CD Enhanced Apparent Solubility of Parameters of Different PAHs Determined in this Study

Polyaromatic Compound	CD	10% CD Enhancement Factor		Log K _{cw}		Apparent Solubility	
		Avg.	Stdev	Avg.	Stdev	Avg. mg/L	Stdev
Naphthalene	HP α CD	19.6	0.5	2.27	0.026	620	16
Naphthalene	HP β CD	23.3	0.2	2.35	0.003	720	5
Naphthalene	HP γ CD	29.8	1.6	2.46	0.024	923	50
Acenaphthene	HP α CD	86.2	1.5	2.93	0.006	356	6
Acenaphthene	HP β CD	89.7	1.5	2.95	0.007	372	6
Acenaphthene	HP γ CD	94.9	0.6	2.97	0.001	392	2
Fluorene	HP α CD	63.3	1.5	2.79	0.012	140	3
Fluorene	HP β CD	66.2	0.6	2.81	0.004	146	1
Fluorene	HP γ CD	74.4	1.0	2.87	0.005	165	2
Dibenzofuran	HP α CD	49.3	1.0	2.68	0.008	207	4
Dibenzofuran	HP β CD	51.9	1.2	2.71	0.010	217	5
Dibenzofuran	HP γ CD	64.2	1.2	2.80	0.007	269	5
Anthracene	HP α CD	269	1	3.43	0.001	12.9	0.1
Anthracene	HP β CD	284	2	3.45	0.003	14	0
Anthracene	HP γ CD	299	1	3.47	0.002	14.3	0.1
Fluranthane	HP α CD	243	3	3.38	0.006	42.8	0.5
Fluranthane	HP β CD	278	3	3.44	0.003	49.1	0.4
Fluranthane	HP γ CD	278	1	3.44	0.002	49.2	0.2
Chrysene	HP α CD	1372	46	4.14	0.014	2.06	0.07
Chrysene	HP β CD	1567	15	4.19	0.003	2.35	0.02
Chrysene	HP γ CD	1741	23	4.24	0.007	2.61	0.03
Benzo(k)Fluranthane	HP α CD	3831	170	4.58	0.019	4.17	0.19
Benzo(k)Fluranthane	HP β CD	4031	192	4.60	0.020	4.39	0.21
Benzo(k)Fluranthane	HP γ CD	4136	70	4.62	0.007	4.50	0.08

The greatest enhancement performance by HP γ CD implies that the larger CD cavities for HPCDs molecules, improve the rate of PAH complexation, but that rate of improvement is marginal (cavity diameters for HP α CD, HP β CD and HP γ CD are 4.5 (Å), 7.0 (Å), and 8.5 (Å) respectively) (Bender & Komiyama, 1978). For all three types of cyclodextrins the benzo (k)

fluoranthene shows highest enhancement factor (3831, 4031 and 4136 for HP α CD, HP β CD and HP γ CD) and naphthalene shows lowest enhancement factor (19.6,23.3 and 29.8 for HP α CD, HP β CD and HP γ CD). Previously the enhancement factors for Naphthalene and Anthracene has been determined by McCray et al.(2000) only with 10% HP β CD. Table - 6 compares the enhancement factors of these two compounds for 10% HP β CD obtained by McCray versus this experiment. The anthracene enhancement factor obtained by McCray et al. (2000) is 4.5% greater than the anthracene enhancement factor obtained in this experiment. The naphthalene enhancement factor obtained in this experiment is 131.6% less than the enhancement value obtained by McCray et al. The reason for the difference in the enhancement values has been discussed in detail in the discussion section.

Table 5. Comparison of Enhancement Factors Between HP α CD, HP β CD & HP γ CD

Polyaromatic Compounds	% Enhancement Factor difference bet.HP β CD & HP α CD	% Enhancement Factor difference bet.HP γ CD & HP β CD	% Enhancement Factor difference bet.HP γ CD & HP α CD
Acenaphthene	3.88	5.44	9.11
Anthracene	5.20	5.08	10.02
Benzo (K)Fluranthene	4.95	2.55	7.38
Chrysene	12.46	10.00	21.22
Dibenzofuran	5.01	19.05	23.10
Fluorene	0.00	10.99	10.99
Fluranthene	12.70	0.22	12.89
Naphthalene	15.94	21.87	34.33
Average	7.52	9.40	16.13

Table 6. Average 10% Enhancement Factors for HP α CD, HP β CD, HP γ CD Solutions

Polyaromatic Compound	Avg.10% Enhancement Factor (HP α CD)	Avg.10% Enhancement Factor (HP β CD)	Avg.10% Enhancement Factor (HP γ CD)	Avg.10% Enhancement Factor (HP β CD) from McCray et al.2000
Acenaphthene	86.23	89.71	94.87	
Anthracene	268.76	283.51	298.68	296.00
Benzo (K)Fluranthene	3831.02	4030.73	4136.20	
Chrysene	1371.99	1567.31	1741.44	
Dibenzofuran	49.33	51.93	64.15	
Fluorene	66.23	66.23	74.40	
Fluranthane	242.54	277.82	278.43	
Naphthalene	19.58	23.29	29.82	53.50

Aqueous Solubility Vs. Enhancement Factor Analysis

Enhancement factors of different PAHs determined here shows that enhancement factors decreases as aqueous solubility increases for all three types of cyclodextrins (Figure 3). Based on linear regression analysis performed here to analyze the relationship between log aqueous solubility and log enhancement factors for three types of cyclodextrins, there is a close relationship exists between enhancement factors and aqueous solubility as shown in the high levels of correlation between Log E and Log Aqueous solubility (RSQ 0.962, 0.965 and 0.967 for HP α CD, HP β CD and HP γ CD respectively) (Table 7). The difference between solubility enhancements of the three types of cyclodextrins was minimal with HP γ CD works better than other two types of cyclodextrins (Table-7) where slope for gamma is slightly steeper and intercept slightly higher.

Table7. Log E vs. Log Aqueous Solubility Analysis

	Slope	Intercept	RSQ
HP α CD	-0.454	2.011	0.962
HP β CD	-0.453	2.049	0.965
HP γ CD	-0.439	2.102	0.967

Table 7 cont.

Slope Avg.	Slope Range	Int. Avg.	Int. C.O.V.

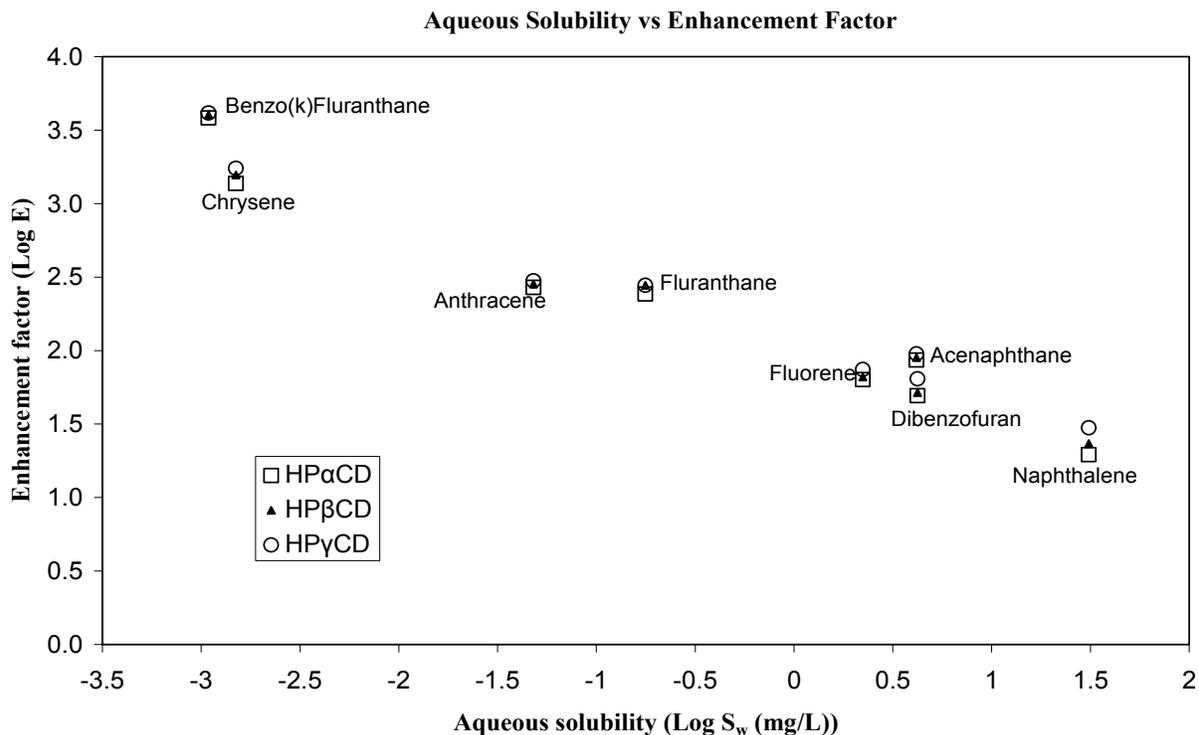


Figure 3. Aqueous Solubility Versus Enhancement Factors Obtained in this Study for HPαCD, HPβCD, and HPγCD

Enhancement Factors Vs. Molecular Masses Analysis

Enhancement factors of different PAHs shows that enhancement factors increases exponentially with molecular mass of the PAH for all three types of cyclodextrins (Figure 4)

The relative relationship between molecular mass and cyclodextrin enhancement factor is not as close as (0.934, 0.934 and 0.935 for HPαCD, HPβCD and HPγCD) (Table 8) that with aqueous solubility (0.962, 0.965, 0.967 for HPαCD, HPβCD and HPγCD). For all three types of cyclodextrins the results of linear regression show that the enhancement factors increases as the

molecular weights of the PAHs increase. Similar to aqueous solubility HP γ CD works better than HP β CD and HP β CD works better than HP α CD as shown in the slope and intercepts (Table 7) of Log E versus molecular weight analysis.

Table 8. Log E Vs. Molecular Weight Analysis

	Slope	Intercept	RSQ
HP α CD	0.0183	-1.094	0.934
HP β CD	0.0182	-1.047	0.934
HP γ CD	0.0176	-0.896	0.935
Slope Avg.	Slope Range	Int. Avg.	Int. C.O.V.
0.018	0.1%	0.934	0.1%

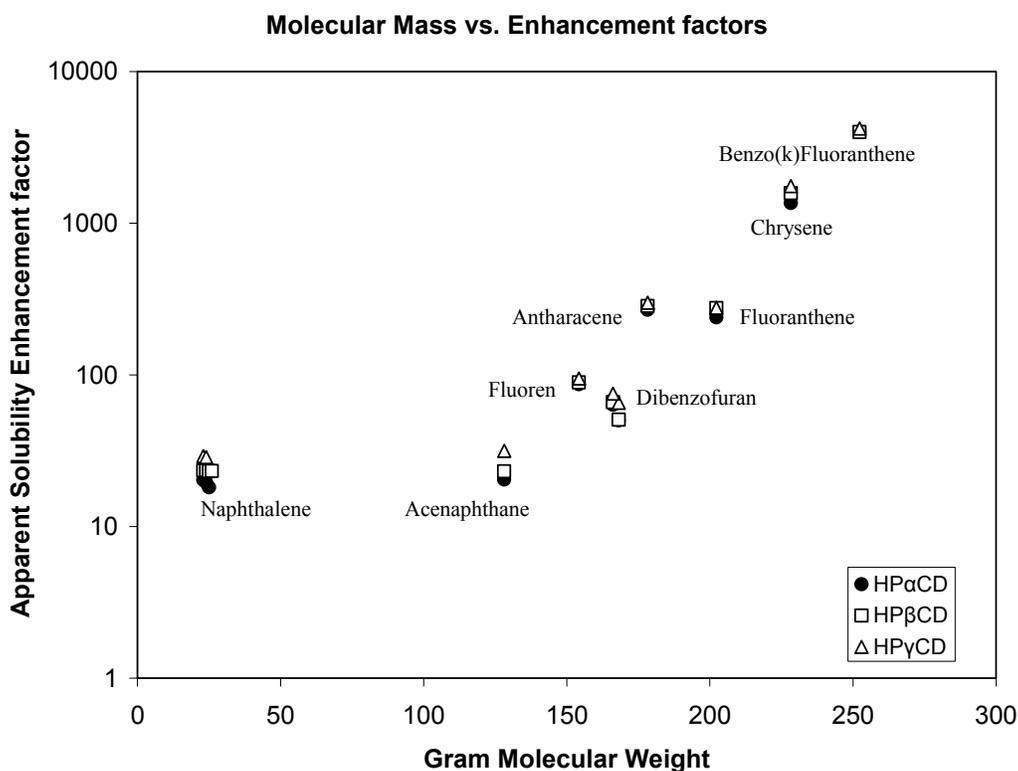


Figure 4. Molecular Mass Versus Enhancement Factors

The apparent solubility enhancement for all PAHs generated by HP γ CD is better than HP β CD and HP α CD. But, no trend was seen in the results to show that the degree to which HP γ CD outperforms HP β CD is greater when considering higher molecular weight PAHs. A comparisons between the slopes and intercepts of the linear regression analysis of Log E with molecular weight data for the three HPCDs shows that there is little difference between the slopes (~2%), but relatively large difference between the intercepts (~9%). In other words, while the average enhancement solubility increase by HP γ CD over HP β CD is 16.13%, the average enhancement solubility increase by HP β CD over HP α CD is 7.52% (Table 5) for the eight PAHs tested. However, the enhanced performance is seen is not related to molecular weight of PAHs.

This also occurs for aqueous solubility and hydrophobicity. No trend has been observed to show that the degree to which HP γ CD outperforms HP β CD is greater when considering PAHs with higher aqueous solubility and higher hydrophobicity (higher Kow values).

Cyclodextrin Enhancement vs. Hydrophobicity Analysis

The hydrophobicity values (Kow) of the PAHs obtained from the literature were plotted against the cyclodextrin enhancement (Kcw) values obtained from this experiment. The Kcw values were calculated using the apparent solubility equation proposed by McCray et al.(2000) ($S_a = ES_w = (1+K_{CW}C_H) S_w$, where S_a is apparent enhanced solubility, E is the enhancement factor, S_w is aqueous solubility, K_{CW} is the Cyclodextrin/water partitioning coefficient and C_H is the Cyclodextrin concentration in wt./vol). Log Kow linearly increases with Log Kcw for eight different compounds (Figure 5). The correlation values (HP α CD -0.922, - HP β CD 0.9284, - HP γ CD 0.9236) (table 9) between these Log Kow and Log Kcw implies that more hydrophobic compounds (as shown by larger Kow values) are more strongly attached to the nonpolar cyclodextrin cavity.

Table 9. Log K_{ow} vs. Log K_{cw} Analysis

	Slope	Intercept	RSQ
HP α CD	0.7791	0.3746	0.9223
HP β CD	0.7807	0.3519	0.9284
HP γ CD	0.7486	0.1474	0.9236
	Slope AVG.	Intercept Avg.	RSQ C.O.V
	0.769467	0.2913	0.0061

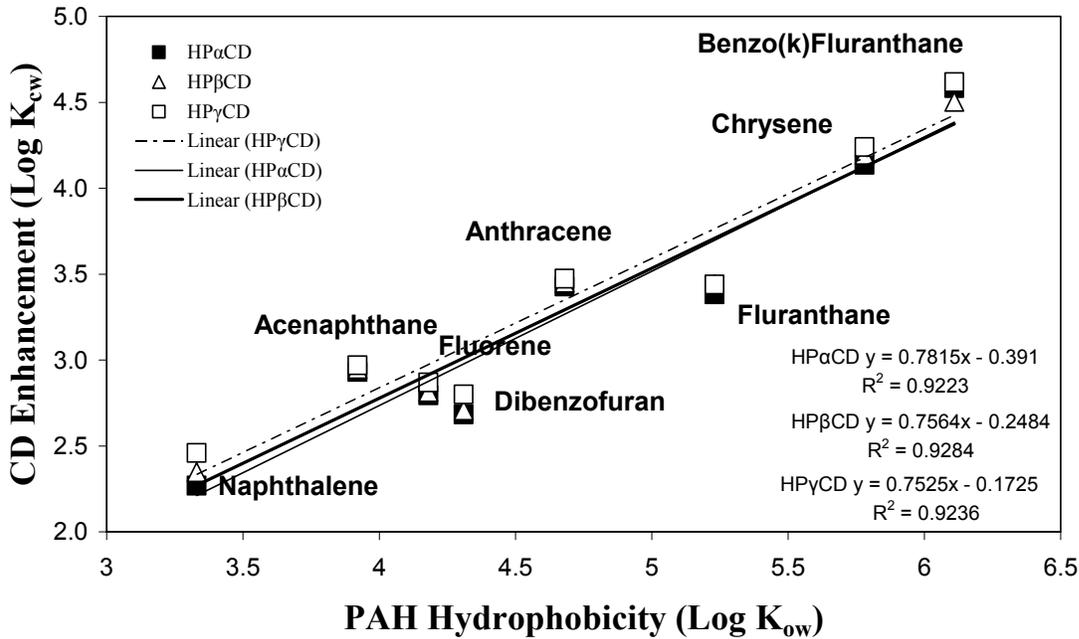


Figure 5. HPCD Enhancements Versus Hydrophobicity

Contaminant to Cyclodextrin Ratio Vs. Aqueous Solubility Analysis

The relationship between aqueous solubility and the contaminant to CD mole ratio shows that the more soluble a PAH is in water the more likely it is to become complexed within cyclodextrin and this phenomena increases exponentially (Figure 6).

Contaminants are more likely to complex as the size of the cyclodextrin cavity increases. This result can also be shown by comparing the mass of the PAH within solution to the mass of cyclodextrin. This shows that HPβCD performs 8.5% better than HPαCD for the PAHs within this study on average of eight compounds. And for HPγCD performs 10.2% better than HPβCD on average of eight compounds. This trend is more correlated if the solubilized contaminant to solubilized cyclodextrin ratio is done on a mole basis. In this case HPβCD performs 22.4% better than HPαCD and HPγCD perform 22.3% better than HPβCD.

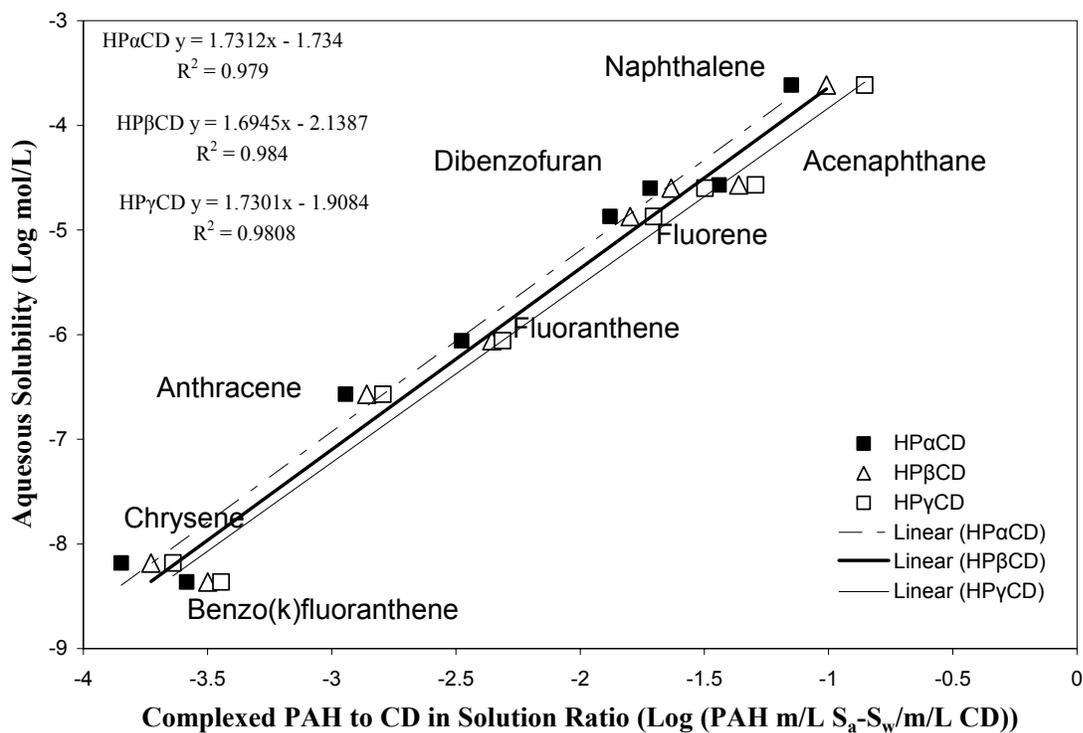


Figure 6. PAH to HPCD Molar Ratio Comparison

A trend was expected to exist where the size of the PAH contaminants increased the solubility enhancement advantage of HPγCD over HPβCD and HPβCD over HPαCD. Based strictly on molecular mass, no trend was observed. In the future, molecular volumes of PAHs should be evaluated to examine whether steric hindrances exist in the complexation of PAHs by

CDs. While the larger the cyclodextrin cavity translates into more of a particular type of PAH entering the cavity, there is no observable trend between increasing molecular weight of the PAHs tested and increased difference in the solubility enhancement for the larger cavity cyclodextrins.

Column Studies

Soil Contamination Analysis

The analysis of creosote contaminated soil by GCMS quantified the contamination level of eighteen PAHs and twenty-eight n-alkane organic compounds (Table 10). PAHs ranged from 2 to 6 rings of carbons and the n-alkanes from 10 to 35 carbons. Results of the three soil sample found a large degree of variability (11%-61%) between the three subsamples for all the contaminants targeted for analysis. Therefore, the initial mass of contaminants in the series of column studies varied. This in turn impacted the level with which comparisons of performance could be made between the HPCDs and water as solubility agents for remediating creosote contaminated aquifers based on the column experiments.

The results of GCMS analysis of the three subsamples of the untreated soil shows that three and four rings PAHs are the most prevalent types among the eighteen targeted PAHs detected in the soil samples (Table 10). In percentage terms of mass abundance of individual PAH, fluoranthene (19.30%) is the most common followed by phenanthrene (16.33%), pyrene (12.53%), fluoroene (9.18%), and anthracene (7.84%). Less prevalent are anthracene chrysene (5.05%), naphthalene (4.43%), benzo (a) anthracene (3.2%) and dibenzothiophene (2.14%) and only minor levels of highly toxic compound benzo (a) pyrene (1.02%) present in the soil sample (Table 10). This shows that the vast majority of PAHs of those analyzed contaminants are composed of three rings (43.23%) and four ring (49.54%) PAHs (Table 11). There were seven

PAHs, which were analyzed, that have five rings and the total of those five PAHs is only 2.2% of the total of the PAHs quantified. Only one six ring PAH was quantified (benzo (g,h,i) perylene). That compound composed on average for the three soil samples approximately 0.2% of the total contamination. However, it should be noted, that in all likelihood many more six ring PAHs are likely present, but either the GCMS analysis technique was incapable of quantifying them because they were below detection level.

Table 10. Concentration of PAHs in Creosote Soil Used in Column Test

Poly Aromatic Compound	Soil Sample1	Soil Sample2	Soil Sample3	Avg.	C.O.V.
	µgPAH/gSoil	µgPAH/gSoil	µgPAH/gSoil	µgPAH/gSoil	
Naphthalene ²	453	260	332	348	28%
Fluorene ³	844	591	731	722	18%
Dibenzothiophene ³	191	141	173	169	15%
Phenanthrene ³	1810	879	1141	1277	38%
Anthracene ³	750	409	690	616	30%
Fluoranthene ⁴	1900	1211	1443	1518	23%
Pyrene ⁴	1100	856	1001	985	12%
Naphthobenzothiophene ⁴	103	113	128	115	11%
Benzo (a) Anthracene ⁴	220	255	288	254	13%
Chrysene ⁴	361	385	445	397	11%
Benzo (b) Fluoranthene ⁵	60	168	160	129	47%
Benzo (k) Fluoranthene ⁵	30	126	110	89	58%
Benzo (e) Pyrene ⁵	28	81	75	62	47%
Benzo (a) Pyrene ⁵	36	107	98	81	48%
Perylene ⁵	8	33	31	24	58%
Indeno (1,2,3 - cd) Pyrene ⁵	11	35	34	27	50%
Dibenzo (a,h) anthracene ⁵	3	11	12	9	61%
Benzo (g,h,i) perylene ⁶	9	26	23	19	48%

Superscript on PAHs is the number of poly aromatic rings

Table 11. Concentration of Organic Contaminants by Group in Creosote Soil Used in Column Test

Contaminant Group	Soil Sample1	Soil Sample2	Soil Sample3	Avg.	C.O.V.
	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	
2 ring PAH totals	4.96%	4.03%	4.14%	4.43%	11%
3 ring PAH totals	47.60%	37.64%	42.75%	43.23%	12%
4 ring PAH totals	46.40%	53.78%	49.71%	49.54%	7%
5 ring PAH totals	0.95%	4.15%	3.11%	2.56%	64%
6 ring PAH totals	0.10%	0.40%	0.29%	0.25%	63%
total PAHs	100%	100%	100%	100%	

To evaluate the variability among the three soil subsamples taken from the uniformly mixed standards, the concentration variability of PAHs and n-alkanes among these subsamples were analyzed. To determine variation among the soil subsamples the statistical function coefficient of variation (COV) was used. This term is the standard deviation of the contaminant concentration of the three soil samples normalized by the average contaminant concentration of the three soil samples. COV is given as a percentage and shows that the variability among all the PAHs was at least 11% (naphthobenzothiophene, chrysene) and was at most 61% (dibenzo (a,h) anthracene) (table 10). The largest molecular weight contaminants, the five and six ring PAHs, which compose less than 2.5% of the total PAHs, are the most variable from sample to sample. But, even for the five most common PAHs the variability from sample to sample is at least 12% (pyrene) and at most 38% (phenanthrene). The variability among the pretreated soil subsamples makes the initial levels of contamination among the column studies imprecise. Despite the undesired variability in the soil contamination the fact that all the soil subsamples showed high levels of contamination among all the PAHs examined, some basic conclusions about HPCD performance can be found from the soil flushing studies.

HP α CD, HP β CD Post Extraction Soil Analysis

Post extraction analysis of soil was done to measure the mass removal performances after flushing 0.5 L, 1 L, 2 L, 4L and 7 L HP α CD and HP β CD solutions through the creosote contaminated soil (Tables 12 & 13).

Table 12. Concentration of Selected PAHs in Creosote Soil After HP α CD Flushing Test

Cyclodextrin	HP α CD							
Volume Flushed(L)	0	0.5	1	2	4	7	Avg.	C.O.V.
Poly Aromatic Compound	$\mu\text{g}_{\text{PAH}}/\text{g}_{\text{Soil}}$							
Naphthalene ²	52	13	17	2	4	8	9	0.72
Fluorene ³	107	33	41	4	10	30	24	0.66
Dibenzothiophene ³	25	7	9	1	3	7	5	0.58
Phenanthrene ³	189	67	88	9	21	68	51	0.66
Anthracene ³	91	55	69	14	25	69	47	0.55
Fluoranthene ⁴	225	56	80	30	52	98	63	0.42
Pyrene ⁴	146	39	57	24	48	97	53	0.51
Naphthobenzothiophene ⁴	17	5	7	6	5	12	7	0.41
Benzo (a) Anthracene ⁴	38	12	17	11	10	27	15	0.46
Chrysene ⁴	59	18	26	23	25	44	27	0.36
Benzo (b) Fluoranthene ⁵	19	5	6	11	11	7	8	0.34
Benzo (k) Fluoranthene ⁵	13	4	7	8	8	5	6	0.28
Benzo (e) Pyrene ⁵	9	3	4	6	7	4	5	0.42
Benzo (a) Pyrene ⁵	12	4	6	7	9	5	6	0.31
Perylene ⁵	4	1	2	2	3	1	2	0.41
Indeno(1,2,3 -cd) pyrene ⁵	4	1	2	3	4	2	2	0.42
Dibenzo (a,h) anthracene ⁵	1	0	0	1	1	0	1	0.42
Benzo (g,h,i) perylene ⁶	3	1	1	2	3	1	2	0.53
Superscript on PAHs is the number of poly aromatic rings								

Table 13. Concentration of Selected PAHs in Creosote Soil After HP β CD Flushing Test

Cyclodextrin	HP β CD							
Volume Flushed(L)	0	0.5	1	2	4	7	Avg.	C.O.V.
Poly Aromatic Compound	$\mu\text{g}_{\text{PAH}}/\text{g}_{\text{Soil}}$							
Naphthalene ²	52	29	23	2	6	6	13	0.88
Fluorene ³	107	82	65	5	18	19	38	0.89
Dibenzothiophene ³	25	14	11	1	5	4	7	0.73
Phenanthrene ³	190	170	123	10	42	41	77	0.87
Anthracene ³	92	240	206	14	31	59	110	0.95
Fluoranthene ⁴	225	240	214	24	80	49	121	0.81
Pyrene ⁴	146	170	167	21	68	52	96	0.72
Naphthobenzothiophene ⁴	17	18	16	4	9	5	10	0.62
Benzo (a) Anthracene ⁴	38	39	36	7	21	8	22	0.67
Chrysene ⁴	59	66	64	17	34	21	40	0.57
Benzo (b) Fluoranthene ⁵	19	10	10	11	11	7	10	0.19
Benzo (k) Fluoranthene ⁵	13	7	6	8	9	4	7	0.28
Benzo (e) Pyrene ⁵	9	5	5	6	6	4	5	0.12
Benzo (a) Pyrene ⁵	12	8	7	6	7	5	7	0.14
Perylene ⁵	4	1	1	2	1	1	2	0.14
Indeno (1,2,3 - cd) Pyrene ⁵	4	2	2	2	3	3	2	0.09
Dibenzo (a,h) anthracene ⁵	1	0	0	1	1	0	1	0.28
Benzo (g,h,i) perylene ⁶	3	2	2	2	2	2	2	0.10
Superscript on PAHs is the number of poly aromatic rings								

The PAH mass removal percentages by HP α CD solutions increases significantly from 0.5 L to 2 L flushing (84.1%) (Table 14). Further flushing did not remove significant amount of contaminant. The percent contaminant removed by different volumes of HP α CD solutions was calculated by subtracting the post extraction PAH concentrations from their initial concentrations

in the pretreated soil. The 4L flushing removes ~75% of the contaminant and 7L flushing removes ~60% contaminants. The reason for the decrease in the removal rate is discussed in detail in the discussion section.

Table 14. Fraction of PAH Removed by Group in Soil After HP α CD Flushing

Cyclodextrin	HP α CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V.
2 ring PAH totals	0.0%	71.3%	64.0%	96.9%	91.7%	87.3%	82.23%	44%
3 ring PAH totals	0.0%	55.8%	46.7%	93.1%	85.5%	65.4%	69.28%	48%
4 ring PAH totals	0.0%	69.6%	59.1%	81.0%	70.8%	53.1%	66.72%	43%
5 ring PAH totals	0.0%	66.1%	54.7%	39.2%	32.2%	69.0%	52.23%	49%
6 ring PAH totals	0.0%	69.0%	59.2%	30.4%	NA	61.9%	55.13%	52%
Total PAHs	0.0%	63.8%	54.0%	84.1%	75.3%	60.8%	67.61%	44%
NA the variability in the starting levels of contamination of this sample are too great to permit accurate evaluation of removal								

The PAH mass removal percentages by HP β CD solutions after flushing different volumes of HP β CD solutions through creosote contaminated soil shows that 2L HP β CD flushing removes ~84% contaminants but after that the mass removal percentages decreases for 4L(~62%) and 7L (~74%) solutions (table 14)

Table 15. Fraction of PAH Removed by Group in Soil After HP β CD Flushing

Cyclodextrin	HP β CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V.
2 ring PAH totals	0.0%	47.7%	56.9%	94.7%	87.1%	89.4%	75.17%	48%
3 ring PAH totals	0.0%	NA	NA	91.7%	74.7%	73.8%	80.09%	51%
4 ring PAH totals	0.0%	NA	NA	83.0%	52.4%	75.4%	70.27%	53%
5 ring PAH totals	0.0%	48.4%	49.0%	36.9%	31.7%	64.1%	46.02%	48%

Table 15 cont.

6 ring PAH totals	0.0%	43.6%	45.9%	28.9%	23.8%	38.2%	36.06%	47%
Total PAHs	0.0%	NA	NA	84.2%	62.0%	74.7%	73.62%	52%
NA the variability in the starting levels of contamination of this sample are too great to permit accurate evaluation of removal								

Table 15 shows the post extraction masses of the different PAHs by groups and Table 16 shows the % PAH mass remains after flushing with different volumes of HP α CD solutions.

Table 16. Mass of Organic Contaminants by Group in Soil After HP α CD Flushing

Cyclodextrin	HP α CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V
Poly Aromatic Compound	μg_{PAH}							
2 ring PAH totals	7560	2167	2722	238	628	962	9	72%
3 ring PAH totals	60457	26721	32237	4190	8784	20945	1857 5	59%
4 ring PAH totals	71012	21616	29052	13477	20717	33304	2363 3	38%
5 ring PAH totals	8919	3019	4042	5427	6047	2769	4261	37%
6 ring PAH totals	420	130	171	292	437	160	2	53%
Total PAHs	148368	53653	68224	23623	36614	58140	402	41%
Total Alkanes	22172	6793	10185	2887	15397	6953	58	53%

Table 17. Fraction of PAH Contaminants by Group in Soil After HP α CD Flushing

Cyclodextrin	HP α CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V.
2 ring PAH totals	5.1%	4.0%	4.0%	1.0%	1.7%	1.7%	2.48%	67%
3 ring PAH totals	40.7%	49.8%	47.3%	17.7%	24.0%	36.0%	34.96%	37%
4 ring PAH totals	47.9%	40.3%	42.6%	57.0%	56.6%	57.3%	50.76%	15%

Table 17 cont.

5 ring PAH totals	6.0%	5.6%	5.9%	23.0%	16.5%	4.8%	11.16%	68%
6 ring PAH totals	0.3%	0.2%	0.3%	1.2%	1.2%	0.3%	0.64%	77%
Total PAHs	100%	100%	100%	100%	100%	100%	100%	0%

Tables 17 and 18 are the equivalent tables for HP β CD. The results in these tables show that majority of the contaminants (35%-50%) remain after different volumes of HP α CD and HP β CD solution flushing are dominated by three and four ring PAHs. The ranges of remaining total three ring is ~34% and four ring total is ~50% (Table 17; figure 7) for HP α CD flushing. The range of remaining total three ring is ~35% and four ring total is ~51% (Table 18; figure 8) for HP β CD flushing. The remaining total two ring and six ring compounds are considerably lower (~2% for two ring and ~0.5% for six ring) for both HP α CD and HP β CD flushing. However, the creosote contaminated soil was initially contaminated with higher percentages of three rings and four rings PAHs and lower concentrations of two rings and six rings PAHs

To evaluate the PAHs mass removal performances by different volumes of HP α CD and HP β CD solutions, comparison between PAH mass removal after different volumes of HP α CD and HP β CD solution flushing was done (Figures 9 & 10). The mass of two ring, three ring and four ring compounds decreases up to 2 L flushing for both HP α CD and HP β CD solution but after that the remaining mass increases for 4L and 7L solutions. Ideally, the 4L and 7L of cyclodextrin solutions should remove more mass of PAHs and remaining mass should be lower than 0.5L, 1 L and 4 L masse. However, the results do not show this because the amount of contamination in the columns is different due to the lack of homogeneity of the creosote soil. The other reasons for less mass removal performances by 4L and 7L solutions discussed in detail in the discussion section.

Table 18. Mass of Organic Contaminants by Group in Soil After HP β CD Flushing

Cyclodextrin	HP β CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V.
Poly Aromatic Compound	μg_{PAH}							
2 ring PAH totals	6989	3654	3010	367	902	744	2611	97%
3 ring PAH totals	55891	64276	52528	4624	14120	14635	34346	76%
4 ring PAH totals	65649	67613	64742	11137	31238	16181	42760	62%
5 ring PAH totals	8246	4255	4207	5203	5630	2958	5083	36%
6 ring PAH totals	388	219	210	276	296	240	271	24%
Total PAHs	137162	140016	124696	21607	52186	34758	85071	64%
Total Alkanes	2020	1019	9219	2590	13014	10386	6375	80%

Table 19. Fraction of PAH Contaminants by Group in Soil After HP β CD Flushing

Cyclodextrin	HP β CD							
Volume Flushed	0	0.5	1	2	4	7	Avg.	C.O.V.
2 ring PAH totals	5.1%	2.6%	2.4%	1.7%	1.7%	2.1%	2.12%	60%
3 ring PAH totals	40.7%	45.9%	42.1%	21.4%	27.1%	42.1%	35.72%	28%
4 ring PAH totals	47.9%	48.3%	51.9%	51.5%	59.9%	46.6%	51.63%	9%
5 ring PAH totals	6.0%	3.0%	3.4%	24.1%	10.8%	8.5%	9.96%	79%
6 ring PAH totals	0.3%	0.2%	0.2%	1.3%	0.6%	0.7%	0.57%	75%
Total PAHs	100%	100%	100%	100%	100%	100%	100%	0%

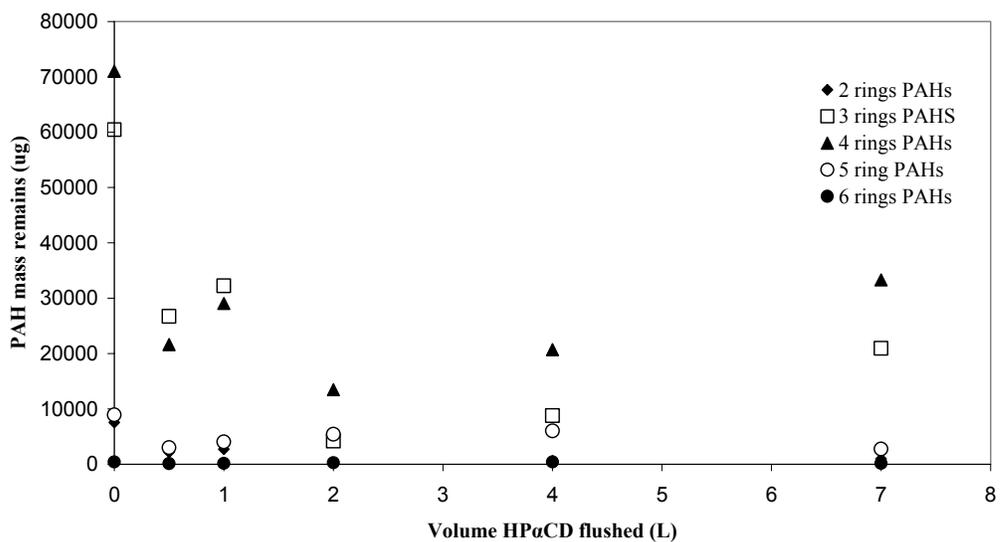


Figure 7. PAH Mass Remains After HPαCD Flushing

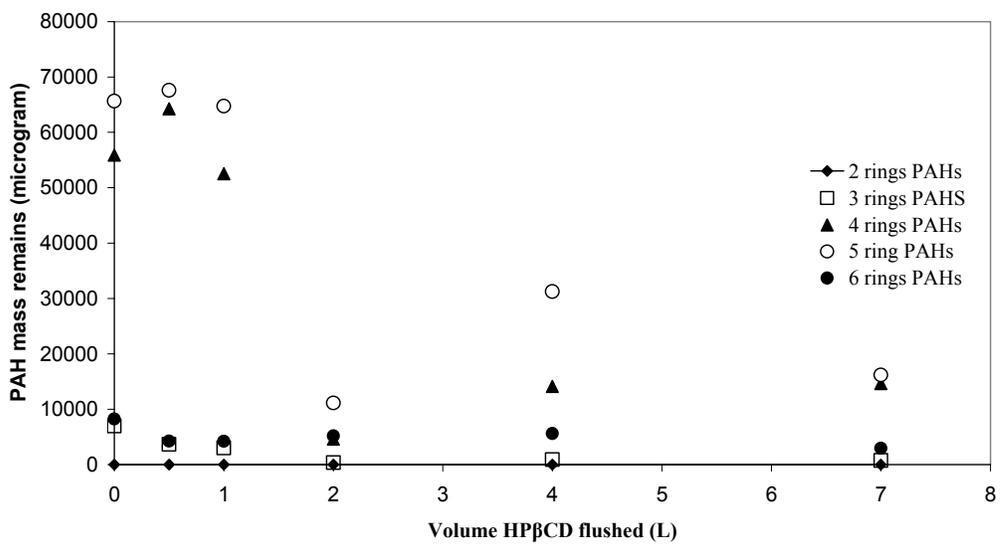


Figure 8. PAH Mass Remains After HPβCD Flushing

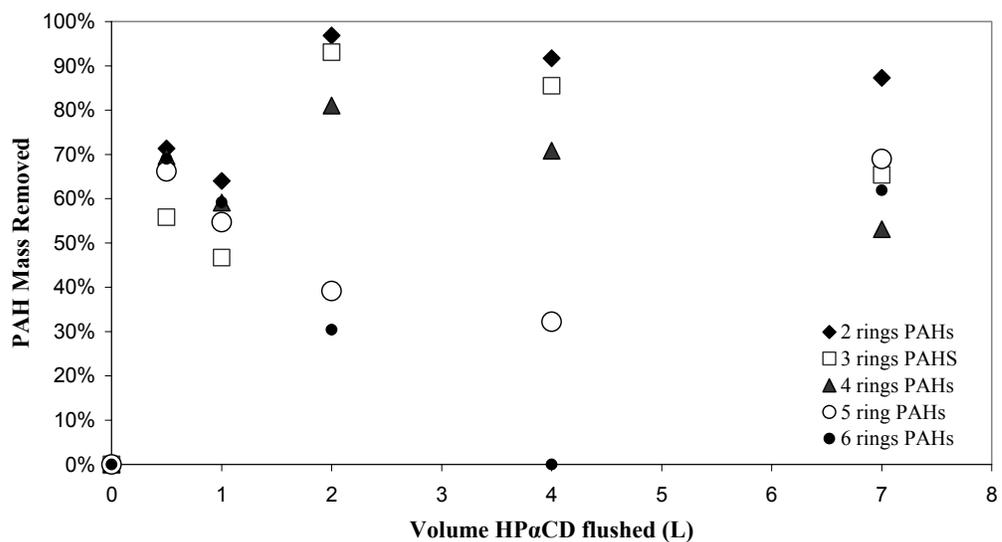


Figure 9. PAH Mass Removed After HP α CD Flushing

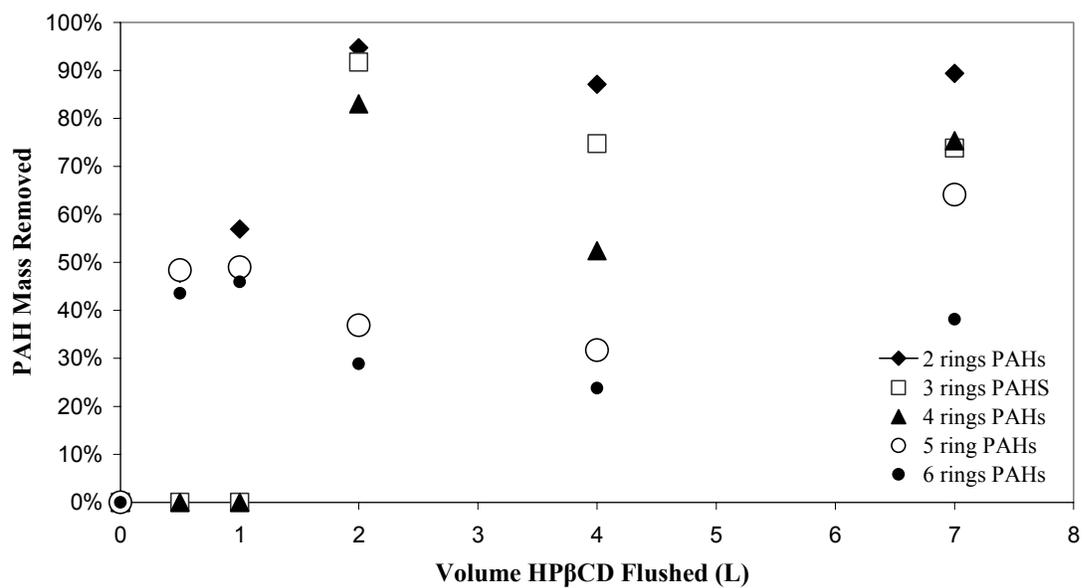


Figure 10. PAH Mass Removed After HP β CD Flushing

2 L HPCDs and Water Flushing Comparison

The contaminant mass removal percentages by three HPCDs and water have been compared for the four compounds which show highest concentrations in the pretreated soil. The concentrations of these compounds are fluoranthene ~ 19%, phenanthrene ~ 16%, pyrene ~ 12%, fluorene ~9% (table 10).

The percentage mass removal rate by HP α CD and HP β CD is much higher in comparison to water and HP γ CD (table 20, 21 and figure 11). For all four compounds the mass removal percentages by HP α CD and HP β CD is close to 80%. (Table 21) The mass removal percentages for these four compounds for water lie between 30-50% and for HP γ CD lies between 40-60%.

Table 20. Post Extraction Removal for Organic Contaminants by Group in HPCD and Water Flushing Column Tests

Contaminant Group	HP α CD 2 L	HP β CD 2 L	HP γ CD 2 L	Water 2L	Avg.	C.O.V.
	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	$\mu\text{gPAH/gSoil}$	
2 ring PAH totals	96.6%	94.7%	58.8%	82.5%	83.1%	21%
3 ring PAH totals	90.9%	90.2%	29.2%	18.5%	57.2%	68%
4 ring PAH totals	76.1%	79.6%	57.7%	52.5%	66.5%	20%
5 ring PAH totals	32.0%	38.1%	46.8%	30.9%	37.0%	20%
6 ring PAH totals	24.5%	28.6%	87.5%	33.0%	43.4%	68%
Total PAHs	82.1%	83.7%	45.2%	38.5%	62.4%	38%
Total Alkanes	85.9%	87.3%	50.3%	45.4%	67.2%	33%

Table 21. Post Extraction Removal Comparison 2L Solutions

	HP α CD 2 L	HP β CD 2 L	HP γ CD 2 L	Water 2L
Fluorene	96%	95%	52%	34%
Phenathrene	83%	94%	40%	23%
Fluoranthene	86%	88%	61%	57%
Pyrene	79%	82%	60%	53%
Total PAHs	82%	84%	45%	39%

Amount of PAHs Removed by Flushing CDs and Water

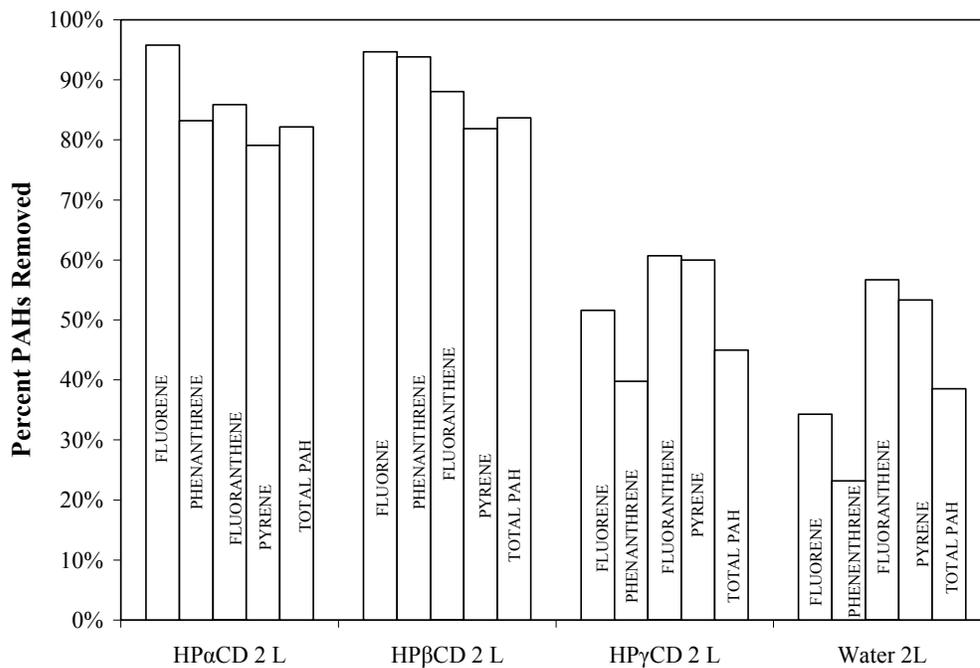


Figure 11. Amount of PAHs Removed by Flushing HPCDs and Water

CHAPTER 5: DISCUSSION

The results of the laboratory batch solubility tests and columns experiments showed that the three hydroxypropyl cyclodextrins demonstrated an enhanced ability to solubilize the tested polyaromatic compounds and increase their removal from contaminated soil. In the batch solubility tests, the three cyclodextrin were evaluated (HP α CD, HP β CD and HP γ CD) to enhance the apparent solubility of the eight tested poly aromatic compounds. Correlations with the degree to which these CDs enhanced the apparent solubilities were found with the aqueous solubility, molecular weight, and hydrophobicity of the PAHs. Also, a strong correlation was found between these same variables and the ratio of the molar concentrations of the individual PAHs and HPCD in solution under equilibrium conditions. The column studies show that all three types of cyclodextrins work better than water for the extraction of PAHs from the creosote contaminated soil.

The equilibrium apparent solubility of the subject PAHs in the cyclodextrin solutions was determined through batch tests where equilibrium was established through prolonged exposure of the PAHs to HPCD aqueous solutions. The batch tests were conducted by adding the excess amounts of the PAHs to 18 ml of 30% wt./vol. aqueous solutions of technical grade HP α CD, HP β CD, and HP γ CD for thirty six days. The concentration of PAHs in the HPCD solutions was measured with a spectrofluorophotometer. The variation of the batch experiments was determined by performing the tests in triplicate.

The results of the solubility studies indicate that the apparent solubility of the PAHs increase for three types of cyclodextrin. The degree of enhancement was also found to increase with the cavity size of the cyclodextrin molecule.

On average, the HP γ CD enhanced the apparent solubility the eight PAHs by 16% over HP α CD, HP γ CD performs 9% better than HP β CD and HP β CD performs 7% better than HP α CD. The better performance of HP γ CD in comparison to other to types of CDs is apparently linked to cavity size. The cavity diameters of HP α CD, HP β CD, and HP γ CD are 4.5, 7.0 and 8.5 Å respectively. The HP γ CD generated greater solubility enhancement values demonstrate the fact that larger the cavity size, more PAH molecules will partition into it and enhancement factors for the PAHs will be increased.

The degree of substitution is the amount of hydroxypropyl (HP) functional groups present in the cyclodextrin molecule. The primary benefit of using cyclodextrins substituted with hydroxypropyl groups is increase in the aqueous solubility of the cyclodextrin molecule Each glucopyranose subunit has three potential sites for substitution. In the three cyclodextrins used in this study the average total number of hydroxypropyl groups per molecule were, 4.50, 5.25, and 4.96 respectively for HP α CD, HP β CD, and HP γ CD. The average number of hydroxypropyl groups for glucopyranose unit on the cyclodextrins is 0.75, 0.75, and 0.62 respectively for α CD, β CD, and γ CD. For the compound β -Lap the results Nasongkla et al. (2003) show that substitution of hydroxypropyl groups on β -cyclodextrin slightly decreased the favorability of the cyclodextrin for the inclusion of that compound. The results of Nasongkla et al.(2003) indicate that substitution of hydroxypropyl functional groups on the β -CD molecule slightly reduce the degree that β -Lap, a hydrophobic compound, partition into the β -cyclodextrin molecules. They also found that β CD forms complexes with this same compound more readily than α CD and γ CD. Nasongkla et al. speculated from their results that cavity size was responsible for differences between their results for α CD and β CD, but they did not have an explanation for the lower rate of complexation of β -Lap by γ CD versus β CD. Without a more fundamental

understanding of the nature of the contaminant/host cyclodextrin complex the cause(s) of the differences in degree of complexation formation between the different cyclodextrins cannot be truly explained.

Solubility enhancement factors for two of the eight PAHs evaluated in this experiment have been determined by other researchers for HP β CD. Wang and Brusseau (1993) and McCray et al. (2000) determined the solubility enhancement factors for naphthalene and anthracene. Table 22 compares the enhancement factors obtained by these researchers and the values obtained in this experiment. The anthracene enhancement factors obtained by Wang and Brusseau and McCray et al. are 3.6% and 4.5% greater than the enhancement factors obtained in this experiment. While these differences are relatively small, the naphthalene enhancement factors obtained by Wang and Brusseau and McCray et al. are substantially different, 128.5% and 131.6% greater than the enhancement factors obtained in this experiment.

Table 22. Comparison of Enhancement Factors

PAHs	Enhancement Factors obtained in this experiment	Enhancement Factors projected from Wang & Brusseau(1993)	Enhancement Factors by McCray et al. (2000)
Naphthalene	23.1	52.8	53.5
Anthracene	283	293.3	296

Other researchers have followed a slightly different method than the method employed in this experiment. For solubility measurements they added the selected organic contaminants in excess (PAH quantities in excess of those capable of being dissolved) to varying concentrations of HP β CD solution. They exposed the PAHs to the cyclodextrin solution for 2 days on a reciprocating shaker in an effort to achieve equilibrium. After 2 days, the samples were

centrifuged at 7500 g for 20 minutes and aliquots of the supernatants (0.5 ml) were diluted with 50:50 methanol/water solution. Samples were analyzed by UV-VIS spectrophotometry. A generator column approach was used for the compounds that exist as solids at room temperature for solubility measurements. The generator column (a glass distillation column, 30 cm long and 2 cm. i.d.) packed with glass beads and coated with excess chemical. The column was plugged with glass wool at both ends and HP β CD solutions were passed through the columns and the effluents were analyzed continuously for solute concentrations using UV-VIS or fluorescent spectroscopy until a relative constant effluent concentration was obtained. The samples were done in triplicates, but only the averages are reported.

Wang and Brusseau (1993) report the results of their experiments with where concentration of HPBCD varied between 0 and 7% wt./vol. The apparent solubility values for these compounds for 10% wt./vol. HP β CD solutions were projected from their results. The linear increase in naphthalene and anthracene solubility enhancement by HPBCD solutions (R^2 from linear regression is 0.99 for both naphthalene and anthracene) enabled the accurate projection of enhancement values outside their experimental range for a 10% solution.

The apparent differences in the enhancement values obtained in this experiment versus the values obtained by the other researchers can be explained by several factors. First of all, the experimental procedure followed in this experiment is slightly different than their method. For instance the usage of the generator column approach may lead to more saturation of the cyclodextrin solution. In this experiment greater exposure time was the means to achieve equilibrium. To better evaluate if equilibrium was achieved followup studies should be conducted where the concentration of the PAHs in the cyclodextrin solution is tracked over time.

Another potential reason for the difference in determined enhancement factors for anthracene and naphthalene could lie with other experimental conditions. The other researchers used concentration of HP β CD between 0 and 10% wt./vol., while the results here are from experiments performed with 30% wt./vol. solution. This higher cyclodextrin concentration would require additional PAH dissolution to achieve saturation. Because equilibrium is obviously not reached instantaneously, but it is rate limited, more than even 36 days maybe required to saturate the cyclodextrin solutions with the subject PAHs. Other reasons could include the differences in the quality of the cyclodextrin solutions and the temperatures of the studies. The other researchers also did not report their standard deviation values for these compounds though they made triplicates of their samples. If their results are highly variable, the results of this study could fall within the range of their experimental results. In this study, the experiments were fairly consistent with the coefficient of variation (COV) for all the studies being on average 1.8% and at most 5%.

Another potential reason for the difference in the values could be due to experimental error. When measuring the concentration of the PAHs in the cyclodextrin solution dilution was needed to lower the PAH concentration to fall with the range of calibration standards. The cyclodextrin solutions were diluted over a range to produce concentrations of PAHs that fall within the different range of quantification limits for the different PAHs. Those ranged from 0.1mg/L to 120 mg/L. Table 23 shows the dilution factors and resulting different concentrations. The experimental error during this dilution process may produce such erroneous result.

Table 23. Dilution Factors Used for Obtaining Different Targeted Concentrations

Stock Conc.	Target Conc.	Dilution Factor	Vol. Stock Solution added	Vol. water added	Final Concentration
mg/L	mg/L		ml	ml	mg/L
120	0.1	1200	0.02	19.98	0.1

Table 23 cont.

120	0.2	600	0.03	19.97	0.2
120	0.5	240	0.08	19.92	0.5
120	1	120	0.17	19.83	1
120	3	40	0.50	19.50	3
120	5	24	0.83	19.17	5
120	7	17.14	1.17	18.83	7
120	20	6	3.33	16.67	20
120	30	4	5.00	15.00	30
120	40	3	6.67	13.33	40
120	50	2.4	8.33	11.67	50
120	60	2	10.00	10.00	60
120	100	1.2	16.67	3.33	100
120	120	1	20.00	0.00	120

The nonlinear calibration curves may be another source of error. However, in this experiment the calibration curves for these compounds are linear (Figure 12 & 13).

Thus eliminate the possibility for error due to the nonlinear calibration curve.

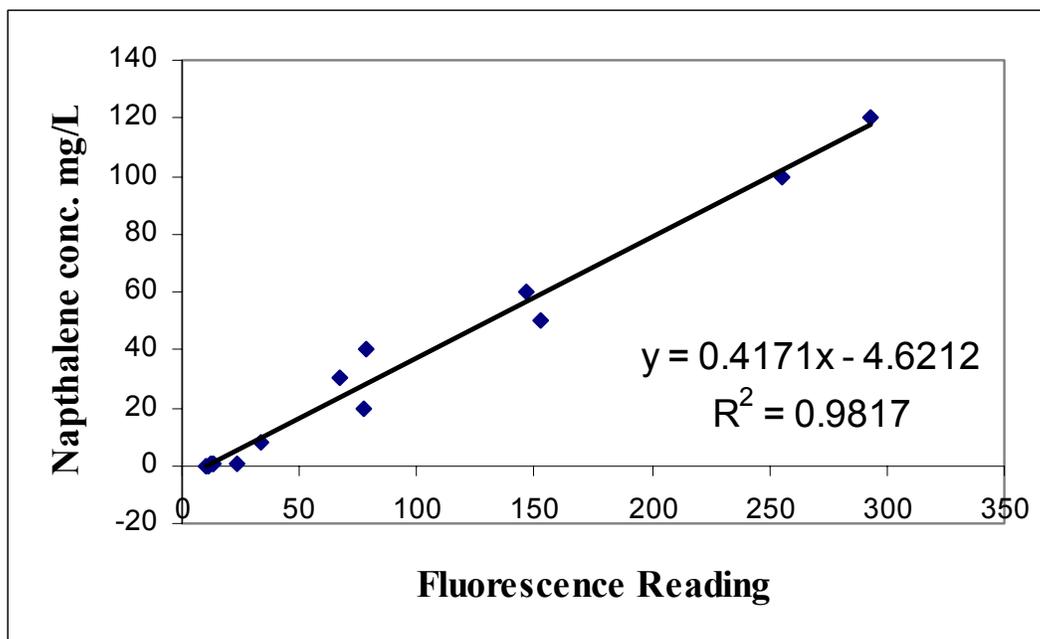


Figure 12. Naphthalene Calibration Curve

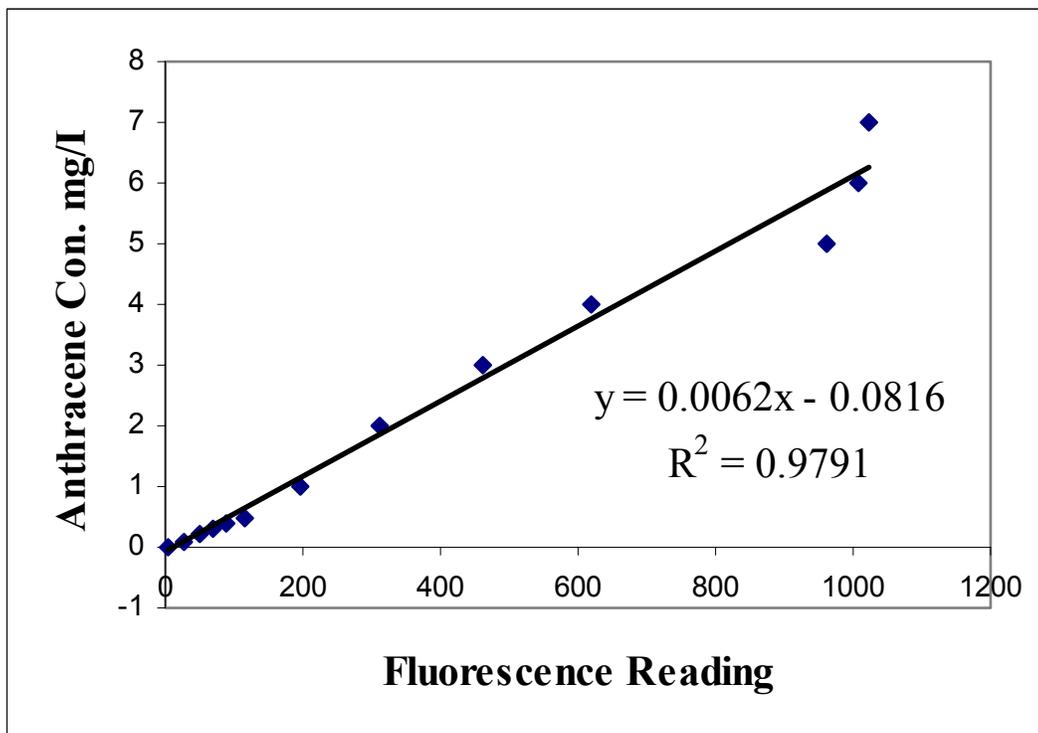


Figure 13. Anthracene Calibration Curve

Another experimental error could be due to the volatilization of PAH from the cubate reservoir during analysis with the fluorescence spectrophotometer. Naphthalene with its high vapor pressure (23×10^{-2} mmHg) may be especially prone to loss during analysis. If the methods of the other researchers resulted in less volatilization then that may partially explain some of the difference in experimental results for naphthalene.

The variability in the precision of spectrofluorophotometer machine could be another source of error. The spectrofluorophotometer may produce different readings for calibration standards versus the samples. The enhancement factors calculated on the basis of these readings may be grossly erroneous due to lack of precision of the machine.

The fluorescence produced by the cyclodextrin solutions for different excitation, emission of the PAHs could be another source of error. However, the background fluorescence for the

cyclodextrin solutions tested for different excitation emission wavelengths of eight PAHs were negligible. Thus, eliminates this possible source of error.

Additional comparisons can be drawn between the solubility, molecular weight and hydrophobicity of the subject PAH with the degree to which their apparent solubility was increased by the cyclodextrin solutions. Analysis of the results indicate that the relationship between the degree of apparent solubility of the PAH is increased is inversely related to the aqueous solubility of the PAH. For the eight PAHs the results show a strong correlation between an exponential increase in the apparent solubility enhancement factor and an exponential decrease in the PAH aqueous solubility. This relationship is true for all three types of CDs. McCray et al.(2000) observed a similar result in the hydrophobic compounds they tested. This relationship can be explained by the fact that, the more hydrophilic a compound the more soluble in water it will be, but also less likely it is partition into the hydrophobic interior of the CD cavity.

More directly on the subject of PAH hydrophobicity comparisons can be drawn to the octanol/water partitioning coefficient (K_{ow}) of the PAHs and the cyclodextrin/water partitioning coefficient (K_{cw}). A comparison between the values from the literature of K_{ow} and the measured results K_{cw} of the eight PAH show a close correlation between exponential increases among the target PAH hydrophobicity and a exponential increases in their tendency to partition into the cyclodextrin cavities. This result is a true of all three tested cyclodextrins and again closely agrees with the results of McCray et al. (2000).

The PAH, CD complexation ratio versus aqueous solubility shows that complexation ratio increases exponentially when aqueous solubility increases. This phenomenon can be explained

by the fact that more hydrophilic a compound will be, more likely that it will enter into the aqueous phase and more it will form inclusion complexes with the CD.

Column Studies

The concentrations of PAHs in the pretreated soil samples were analyzed using GCMS. The soil samples were mostly concentrated in three and four rings compounds such as fluoranthene(19%), phenanthrene (16%), pyrene (12%), fluorene (9%). Large degree of variability in PAH concentrations was observed in the soil analysis values. The degree of variability was highest for dienzo(a,h) anthracene (61%) and lowest for two compounds chrysene and naphthobenzothiophene (11%).The degree of variability is higher for five and six ring compounds (benzo(k) fluoranthane 58%, benzo(b) fluorantahne 47%, perylene 58%, benzo(g,h, I) perylene 48%). The degree of variability is relatively lower for three rings and four rings compounds.The degree of variability is relatively lower for fluoranthane (11% lower from the average PAH variability) which shows the highest concentrations among all other PAHs. The degree of variability is also relatively lower for other two highly concentrated compounds such as phenanthrene (4% above average PAH variability) and pyrene (22% lower than average PAH variability).

The degree of variability of PAHs concentrations in the pretreated soil sample may results from lack of homogenization of soil samples. Though the pretreated soil was stirred for an hour for proper homogenization, the GCMS analysis shows that the soil was not homogenous. The lack of homogeneity of the soil samples contributes to the erroneous comparison between extraction potentiality between cyclodextrin solutions and water.

The PAH concentration analysis of the cyclodextrin and water treated soil shows that ~85% of the contaminants were removed by HP α CD and HP β CD solutions during 2 L flushing.

The contaminant removal rate was only ~65% during 4L and 7L flushing of HP α CD and HPBCD solutions. Water removed ~55% of the contaminants and HP γ CD removed ~60% of the contaminants during 2L flushing. The contaminant removal rate by 2L water was better than expected. Water removed roughly half as much contaminants as HPCD solutions removed. The contaminant removal rate was unexpectedly lower for HP γ CD. This unexpected behavior of water and HP γ CD can be linked to the initial nonhomogenization of the soil and mobilization of the contaminants during 2L flushing. The PAH removal performances by same volume (2 L) HPCD solutions and water is inappropriate because of the lack of homogeneity of the pretreated soil. The concentrations of PAHs in the soil treated with HP γ CD may be higher than the soil treated with HP α CD and HP β CD.

The significant PAH removal performance by water can be linked to the mobilization of the contaminants. Due to the mobilization the loose contaminant particles removed from the soil by water flushing and accumulate in the waste solution. As a result of that it seems that water has removed significant amount of contaminants but in reality only loose contaminants are removed. This mobilization of the contaminants not only induced by water flushing but also generated by HPCD solution flushing. The initial mobilization of the contaminants during first 2L flushing of HPCD solution produces lower concentrations of contaminants in the soil. The additional volume flushing of (4L and 7L) HPCD solutions through the soil column does not remove as much contaminants as expected because the soil column has lost most of its contaminants due to mobilization during first 2L flushing.

To evaluate the PAH removal performances by same volumes of HPCD solutions and water more standardize approach should be adapted. The biggest shortcoming of this experiment was lack of standardization in the PAH concentrations of the pretreated soil. To overcome that

problem the pretreated soil should be artificially contaminated with known amount of contaminant.

To prevent the problem of homogenization well sorted sand should be used for the experiment rather than natural soil. The natural soil is poorly sorted and larger particles are likely to be more mobile than finer particles. The finer sand particles tend to be less mobile during solution flushing. Another problem of using natural soil is that, it tends to be more contaminated than artificially contaminated soil. Using a porous media like sand is advantageous because it is less contaminated than natural soil and contaminants are well bonded to the sand. Besides, in case of artificial contamination, the sand can be contaminated artificially with single component.

The single component can be analyzed using spectrofluorometer. If the sand is artificially contaminated with more than one component, the fluorescence readings should be evaluated properly in order to avoid the problem of interferences with fluorospectrometric readings for individual PAHs. If the soil is contaminated with more than one component and cyclodextrin solution is flushed through the contaminated sand, the ideal concentrations of each contaminant in the cyclodextrin solution can be determined using modified Raoult's Law proposed by McCray et al. (1999), $C_i^{A*} = X_i^N E_i S_i^W$, where C_i^{A*} is the ideal equilibrium aqueous concentration of organic contaminant i in a cyclodextrin solution, E is the enhancement parameter for particular contaminant generated by the cyclodextrin, X_i^N is the mole fraction of that particular contaminant in cyclodextrin solution, S_i^W is the aqueous solubility of the contaminant. The ideal equilibrium concentrations of the contaminants can be compared with the measured concentrations of the contaminants after cyclodextrin flushing to project whether cyclodextrin solution increases the rate of rate limited dissolution of the contaminants in the cyclodextrin solution as observed by McCray et al. (1999).

CHAPTER 6: CONCLUSIONS

The apparent solubility enhancement results obtained in this experiment shows that HP γ CD with largest CD cavity works relatively better than other two types of HPCDs with smaller cavity sizes. It is concluded that cyclodextrin cavity sizes has a small influence on the PAH complexation ratio. A comparison between the apparent solubility enhancement factors of the eight PAHs tested in this study and their aqueous solubility shows that there is an inverse correlation (RSQ 0.962, 0.965, 0.967 for HP α CD, HP β CD, and HP γ CD) between the logarithm of aqueous solubility and logarithm of solubility enhancement factors. From this result, the apparent solubility can be projected of other PAHs whose aqueous solubility is known.

The molecular mass of the selected PAHs also increases exponentially with enhancement factors for all three types of HPCDs. The enhancement factors of a molecule with known molecular weight can be projected from this result. The analysis of PAH to cyclodextrin ratio versus aqueous solubility shows that the more soluble a PAH is in water the more likely it is to become complexed within cyclodextrin and this phenomena increases exponentially. This mole to mole comparison shows that HP γ CD induced complexation ratio is significantly better than both HP α CD and HP β CD. This analysis supports the suggestion that apparent solubility enhancement factors influenced by the cavity sizes of the cyclodextrin molecules.

Column tests with pretreated soil contamination shows that the n-alkanes and PAHs concentrations shows large degree of variability for all three soil sub samples analyzed for this experiment. The soil was rich in silica (~98%). The amount of clay was low in the soil (~2%). Even after attempts of homogenization, the concentrations of targeted contaminants show a high degree of variability. This suggest that the experiment should be done with known amount of contaminants to avoid the difficulty of attempting to homogenize naturally contaminated soil.

The soil contamination analysis for both pretreated and post treated soil shows that three and four ring PAHs (fluorene, fluoranthene, anthracene, chrysene) are the major constituents of the soil. The apparent solubility enhancement of PAHs obtained in these experiments shows that all three types of HPCDs are capable of enhancing the apparent solubility of these compounds. Thus, it is concluded that all three types of HPCDs can be considered as potential remediating agents for cleaning up creosote contaminated site because they increase the apparent solubility of the PAHs, major constituents of the creosote.

The comparison between the mass removal rates by three types of HPCDs and water shows that all three types of cyclodextrin works better than water. The conventional cleaning up technologies such as pump and treat is entirely dependent on water for contaminated site remediation. The better performance of HPCDs in comparison to water can be employed in the creosote contaminated sites for better remedial outcomes.

CHAPTER 7: FUTURE WORK

To evaluate the potential for cyclodextrin as a remedial agent for creosote contaminated sites additional work needs to be completed. The solubility enhancement of more PAHs and other components such as n-alkanes needs to be determined. Also, additional forms of cyclodextrin (carboxymethyl beta cyclodextrin, methyl beta cyclodextrin) need to be tested for their enhancement of apparent solubility of the toxic components of creosote.

To address a shortcoming of this work, new column studies need to be performed with artificially contaminated soil to minimize the amount of contaminant variability in the soil. The mineralogical properties of the soil need to be evaluated before column studies. Also, methods need to be developed to analyze the concentration of different PAH in post-soil flushing cyclodextrin solutions. This method can be used to determine the variation in the concentration of the different PAHs as CD solutions are passed through contaminated soil in laboratory and more importantly extrapolated to field experiments. Additional laboratory studies need to be completed to evaluate if standard methods such as activated carbon can be employed to extract PAHs from cyclodextrin solutions enabling the reuse of these solutions. Finally several field demonstrations under a variety of conditions need to be performed and these results need to be incorporated in hydrogeologic models to predict the remediation time, effort, and cost to implement cyclodextrin as a remedial solution for creosote contaminated aquifers.

The apparent solubility enhancement factors for additional PAHs such as pyrene, phenanthrene, benzo(a)anthracene, benzo(e) pyrene, perylene, benzo(g,h,i) perylene, naphthbenzothiophene, dibenzothiophene, decacyclene, pentachlorophenol, coronen should be determined. Because these PAHs are common components of creosote and can be detected in the GCMS analysis. The solubility enhancement factors of several n-alkanes, which are common

components of creosote, need to be determined. Other researchers have determined the apparent solubility enhancement factors of some selected n-alkanes, such as decane, undecane, octadecane. The solubility enhancement factors of tricosane, nanodecane, tetradecane etc. should be evaluated because they are the major constituents of creosote.

Brusseau et al.(1997) has demonstrated the ability of carboxymethyl- β -cyclodextrins (CMCD), a modified form of cyclodextrin to enhance the desorption and elution of heavy metals and phenanthrene (a low polarity PAH) from the soil. Boving et al. (1999) has demonstrated the ability of methyl- β -cyclodextrin (MCD) to enhance the apparent solubility of chlorinated solvents. CMCD and MCD could be applied on different PAHs and alkenes in order to determine the performance of these CDs on these compounds.

Field testing of cyclodextrin as a remedial agent should be performed at several field sites under different hydrogeological and geochemical field conditions. In these studies effort should be spent on analyzing the ability of cyclodextrin solutions to extract contaminants from the subsurface, but also leading to greater rates of biodegradation due to enhanced bioavailability generated by the increased apparent solubility of the creosote components by cyclodextrin. This work in turn needs to be followed by computer simulations based on the lab and field pilot-scale studies to estimate the performance and cost of full-scale application of cyclodextrin as a remedial agent. Finally, to judge the efficacy of cyclodextrin as a remedial agent for creosote contaminated sites the cost and performance simulations need to be compared to similar simulations of other currently and potentially used remediation.

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