

# EVALUATION OF SURFACTANTS/COSOLVENTS FOR DESORPTION/SOLUBILIZATION OF PHENANTHRENE IN CLAYEY SOILS

RICHARD E. SAICHEK and KRISHNA R. REDDY\*

*University of Illinois at Chicago, Department of Civil and Materials Engineering, 842 West Taylor Street, Chicago, Illinois 60607, USA*

*(Received June 20, 2002; In final form February 27, 2004)*

Throughout the USA, numerous sites exist where the soils have been contaminated by polycyclic aromatic hydrocarbons (PAHs). These compounds may be toxic, mutagenic and/or carcinogenic, so these sites threaten human health and the environment and prompt remediation is warranted. In situ flushing with surfactants/cosolvents has shown promise for treating PAH-contaminated soils that are uniform and possess a high permeability, but the efficiency of this process is severely limited when heterogeneous and/or low permeability soils are present. For these difficult situations, electrokinetically enhanced in situ flushing offers great potential, but this method is highly dependent on the type of purging agent that is used. Thus, in this laboratory investigation, batch desorption experiments were conducted to evaluate different surfactants/cosolvent solutions for use in electrokinetically enhanced in situ flushing. The surfactants/cosolvents were evaluated on their ability to desorb and solubilize phenanthrene, a representative PAH, from two widely varying clayey soil types. The soils were artificially contaminated at four PAH concentrations, and batch tests were conducted using six different surfactant/cosolvent solutions. The results indicated that phenanthrene was more strongly bound to the soil with the higher organic content, and the surfactants with a higher hydrophile – lipophile balance number (HLB) caused greater PAH desorption and solubilization. Furthermore, the surfactant solutions performed better when they were used at a higher concentration. Compared to the cosolvent solution or a combined mixture of the cosolvent and surfactant solutions, greater desorption and solubilization of the contaminant occurred when the surfactant solution was used by itself.

*Keywords:* PAHs; Soils; Clays; Surfactants; Desorption; Solubilization; Remediation

## 1. INTRODUCTION

It has been well established that polycyclic aromatic hydrocarbons (PAHs) are present at numerous contaminated sites throughout the USA [1], and these compounds threaten human health and the environment because they are commonly toxic and many have been identified as mutagens and/or carcinogens [2–6]. Moreover, PAHs are hydrophobic and resistant to degradation, so they are generally immobile; however, they still pose a major threat to the environment because they slowly leach into groundwater or surface water, and this contamination may continue for as long as 100 years [7].

---

\*Corresponding author. E-mail: kreddy@uic.edu

The hydrophobicity and persistence of PAH compounds causes them to be difficult contaminants to remediate, especially when they are present in subsurface environments that possess heterogeneous and/or low permeability soils. In situ flushing with surfactants/cosolvents has shown the ability to remediate PAH-contaminated soils that are uniform and have a fairly high hydraulic conductivity [8–10], but this remediation technique is often ineffective for heterogeneous and/or low permeability soils, especially when the hydraulic conductivities are less than about  $10^{-5}$  cm/s in magnitude. Under low permeability conditions, the electrokinetically enhanced in situ flushing technique has the potential to improve soil–solution–contaminant interaction and contaminant removal, but this process is highly dependant on the type of purging solution [11].

A complete review of the electrokinetic method, and the physico-chemical processes and contaminant transport mechanisms that are involved, is beyond the scope of this paper, but many studies, such as those by Eykholt and Daniel [12], Yeung [13] or Acar *et al.* [14], have adequately provided information on the basics of this technology. Furthermore, several researchers, such as Bruell *et al.* [15], Acar *et al.* [14] or Shapiro and Probstein [16], have performed laboratory investigations and have found that electrokinetics is applicable for the remediation of organic contaminants. Nevertheless, the success of remediation processes, such as in situ flushing or electrokinetically enhanced in situ flushing, depends on the solubility of the contaminants, and, for hydrophobic compounds such as PAHs, surfactants/cosolvents are commonly used as flushing solutions to substantially increase desorption and solubilization through micellization and surface tension reduction [8,9,11,17].

The solution chemistry of surfactants/cosolvents and the solubilization of PAH compounds involves many considerations, such as the thermodynamics, molecular structures, forces and kinetics. For the purposes of this investigation, however, only a brief overview of the solution chemistry is provided herein to facilitate a better understanding of the surfactant/cosolvent properties. For cosolvents, the co-dissolved organic molecules generally reduce the polar interactions between the water molecules [18], and the total mixture attains an organic character that is more conducive to PAH solubilization. As opposed to cosolvents, surfactants increase PAH solubilization through the formation of micelles, which are essentially aggregates of surfactant molecules that create a hydrophobic region in which PAH molecules may reside [19,20]. The formation of micelles, begins at a specific surfactant concentration termed the critical micelle concentration (CMC), where the physical properties of the solution, such as interfacial tension, electrical conductivity, and light scattering behaviour, often changes abruptly due to the existence of micelles [20]. Surfactants are commonly classified according to the balance between the hydrophilic and hydrophobic, or lipophilic, portions of the surfactant molecule. A lipophilic substance is one with a high affinity for fatty or organic solvents and it is essentially a hydrophobic substance [19]. Surfactants with a high hydrophile-lipophile balance (HLB) number are more soluble in water, and a low HLB indicates the surfactant is more soluble in an organic solvent [21].

It should be noted that in situ flushing investigations are usually performed on high permeability soils such as sands. Sandy soils however, may be considerably easier to remediate than clays, because PAH sorption often predominates in soils that possess substantial quantities of organic matter and/or clay/silt-sized particles. Organic matter contains substances that have hydrophobic characteristics that are similar to PAHs, and clay/silt-sized particles have large surface areas as well as electrical charges associated with them [22]. Furthermore, sufficient soil–solution interaction usually occurs in sandy soils, whereas low permeability clayey soils commonly need alternative methods, such as electrokinetics or a high hydraulic gradient, to achieve adequate soil-solution interaction.

The primary objective of this paper was to assess and compare the ability of various types of surfactant/cosolvent purging solutions to desorb and solubilize a representative PAH

contaminant, phenanthrene, from different types of clayey soils. Initially, potential surfactants/cosolvents were identified from recent published literature and they were selected according to the specific criteria described in the following section of this paper. Based on the criteria, six different types of surfactant/cosolvent solutions were chosen for use in batch desorption tests for two different artificially contaminated clayey soils, kaolin and glacial till. These particular soils were used because they possessed different soil properties and mineral compositions to account for the wide range of subsurface environments that are present at contaminated sites. After the batch tests were completed, the results were used to determine desorption isotherms, which were useful for examining solution and contaminant behaviour and analysing surfactant/cosolvent performance under the different soil conditions.

## 2. BACKGROUND

Candidate surfactants/cosolvents were selected based on solution chemistry, proven ability to desorb/solubilize PAH compounds in previous studies, human health and environmental protection, and compatibility with the electrokinetically enhanced in situ flushing remediation technique. One of the primary drawbacks of remediation processes, such as in situ flushing, is the possibility that the contaminants and/or the flushing solution will migrate beyond the zone of influence of the extraction well or wells. Furthermore, even though extensive flushing with plain water is commonly performed after surfactant/cosolvent flushing is completed, there is a high probability that there will be some residual or adsorbed surfactant/cosolvent solution left in the soil after the remediation process is finished. Therefore, the optimal surfactant/cosolvent would be one that was proven to be effective on PAHs yet is fairly non-toxic and will not pose a threat to human health or the environment. Moreover, it is beneficial if the surfactant/cosolvent is readily available, economically priced and recyclable. Although it is advantageous if the surfactant/cosolvent is biodegradable, it is important to ensure that the solution is well-matched with the flushing technique and the subsurface environment, so advection and biodegradation are controlled and microbial activity does not overwhelm the process or biofoul and clog pore spaces and/or the injection/extraction wells [23].

In a previous study at the University of Illinois at Chicago (UIC), a variety of different cosolvents were investigated, but they were only moderately effective at removing phenanthrene from a glacial till soil [17]. It was evident from this previous study that cosolvents, such as *n*-butylamine, acetone, and tetrahydrofuran (each at a 20% concentration), may significantly increase phenanthrene solubility, but these cosolvents are generally not used for in situ flushing applications due to their toxicity and/or volatility. Typically, the main cosolvents that are employed for in situ flushing are miscible alcohols [24], such as ethanol, methanol and isopropyl alcohol, since they are considerably less hazardous for the environment.

The US National Toxicology Program (NTP), which is a division of the National Institute of Environmental Health Sciences (NIEHS) [6], compiles a chemical health and safety database that provides physical and chemical data and toxicological information on nearly 2000 chemicals. For many chemicals, this database lists the dosage of the chemical that produces the death of 50% of a particular species, also known as Lethal Dose 50 or LD<sub>50</sub>. Usually, a low LD<sub>50</sub> corresponds to a more toxic chemical, since a smaller dose of the chemical is needed to cause 50% of the particular species to die. For a rat species with an oral mode of chemical intake, chemicals such as *n*-butylamine and tetrahydrofuran had relatively low LD<sub>50</sub> doses of 380 and 2816 mg/kg, respectively, whereas alcohols such as isopropyl alcohol, methanol, and ethanol had LD<sub>50</sub> doses of 5045, 5628 and 7060 mg/kg, respectively.

Through this same database, acetone was found to have a relatively high rat oral LD<sub>50</sub> of 5800 mg/kg, but the volatility of acetone (180 mm Hg at 20°C) was high compared to miscible alcohols such as ethanol (40 mm Hg at 19°C). Although both ethanol and acetone are flammable liquids, the higher vapor pressure of acetone may cause it to be more susceptible to losses due to evaporation and there may be a greater risk for fires or explosions. Li *et al.* [16] determined that the miscible alcohols, namely, ethanol, methanol and isopropyl alcohol, had similar phenanthrene solubilities of  $1.36 \times 10^4$ ,  $1.38 \times 10^4$  and  $1.4 \times 10^4$  mg/l, respectively. However, ethanol was chosen for the present study because it has a higher LD<sub>50</sub> than the other alcohols, and, since it is used in alcoholic beverages, it appears as though ethanol would generally be less harmful to human health and the environment. This is important since research has shown that high cosolvent concentrations may be necessary for contaminant removal [25], and high ethanol concentrations have exhibited success at solubilizing non-aqueous phase liquids (NAPLs) [7,26].

Choosing the best surfactant solution for desorbing and solubilizing phenanthrene can be a daunting task since over 700 different types of surfactants are commercially available [19]. Furthermore, even after a potential surfactant has been identified, the optimal concentration still needs to be determined. In addition, surfactant and cosolvent mixtures may be used, but organic additives will change solution properties, such as the CMC of the surfactant [20], so this can significantly complicate the selection process. Since the ultimate intent of this study is to select the surfactants for electrokinetically enhanced in situ flushing, it was decided that non-ionic surfactants would be best because they would not counteract the electroosmotic flow like anionic surfactants [11,27,28]. Moreover, cationic and zwitterionic surfactants were rejected because of their possible strong adsorption and/or complexation with soil minerals [29]. Published literature revealed that the following surfactant trade names are strong candidates for soil remediation: Brij 35, Igepal CA-720, Triton X-100, and Tween 80 [9,30,31,32,33].

For in situ flushing, it is desirable to select surfactants that will not adsorb to the soil particles, because surfactant adsorption could reduce the micellization and solubilization capacity of the surfactant, and it could result in the contaminant partitioning to the adsorbed surfactant molecules [34,35]. Clearly, if a substantial amount of surfactant molecules are adsorbed to the soil surface, less of them will be available for micelle formation and for PAH solubilization. Therefore, it was assumed that high surfactant adsorption would result in poor flushing solution performance, and, although surfactant adsorption was a concern, the emphasis for the present investigation was placed on the remediation capability of the different surfactant/cosolvent solutions. Moreover, environmentally friendly surfactant solutions were selected and they were used at low concentrations, so a minor amount of surfactant adsorption was deemed to be acceptable.

Due to the numerous surfactant/cosolvent combinations and concentrations that are applicable for PAH remediation, chemical analyses can become costly and time consuming. Thus, this preliminary investigation was primarily aimed at screening potential flushing solution candidates, and the performance of quantitative analyses on surfactant sorption was presumed to be unnecessary and beyond the scope of this study.

### 3. BATCH DESORPTION EXPERIMENTS

#### 3.1. Materials

Phenanthrene (C<sub>14</sub>H<sub>10</sub>), which is an uncharged organic compound that consists of three aromatic rings, was selected as a representative PAH in this study. It has environmental properties such as aqueous solubility, K<sub>ow</sub>, and vapor pressure that are similar to other PAHs,

TABLE I Properties of soils tested

<i>Property</i>	<i>Kaolin</i>	<i>Glacial Till</i>
Mineralogy	Kaolinite 100% Muscovite: trace Illite: trace	Quartz: 31% Feldspar: 13% Carbonate: 35% Illite: 15% Chlorite: 4–6% Vermiculite: 0.5% Smectite: trace
<i>Particle Size Distribution (ASTM D 422)</i>		
Gravel (%)	0	0
Sand (%)	4	20
Silt (%)	18	44
Clay (%)	78	36
Specific Gravity (ASTM D 854)	2.6	2.7
Hydraulic Conductivity (cm/s)	$1.0 \times 10^{-8}$	$8.8 \times 10^{-8}$
Organic Content (%)	Near 0	2.8
pH (ASTM D 4972)	4.9	8.2
Cation Exchange Capacity [meq/100 g] (ASTM D 9081)	1.0–1.6	13–18
USCS Classification (ASTM D 2487)	CL	CL

such as acenaphthene, fluoranthene, and fluorene [5,36]. Although higher molecular weight and more carcinogenic PAHs, such as benzo (a) pyrene, may have higher  $K_{ow}$  values and lower aqueous solubilities, it was hypothesized that since the parent structures are similar, phenanthrene would be an adequate representative compound that would give a general indication of PAH behaviour. All PAHs are hydrophobic, and phenanthrene has an aqueous solubility of 1.1 mg/l at 25°C [36]. In the environment, phenanthrene has a high fugacity and a tendency to flee aqueous regions, and its  $\log K_{ow}$  value of 4.57 [36] indicates that it will tend to partition to organic matter.

Since the main purpose of the batch test programme was to compare surfactant/cosolvent desorption and solubilization ability, it was advantageous to limit discrepancies due to other parameters, such as differences in soil or contaminant properties. Therefore, it was decided to artificially contaminate the soil with a known PAH contaminant and at known concentrations, so as to avoid concerns about the source, type, and concentration of the contaminant, as well as differences due to aged contamination.

Two clayey soils, kaolin and glacial till, were selected for this study, and the composition and properties of these soils are summarized in Table I. The colloidal laboratory grade kaolin was obtained from VWR Scientific Products and the manufacturer was EM Science, where as the glacial till was obtained from a field location near Chicago, Illinois. These soils were selected to represent the diverse variations of clayey soils that are encountered at contaminated sites. Kaolin mainly consists of the kaolinite clay mineral, while glacial till consists of a combination of different soil minerals including quartz, feldspar, carbonates, illite, chlorite, vermiculite and trace amounts of smectite.

Six different surfactant/cosolvent purging solutions were tested based on several factors discussed in the background section, and these solutions included Igepal CA-720 at two different concentrations, 3 and 5%, 5% Triton X-100, 3% Tween 80, 40% ethanol, and a 40% ethanol and 5% Igepal CA-720 mixture. Brij 35 was found to be relatively ineffective at phenanthrene solubilization during preliminary batch testing, so it was subsequently dropped from the testing programme. Table II shows the individual properties of the

TABLE II Non-ionic surfactants used in this study

<i>Surfactant Trade Name</i>	<i>Structural Chemical Formula</i>	<i>Approximate Molecular Weight</i>	<i>Type of Surfactant</i>	<i>CMC* [mol/L]</i>	<i>HLB**</i>
Igepal CA-720	C <sub>8</sub> PE <sub>12</sub>	735	Octylphenol polyoxyethylene (POE)	$2.3 \times 10^{-4}$	14.6
Triton X-100	C <sub>8</sub> PE <sub>10</sub>	625	Octylphenol polyoxyethylene (POE)	$1.7 \times 10^{-4}$	13.5
Tween 80, Witconol 2722	C <sub>18</sub> S <sub>6</sub> E <sub>20</sub>	1310	Polyoxyethylene (POE) sorbitan monooleate	$1.2 \times 10^{-5}$	15.0

*Notes:* C represents the alkyl chain length ( $-\text{CH}_2-$ ), P represents a phenol ring ( $-\text{C}_6\text{H}_6-$ ), S<sub>6</sub> represents a sorbitan ring ( $\text{C}_6\text{H}_{12}\text{O}_5$ ) and E represents an ethoxylate group ( $\text{CH}_2\text{CH}_2\text{O}$ ).

\* Critical micelle concentration.

\*\* Hydrophile – Lipophile balance.

surfactants selected for the batch desorption tests. The concentrations were selected based on the published surfactant studies as stated in the background section, and a desire to maximize contaminant removal and minimize environmental impact and adverse chemical reactions.

### 3.2. Testing Procedure

The two selected soils were artificially contaminated (spiked) with phenanthrene at initial target concentrations of 100, 300, 500 and 1000 mg/kg. These concentrations were based on the typical PAH concentrations that are found near source zones at contaminated sites [1], and approximately 1.5 kg of each soil was spiked for each target concentration of phenanthrene. Initially, the phenanthrene required to yield the target concentration was measured and then completely dissolved in about 500 ml of hexane. Hexane was used because phenanthrene has an extremely low solubility in water. The hexane–phenanthrene mixture was subsequently mixed with the measured amount of soil and additional hexane was put in so that the soil–hexane–phenanthrene mixture could be easily stirred and blended homogeneously. The mixtures were stirred with stainless steel spoons, and all mixing operations were performed within glass beakers. The motivation for this mixing technique was to ensure that the phenanthrene would be distributed evenly throughout the soil. The soil–hexane–phenanthrene mixture was then placed beneath a ventilation hood for nearly a week until the hexane completely evaporated and the contaminated soil was dry. Occasional stirring was necessary during the drying period to increase the rate of drying and further ensure uniform phenanthrene distribution. A soil sample was taken to determine the actual initial concentration of phenanthrene in the soil, since a portion of the contaminant may volatilize along with the solvent, hexane.

The batch desorption experiments were conducted using a soil to water ratio of 1:5, or, specifically, 5 g of the soil, kaolin or glacial till, were combined with 25 ml of solution. First, 5 g of dry, contaminated soil was measured and placed in a new, clear 40 ml glass vial. Then, 25 ml of the appropriate surfactant/cosolvent solution was measured and added, and the vial was sealed with a Teflon screw-type top. Each vial was then shaken by hand for about a minute to ensure the soil was fully saturated with solution, and the vials were placed on a rotary shaker table at 250 rpm for 24 h. After the shaking was completed, the solution was decanted into a clean polycarbonate centrifuge tube, and the soil-solution mixture was placed

in a centrifuge and centrifuged at 4000 rpm for 28 min. Then, the supernatant was poured through a glass funnel holding a Whatman GF/C glass fibre filter (1.2  $\mu\text{m}$  particle retention) to remove any floating particles or debris, and the effluent from the funnel flowed into a clean 40 ml glass vial. The supernatant from the samples containing kaolin soil was decanted into a clean polycarbonate centrifuge tube and centrifuged again at 4000 rpm for 28 min. This was necessary with the kaolin because, after only one run through the centrifuge, the supernatant still contained fine particles that tended to stay suspended in solution. Once the supernatant was observed to be clear of any suspended particles, the concentration of phenanthrene in the supernatant was determined by liquid–liquid extraction followed by gas chromatography/mass spectrometry (GC-MS) chemical analysis [11].

For each of the four different phenanthrene concentrations in the soil there were six different solutions tested, and this resulted in 24 tests for each soil, kaolin and glacial till, or a total of 48 batch tests. In addition, since duplicate samples were tested to ensure quality control, a total of 96 batch tests were conducted.

### 3.4. Chemical Analysis

To determine the initial phenanthrene concentration in the soil, a dry representative soil sample weighing 10 g was thoroughly mixed with about 10 g of  $\text{Na}_2\text{SO}_4$  (Fisher Scientific), and the mixture was placed into a Whatman cellulose extraction thimble. The phenanthrene was then extracted using a Soxhlet apparatus consisting of a 250 ml flask, a Soxhlet extraction tube, and a bulb-type Allihn condenser. The procedure is outlined in USEPA test method 3540C [37]. The solution used in the Soxhlet extraction process was 190 ml of a 1:1 mixture of hexane and acetone (Fisher Scientific), and the process was operated for at 4–6 cycles/h for at least 24 h. After the extraction was completed, the volume of the solvent remaining in the Soxhlet extraction tube and flask was measured, and GC/MS analysis was performed on a sample of the liquid. The soil was usually highly contaminated with phenanthrene, so the solvent–phenanthrene liquid samples obtained from the Soxhlet extraction could be directly analysed using GC/MS without performing a concentrating procedure.

For the supernatant obtained after the batch tests, a liquid–liquid extraction procedure was adopted in order to extract the phenanthrene from the aqueous surfactant/cosolvent solution into methylene chloride (dichloromethane) (Fisher Scientific GC Resolv grade). The extraction procedure first consists of placing 15 ml of methylene chloride into a clean and empty 40 ml clear or brown glass vial. Then, a 5 ml sample of the supernatant (surfactant/cosolvent-phenanthrene solution) is placed into the vial along with the methylene chloride. This 3:1 ratio was found to reduce emulsion formation problems with the surfactants. The mixture was then sealed in the vial with a screw type Teflon cap and hand shaken. After shaking by hand for a few seconds, the top was opened to release gas generated by the reaction between the methylene chloride and the aqueous surfactant/cosolvent solution. If the gas was not released, high pressure may have resulted, which could have caused the cap to leak or possibly be ejected from the vial. The cap was then tightly re-sealed and the vial was placed on a rotary shaker table at 250 rpm for 24 h. Since phenanthrene has a much higher solubility in the methylene chloride solvent, during the shaking process it was extracted from the surfactant/cosolvent solution into the methylene chloride. Moreover, the greater density of the methylene chloride solvent causes it to sink and form a separate liquid phase beneath the aqueous surfactant/cosolvent solution. After mechanical shaking, a 1.0 ml aliquot of the methylene chloride-phenanthrene solution was removed from beneath the surfactant solution by using a Hamilton glass 1 ml syringe, and the extracted methylene chloride-phenanthrene solution was placed into a 2 ml Target auto-

sampler vial with a Teflon screw cap for injection and GC/MS analysis. Between samples, the syringe was flushed approximately eight times using two flasks of methylene chloride to avoid cross-contamination. Due to the high phenanthrene concentrations, the methylene chloride-phenanthrene solution was directly analysed by the GC/MS without performing a concentrating procedure.

Chemical analysis was performed according to USEPA method 8270C, semivolatile organic compounds by GC/MS [37]. The GC/MS that was used was a Hewlett-Packard Model 5890 Series II GC equipped with a Hewlett-Packard 5971A mass selective detector. The injection volume was 1  $\mu$ ml, and it was injected via an auto-injector at an inlet temperature of 250°C. The mass transfer line was at 300°C. The column used on the GC was an Agilent Technologies HP-5MS (30 M  $\times$  0.250 mm  $\times$  0.25  $\mu$ m) and the MS was run in selective ion mode for  $m/z$  178 and 179. The total run time was 28 min. The oven ramp was started at 50°C (four min) and increased to 310°C at 20°C/min and then held at 310°C till the end of the run time. The instrument was calibrated using calibration points at different concentration levels, and four internal standards were used, which consisted of 1,2 - dichlorobenzene-d4, nitrobenzene-d5, 2-fluorobiphenyl, and p-terphenyl-d14.

### 3.5. Quality Control

Throughout the batch testing and chemical analyses, all the glassware, such as vials and sample bottles, were new from the manufacturer and certified to be clean. The chemicals were new from the manufacturer and they were fresh and of high-grade purity. The deionized water was tested to verify that it had an ionic conductivity near zero. The calibration standards for the phenanthrene analyses by (GC/MS) were prepared in two different concentration ranges, and each series contained at least four standard solutions that covered an order of magnitude in concentration or more. The linearity of the calibration graph was always checked to make sure that the regression coefficient ( $R^2$ ) was close to one, and sample blanks, without contamination, were injected regularly to ensure that the system remained uncontaminated. Duplicate standard samples were commonly injected to certify a uniform response, and to ensure that the calibration graph and the baseline remained stable. The syringe was rinsed with solvent several times between sample injections to reduce contamination carryover.

## 4. RESULTS AND ANALYSIS

The initial phenanthrene target concentrations were 100, 300, 500 and 1000 mg/kg for the kaolin and glacial till soils, but the chemical analysis of the initial dry soil revealed that a significant amount of phenanthrene was volatilized along with hexane during the spiking procedure. The actual initial concentrations in the soils as determined by Soxhlet extraction and GC analyses were 85, 156, 364 and 864 mg/kg for the kaolin soil and 82, 168, 303 and 647 mg/kg for the glacial till soil. The mass of phenanthrene initially present in the soil before batch testing was approximately equal to the actual initial concentration of that particular soil times the 5 g of soil placed into the vial. Then, after batch testing, liquid-liquid extraction and GC analysis of the supernatant was performed to determine the concentration of phenanthrene that was desorbed and solubilized into the aqueous, surfactant/cosolvent, phase ( $C_w$ ). The mass of phenanthrene desorbed and solubilized by the surfactant/cosolvent solution was calculated to be equal to the concentration in the aqueous phase times the 25 ml of solution that was initially combined with the soil. The residual mass of phenanthrene remaining in the soil was then computed by subtracting the mass that was desorbed and

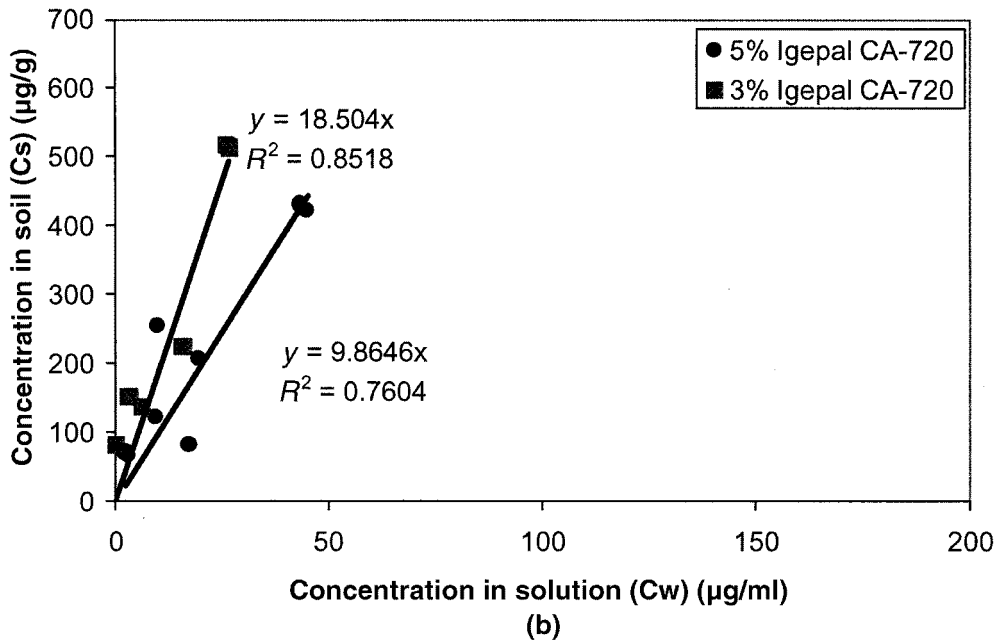
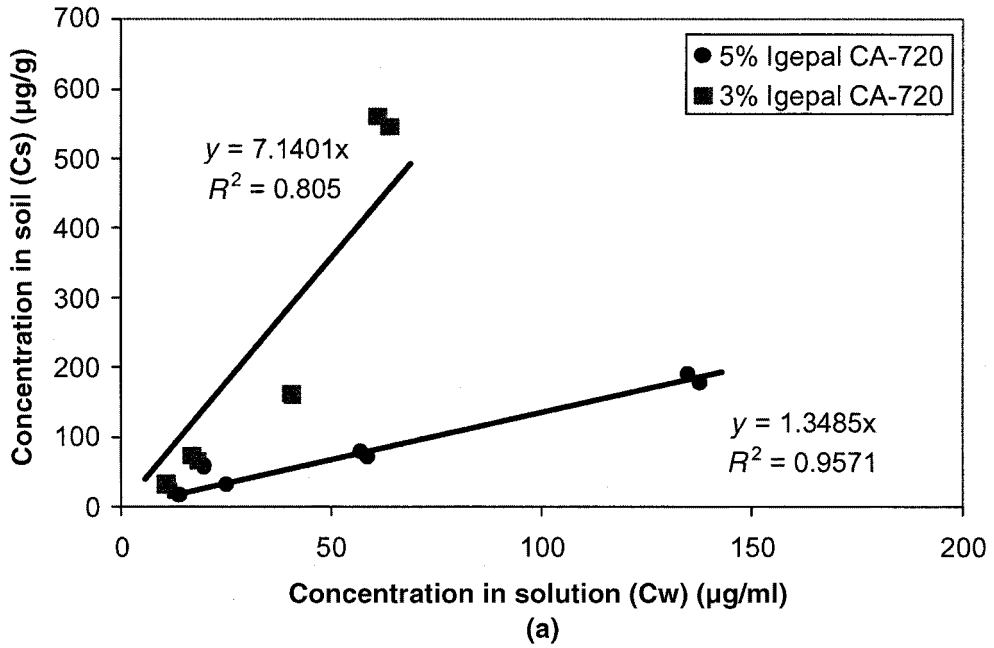


FIGURE 1 Desorption test results with Igepal CA-720: (a) kaolin and (b) glacial till

solubilized into the aqueous phase from the mass that was initially present in the soil. Once the residual mass was determined, the concentration remaining in the soil after batch testing ( $C_s$ ) was computed by dividing the residual mass by the five grams placed into the vial. Thus, for each individual batch test experiment, there were two concentration values representing the concentration of phenanthrene desorbed and solubilized into the aqueous phase ( $C_w$ ) and the concentration that remained in the soil phase ( $C_s$ ). When these points are plotted with the

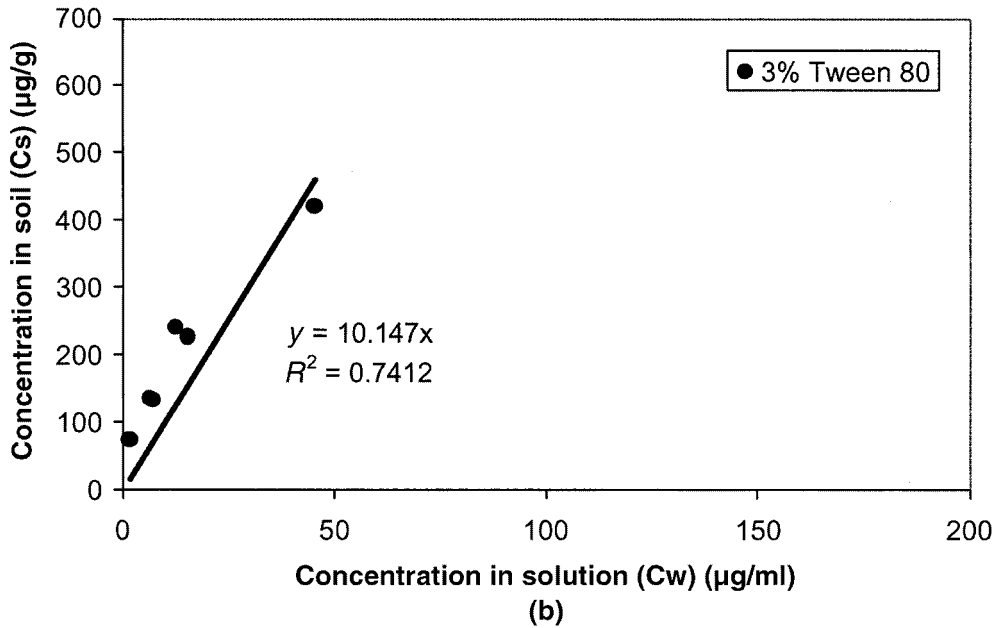
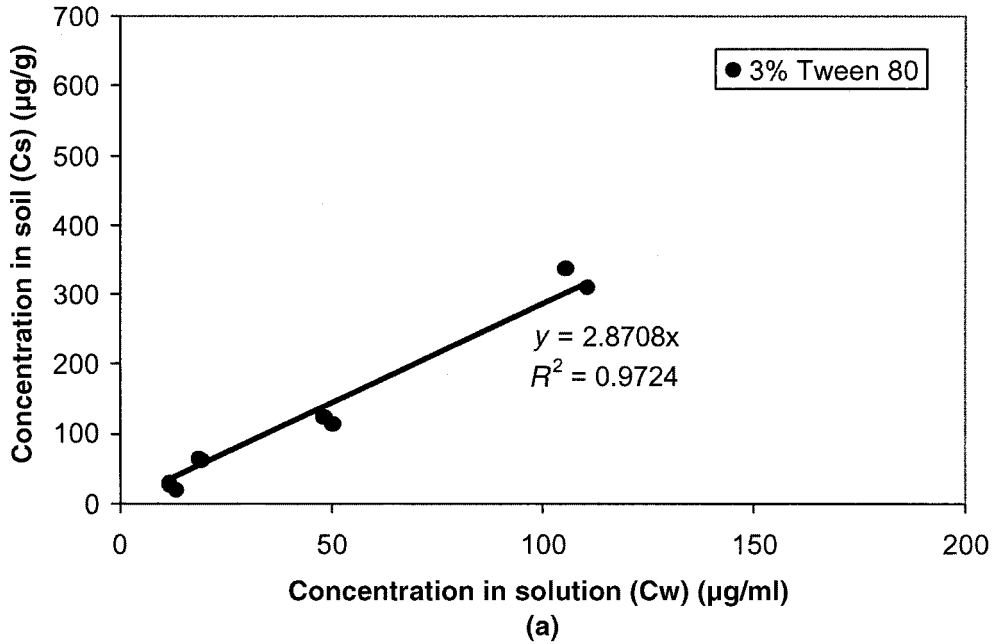


FIGURE 2 Desorption test results with Tween 80: (a) kaolin and (b) glacial till

$C_s$  values corresponding to the y-axis and the  $C_w$  values corresponding to the x-axis, the points may be linearly related by:  $K_d = C_s/C_w$ , and the line plotted through the points is known as a linear desorption isotherm.

Figures 1–4 show the  $C_w$  versus  $C_s$  plots, or the phenanthrene desorption isotherms, for the different surfactant/cosolvent solutions in the kaolin and glacial till soils. The isotherms for each type of soil were plotted to the same scale for comparison, and the  $K_d$  values were

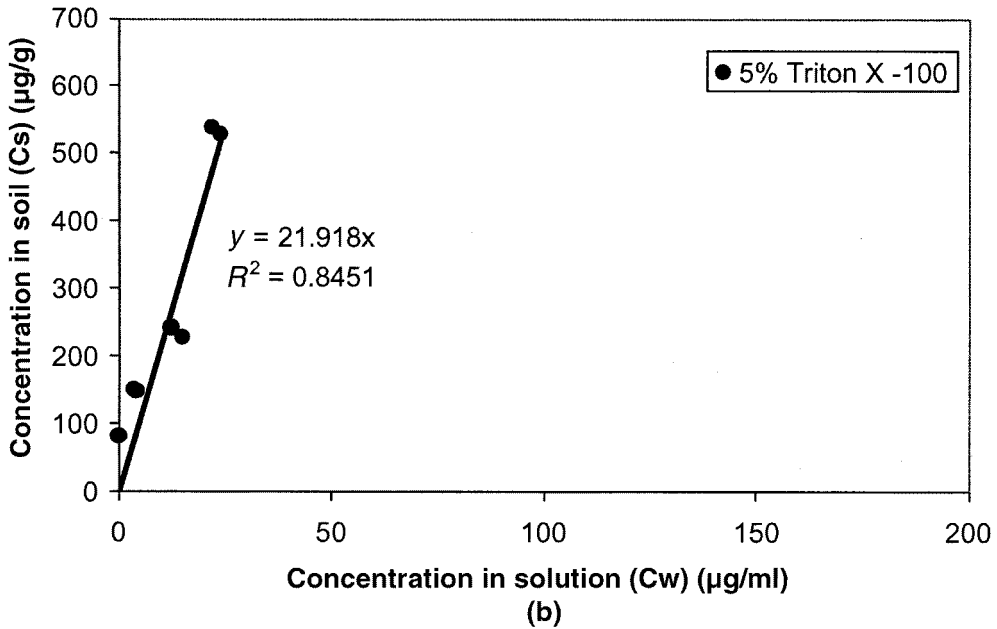
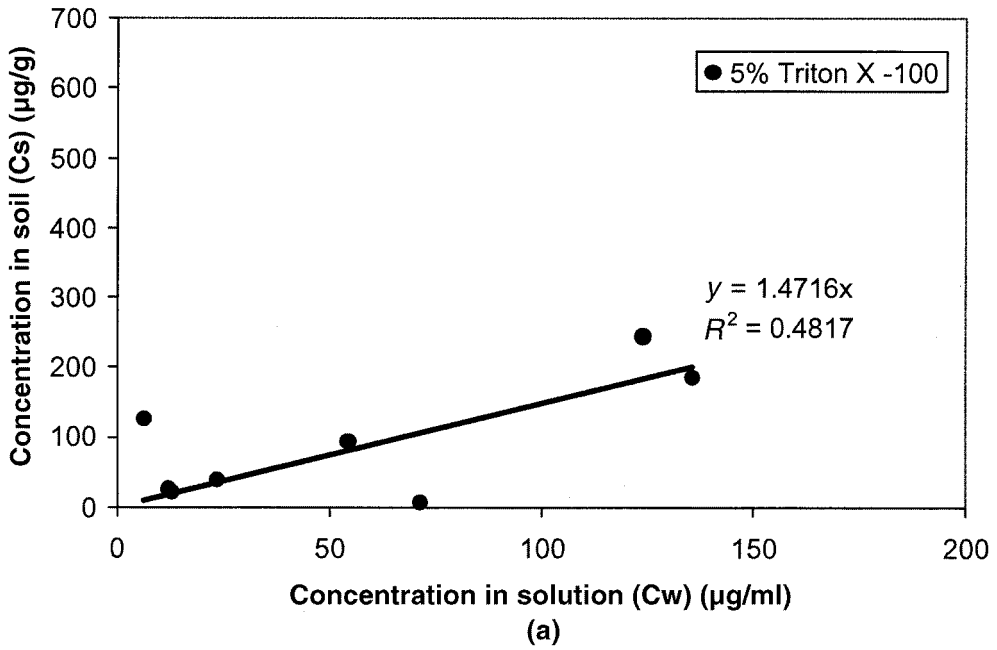


FIGURE 3 Desorption test results with Triton X-100: (a) kaolin and (b) glacial till

calculated using a linear regression analysis. The correlation coefficients ( $R^2$ ) for the surfactant/cosolvent solutions are also shown in the figures. Although this analysis correlated well for the majority of the desorption tests, there were some exceptions where the isotherm deviated from linearity, especially near the highest phenanthrene concentration. Generally, a good agreement was observed between the duplicate samples, but non-uniform contaminant distribution may have caused divergence from the other data values and a linear behaviour.

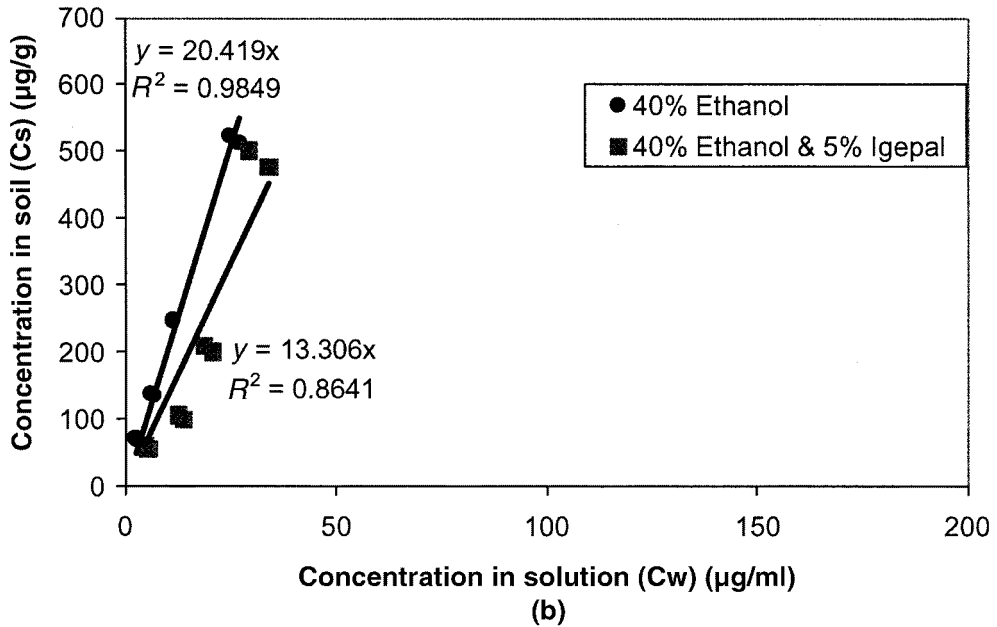
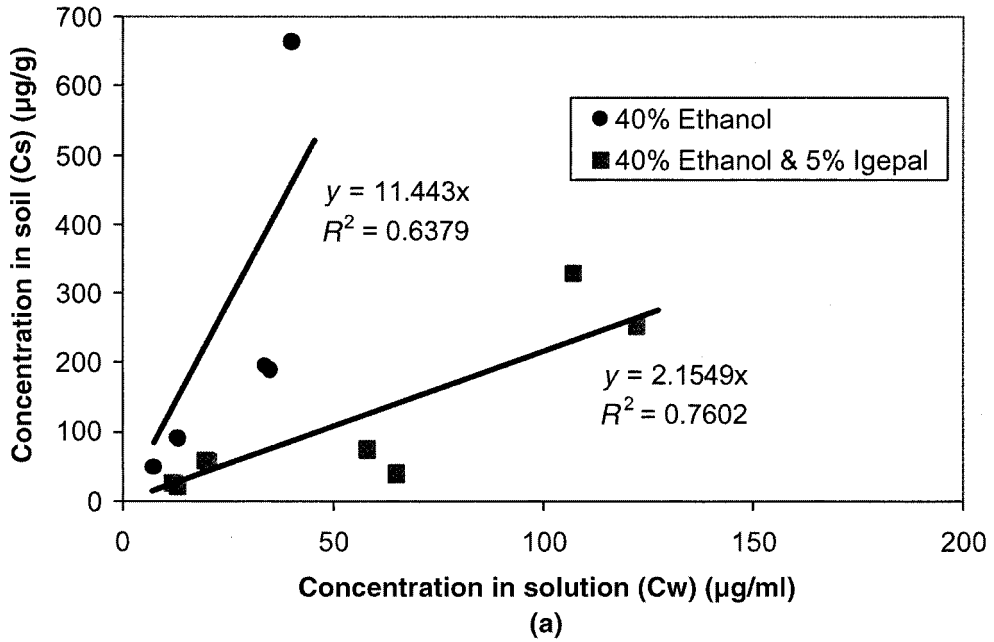


FIGURE 4 Desorption test results with ethanol and ethanol with Igepal CA-720: (a) kaolin and (b) glacial till

The average correlation coefficient of the desorption tests was 0.77 and 0.84 for the kaolin and glacial till soils, respectively.

Table III summarizes the  $K_d$  values for the six different surfactant/cosolvent solutions in the kaolin and glacial till soils. It should be noted that  $K_d$  is based on a linear desorption isotherm, and it has been assumed that  $C_s$  and  $C_w$  vary linearly over this range of concentrations. As discussed earlier,  $C_s$  represents the concentration of phenanthrene sorbed

TABLE III Calculated  $K_d$  Values

Surfactant/cosolvent	$K_d = C_d/C_w$ (ml/g)	
	Kaolin	Glacial till
Deionized Water	N/A	210
5% Igepal CA-720	1.35	9.86
3% Igepal CA-720	7.14	18.50
5% Triton X-100	1.47	21.92
3% Tween 80	2.85	10.15
40% Ethanol	11.44	20.42
40% Ethanol and 5% Igepal CA-720	2.15	13.31

Notes: N/A = not available.

\* Li *et al.* [17].

to the soil and  $C_w$  represents the phenanthrene concentration in the solution. However, with surfactant solutions,  $C_w$  is often thought of as the “apparent” solubility because it refers to the phenanthrene that is dissolved in the aqueous solution as well as the phenanthrene that is solubilized into surfactant micelles, if they are present.

The results indicate that all the surfactant/cosolvent solutions were fairly successful at achieving contaminant removal, and, even with the largest  $K_d$  value, 21.92 ml/g, the 5% Triton X-100 solution greatly enhanced phenanthrene desorption and solubilization from the glacial till soil compared to plain water. Fig. 3 exhibits that when the initial phenanthrene concentration in the glacial till was 647 mg/kg, the solubility ( $C_w$ ) of phenanthrene in the 5% Triton X-100 solution was around 20 mg/l, whereas the solubility of this contaminant in water is only around 1.1 mg/l [36]. Li *et al.* [17] show experimentally and through estimation that the  $K_d$  value for phenanthrene in this glacial till soil with water was about 210 ml/g, so a  $K_d$  of 21.92 ml (for the 5% Triton X-100 solution with glacial till soil) indicates that a significant amount of phenanthrene desorption and solubilization occurred. Incidentally, since phenanthrene has such a low solubility in water, for the present investigation, the contaminant was not detected in the supernatant when a water flushing solution was used, and Li *et al.* [17] employed a procedure using a Kuderna-Danish concentrator in order to measure the small amount of phenanthrene that was solubilized from the glacial till with water.

For both soils, the lowest  $K_d$  values occurred when the 5% Igepal CA-720 solution (Fig. 1) was used, and, for an initial concentration of 865 mg/kg in the kaolin soil, this solution produced an apparent solubility ( $C_w$ ) of about 130 mg/l, which is about a hundred times the solubility of phenanthrene in plain water. Since Igepal CA-720 and Triton X-100 are both octylphenol polyoxyethylene surfactants and have similar structures, they were expected to produce similar results. This expectation was verified by a study conducted by Jafvert *et al.* [36] in which a quantitative structure-activity relationship was developed for the solubilization of non-polar compounds by nonionic surfactants. Jafvert *et al.* [36] show that for phenanthrene, Igepal CA-720 and Triton X-100 have comparable micelle-water partition coefficients (Log  $K_m$ ). For the present study, the desorption tests performed with the 5% solutions of these different surfactants produced nearly identical  $K_d$  values in the kaolin soil (they only differed by about 0.12 ml/g) (Fig 1 and 3). Conversely, Igepal CA 720 has two more ethoxylate (polar) groups than Triton X-100, and this significantly affected the results in the more organic and heterogeneous glacial till soil because, in the glacial till, 5% Igepal CA-720 had less than half the  $K_d$  of the 5% Triton X-100 solution (Fig 1 and 3).

As seen in Table III, it is apparent that all the  $K_d$  values were higher for glacial till as compared to kaolin, and this can be partially explained by a strong sorption of phenanthrene to organic matter. Furthermore, the varied mineralogy of the glacial till as well as the more heterogeneous particle sizes may have also contributed to phenanthrene sorption or reduced removal. However, the effects of other soil properties such as mineralogy and particle size distribution are less understood, and Means *et al.* [39] tested 14 soil samples and only found a correlation with organic content. In addition, since Igepal CA-720 has more polar groups and it is more hydrophilic than Triton X-100, there was probably less surfactant sorption to the organic matter in glacial till, so more micelles were available for solubilizing phenanthrene.

In addition to the effects of soil composition and, particularly, the presence of organic matter, the removal of phenanthrene depends on other parameters, such as the solution chemistry and surfactant/cosolvent concentration. A comparison of the results from the 5% and 3% Igepal CA-720 tests indicates that for either soil the surfactant concentration was a key factor in phenanthrene removal (Fig. 1). At lower concentrations there are less micelles, and, consequently, there was less phenanthrene solubilization. With pure-phase phenanthrene present, above the CMC, the molar increase in phenanthrene solubilization per molar increase in surfactant concentration is a constant value called the molar solubilization ratio (MSR), and Edwards *et al.* [30] determined that Igepal CA-720 has an MSR of 0.104 for phenanthrene. In the absence of pure-phase phenanthrene, however, Edwards *et al.* [31] mention that as the contaminant transfers to the micellar phase, its concentration decreases proportionately in both the aqueous and the soil phases, and this results in a nonlinear MSR, expressed as:

$$\text{MSR} = \frac{X_m}{1 - X_m}$$

where  $X_m$  equals the mole fraction of contaminant in the micellar phase. Edwards *et al.* [34] found that at sub-CMC and small supra-CMC values, the amount of phenanthrene in solution decreased compared to a soil-solution mixture without surfactant because the phenanthrene was sorbing to the sorbed nonionic surfactant molecules. Clearly, this is a disadvantage at low surfactant concentrations, but, with additional increases in surfactant, a point is reached where micellar solubilization begins to dominate, and after this point, the fraction of phenanthrene in the bulk solution increases as surfactant is added. Within this region, where micellar solubilization dominates, the MSR, or the amount of contaminant solubilized per surfactant dose added, is initially high, but, as the fraction of phenanthrene remaining in the aqueous and soil phases diminishes, the MSR value decreases [31,34].

The surfactant concentrations used in the present study ranged 200–2000 times their CMC values (Table II). Therefore, even though a significant amount of surfactant may adsorb to the clay, the surfactant concentration should remain within the region where micellar solubilization dominates. When the maximum initial phenanthrene soil concentrations are used, the results from the 3% and 5% Igepal CA-720 experiments show that the MSR values were approximately 0.0033 and 0.0008 for the kaolin and glacial till soils, respectively. These values are considerably lower than the 0.104 value determined by Edwards *et al.* [30] with pure-phase phenanthrene at much lower surfactant concentrations, and this implies that the MSR curve, or the fraction of phenanthrene in solution versus surfactant concentration curve, could be reaching a range where only a small amount of phenanthrene will be solubilized with further increases in surfactant concentration. Furthermore, the higher MSR value for the kaolin soil compared to glacial till indicates that the higher 5% Igepal CA-720 concentration

was more efficient at phenanthrene removal in kaolin, and this was most likely due to the lower organic content. Since there are a lower number of sites available for phenanthrene adsorption in kaolin, and the contaminant sorption is weaker, these conditions are favorable for micellar solubilization, and the additional surfactant was more efficient.

From Table II, Tween 80 has a lower CMC and a higher HLB value than Igepal CA-720, so Tween 80 micelle formation may begin at a lower surfactant concentration and there could be less Tween 80 sorption to organic matter. These attributes of Tween 80 can be observed when comparing the  $K_d$  results between the 3% Igepal CA-720 and 3% Tween 80 solutions, because Tween 80 produced much more phenanthrene solubilization, and, for either soil, the 3% Tween 80  $K_d$  value was about half the  $K_d$  value of 3% Igepal CA-720 (Figs 1 and 2 and Table III). Ko (1998) found that with Tween 80, the  $K_d$  values decreased with increasing pH, and this was attributed to a lower amount of surfactant adsorption at high pH. Ko *et al.* [33] explain that this happens because the Tween 80 oxyethylene (polar) group bonds to the protonated soil particle surface at low pH. Edwards *et al.* [34] and Rosen [20] report that other researchers have also observed the sorption of nonionic surfactants to silica at low pH, and, similarly, they explain that the sorption is probably due to the hydrophilic (polar) oxyethylene group attaching to the soil through hydrogen bonding. Using kaolin soil, Ko [33] determined  $K_d$  values of approximately 130, 29, and 16 ml/g for fixed pH values of 4.6, 6.25 and 7.85, respectively, using about a 0.2% Tween 80 solution. In the present study, the 3% Tween 80-kaolin test resulted in a lower  $K_d$  value of 2.8 ml/g (Fig. 2), but the 3% surfactant concentration used in this study was approximately 15 times greater than the 0.2% concentration used by Ko. The pH values in the present investigation were not fixed, but for the 3% Tween 80-kaolin test, they were mostly in the acidic range and averaged about 4.4. Thus, the 2.8 ml/g  $K_d$  value in this study was much smaller than the 130 ml/g  $K_d$  found by Ko [33] at a slightly higher pH. Apparently using a higher 3% Tween 80 concentration may have significantly affected the solution chemistry, and this can be important because, according to Ko [33], solution chemistry changes, such as a 1.65 rise in pH, can produce a large effect (100 ml/g reduction) on  $K_d$ .

In the kaolin and glacial till soils, the cosolvent, 40% ethanol, performed poorly, because the results show that it had a relatively high  $K_d$  value compared to most of the surfactants (Fig. 4 and Table III). Phenanthrene is very soluble in pure ethanol and it has a solubility of  $1.36 \times 10^4$  mg/l, whereas in an ethanol- water mixture, phenanthrene solubility is significantly reduced, and it was measured as 5.0 mg/l in a 20% ethanol solution [17]. Banerjee and Yalkowsky [40] found that when the concentration of the cosolvent exceeds 10% (v/v), the molar solubility of a PAH in the mixture ( $S_m$ ) could be approximated by the following equation:

$$\ln(S_m) = f_c \ln(S_c) + (1 - f_c) \ln(S_w)$$

where  $f_c$  is the nominal cosolvent volume fraction and  $S_c$  and  $S_w$  are the molar solubilities of the PAH in pure cosolvent and pure water, respectively. Using Banerjee and Yalkowsky's [40] equation, which was developed to estimate the solubility enhancement of a PAH in water by using a cosolvent, the solubility of phenanthrene (MW = 178.2) in the 20% and 40% ethanol mixtures should have been approximately 9.7 mg/l and 83.0 mg/l, respectively, assuming the solubility of phenanthrene in pure ethanol ( $S_c$ ) provided earlier from Li *et al.* [17] and the solubility of phenanthrene in water ( $S_w$ ) provided earlier from Schwarzenbach *et al.* [36]. This equation shows that increasing the ethanol concentration to 40% may enhance the solubility of phenanthrene by over eight times the solubility at the 20% concentration. However, at a 20% ethanol concentration, the phenanthrene solubility measured by Li *et al.* [17] was roughly half the solubility estimated by the equation. By

comparing the maximum  $C_w$  values in the 40% ethanol sorption tests to the estimation values, it can be seen that the presence of soil and organic matter greatly reduce phenanthrene solubility. Fu and Luthy [8] hypothesized that the cosolvent-water mixture could produce a swelling effect on the organic carbon fraction of the soil that subsequently causes greater contaminant sorption. The swelling of the carbon fraction may help explain why the 40% ethanol  $K_d$  value in the glacial till was nearly twice the value in the kaolin, but it does not explain why the contaminant solubility was so much less than expected based on Banerjee and Yalkowsky's [40] equation when high phenanthrene concentrations were present in the kaolin.

The combination of the 40% ethanol solution with the 5% Igepal CA-720 solution greatly improved phenanthrene solubilization over the 40% ethanol by itself (Fig. 4); however, the desorption or removal was still less than that produced when the 5% Igepal CA-720 was used alone. The reason that the 40% ethanol and 5% Igepal CA-720 solution had a lower removal than the 5% Igepal CA-720 solution by itself may be due to the effects on micellization caused by the cosolvent [20]. These effects may have included the reduction of the number of surfactant molecules per micelle or changes to the micelle structure. Some ethanol molecules could have been incorporated into the micelles reducing the capacity for phenanthrene, or the ethanol may have disrupted the soil-micelle-contaminant interaction.

## 5. CONCLUSION

This study was performed to assess the ability of various surfactant/cosolvent solutions to desorb and solubilize a representative PAH contaminant, phenanthrene, from two different clayey soils, kaolin and glacial till. Based on the results from the present investigation, the following conclusions were drawn:

- (1) Soil composition had a profound influence on phenanthrene desorption and solubilization. It was far more difficult to desorb and solubilize the contaminant from the glacial till than the kaolin soil, and this behaviour is attributed to the strong binding characteristics of phenanthrene to organic matter.
- (2) The chemical structure of the surfactant significantly affected phenanthrene removal, and the more hydrophilic surfactants performed better. Hydrophilic surfactants are less prone to sorption, so more surfactant molecules are available for micellar solubilization. Compared to the other solutions tested, 5% Igepal CA-720 produced the largest amount of phenanthrene solubilization in both soils. However, at a 3% concentration, Tween 80, which has a lower CMC and higher HLB, outperformed Igepal CA-720.
- (3) Surfactant concentration had an impact on phenanthrene desorption and solubilization. The desorption tests using the 5% Igepal CA-720 produced significantly lower  $K_d$  values than the tests using the 3% Igepal CA-720, and this was evident in both soils. At higher concentrations there are more micelles available for phenanthrene solubilization, but this has been shown to be a non-linear relationship.
- (4) In the kaolin and glacial till soils, the use of ethanol as a cosolvent yielded a low amount of phenanthrene solubilization. Although cosolvents have been shown to greatly enhance phenanthrene solubility in aqueous systems, it appears that when soil is present, the ethanol was not as effective as the surfactants at desorbing the contaminant from the soil and organic matter.
- (5) The combined mixture of ethanol with 5% Igepal CA-720 improved phenanthrene desorption and solubilization over ethanol by itself, but better results were found when

5% Igepal CA-720 was used alone. The ethanol molecules appear to have an adverse effect on micelle structure and behaviour or soil-micelle-contaminant interaction.

Overall, the results from this research indicated that surfactant/cosolvent chemistry as well as the soil properties and composition greatly affected PAH removal, and, although the present study provides suggestions for the type and concentration of surfactant/cosolvent to use, the actual performance of the flushing solution should be verified by conducting laboratory experiments using the specific soils and contaminants that are present at the site.

## Acknowledgments

Funding for this research was provided by the National Science Foundation, the Gas Research Institute, and the University of Illinois at Chicago.

## References

- [1] USEPA, "A resource for MGP site characterization and remediation," EPA/542-R-00-005, July 2000.
- [2] R.G. Harvey, *Polycyclic aromatic hydrocarbons; Chemistry and carcinogenicity* (Cambridge University Press, New York, 1991).
- [3] C.A. Menzie, B.B. Potocki and J Santodanato, "Exposure to carcinogenic PAH's in the environment," *Environmental Science and Technology* **26**(7), 1278–1284 (1992).
- [4] R.G. Luthy, D.A. Dzombak, C.A. Peters, S.B. Roy, A. Ramaswami, D.V. Nakles and B.R. Nott, "Remediating tar-contaminated soils at manufactured gas plant sites," *Environmental Science and Technology* **28** (6), 266A–276A (1994).
- [5] D.W. Connell, *Basic Concepts of Environmental Chemistry* (Lewis Publishers, New York, 1997).
- [6] National Institute of Environmental Health Science (NIEHS) – National Toxicology Program – "Eighth Report on Carcinogens" (RoC) 1997.
- [7] National Research Council, *Innovations in Ground Water and Soil Cleanup* (National Academy Press, Washington, DC, 1997).
- [8] J. Fu and R.G. Luthy, "Effect of organic solvent on sorption of aromatic solutes onto soils," *Journal of Environmental Engineering* **112** (2), 346–367 (1986).
- [9] S. Ganeshalingam, R.L. Legge and W.A. Anderson, "Surfactant-enhanced leaching of polycyclic aromatic hydrocarbons from soil," *Transactions – Institution of Chemical Engineers* **72**(B), 247–251 (1994).
- [10] D.S. Roote, "In-situ flushing," Technology Overview Report, TO-97-02, Ground-Water Remediation Technologies Analysis Center, June 1997.
- [11] R.E. Saichek, "Electrokinetically enhanced in-situ flushing for HOC-contaminated soils," PhD thesis, University of Illinois at Chicago, Chicago, Illinois, 2001.
- [12] G.R. Eykholt, and D.E. Daniel, "Impact of system chemistry on electroosmosis in contaminated soil", *Journal of Geotechnical Engineering* **120** (5), 797–815 (1994).
- [13] A.T. Yeung, "Electrokinetic flow processes in porous media and their applications," In: (M.Y. Corapcioglu, ed.) *Advances in Porous Media* M.Y. (Elsevier, Amsterdam, 1994).
- [14] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, and R. Parker, "Electrokinetic remediation: Basics and technology status," *Journal of Hazardous Materials* **40**, 117–137 (1995).
- [15] C.J. Bruell, B.A. Segall and M.T. Walsh, "Electrokinetic removal of gasoline hydrocarbons and TCE from clay," *Journal of Environmental Engineering* **118** (1), 68–83 (1992).
- [16] A.P. Shapiro and R.F. Probststein, "Removal of contaminants from saturated clay by electroosmosis," *Environmental Science and Technology* **27**(2), 283–291 (1993).
- [17] A. Li, K.A. Cheung and K.R. Reddy, "Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene," *Journal of Environmental Engineering* **126**(6), 527–533 (2000).
- [18] K.T. Valsaraj, *Elements of Environmental Engineering; Thermodynamics and Kinetics* (CRC Press LLC, Boca Raton, FL, 2000).
- [19] D. Myers, *Surfactant Science and Technology* (VCH Publishers Inc., New York, 1988).
- [20] M.J. Rosen, *Surfactants and Interfacial Phenomena*, 2nd edn (John Wiley and Sons, New York, 1989).
- [21] D.A. Sabatini, R.C. Knox and J.H. Harwell, "Emerging technologies in surfactant-enhanced subsurface remediation," In: (D.A. Sabatini, R.C. Knox and J.H. Harwell, eds) *Chapter 1 in Surfactant Enhanced Subsurface Remediation – Emerging Technologies*, ACS Symposium Series 594 (American Chemical Society, Washington, DC, 1995) pp. 177–190.
- [22] C.T., Johnston, "Sorption of organic compounds on clay minerals: A surface functional group approach," In: (B. Sahwney, ed.) *CMS Workshop Lectures, Vol. 8, Organic Pollutants in the Environment* (The Clay Mineral Society, Boulder, CO, 1996) pp. 2–44.

- [23] J.C. Fountain, C. Waddell-Sheets, A. Lagowski, C. Taylor, D. Frazier and M. Byrne, "Enhanced removal of dense non-aqueous phase liquids using surfactants; Capabilities and limitations from field trials," In: (D.A. Sabatini, R.C. Knox and J.H. Harwell, eds.) *Chapter 13 in Surfactant Enhanced Subsurface Remediation – Emerging Technologies*, ACS Symposium Series 594 (American Chemical Society, Washington, DC, 1995) pp. 177–190.
- [24] D.F. Lowe, C.L. Oubre, C.H. Ward and others, *Surfactants and Cosolvents for NAPL Remediation: A Technology Practices Manual* (Lewis Publishers, Boca Raton, FL, 1999).
- [25] C.A. Staples and S.J. Geiselmann, "Cosolvent influences on organic solute retardation factors," *Ground Water* **26**(2), 192–198 (1988).
- [26] C.T. Jafvert, "Surfactants and cosolvents," Technology Evaluation Report, TE-96–02, Ground-Water Remediation Technologies Analysis Center, December 1996.
- [27] S. Pamukcu, "Electrokinetic removal of coal tar constituents from contaminated soils," Final Report, Electric Power Research Institute, EPRI TR-103320, Project 2879–21, 1994.
- [28] M.R. Taha, "Micellar electrokinetic remediation of TNT from soil," PhD thesis, Dept. of Civil and Environmental Engineering, Louisiana State University and Agricultural and Mechanical College, 1996.
- [29] K.A. Bourbonnais, G.C. Campeau and L.K. MacClellan, "Evaluating effectiveness of *in-situ* flushing with surfactants," In: (D.A. Sabatini, R.C. Knox and J.H. Harwell, eds.) *Chapter 12 in Surfactant Enhanced Subsurface Remediation – Emerging Technologies*, ACS Symposium Series 594 (American Chemical Society, Washington, DC, 1995) pp. 161–176.
- [30] D.A. Edwards, R.G. Luthy and Z. Liu, "Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions," *Environmental Science and Technology* **25**(1), 127–133 (1991).
- [31] D.A. Edwards, Z. Liu and R.G. Luthy, "Experimental data and modeling for surfactant micelles, HOCs, and soil," *Journal of Environmental Engineering* **120**(1), 23–41 (1994).
- [32] M.M. Joshi and S. Lee, "Optimization of surfactant-aided remediation of industrially contaminated soils," *Energy Sources* **18**, 291–301 (1996).
- [33] S. Ko, M.A. Schlautman and E.R. Carraway, "Effects of solution chemistry on the partitioning of phenanthrene to sorbed surfactants," *Environmental Science and Technology* **32** (22), 3542–3548 (1998).
- [34] D.A. Edwards, Z. Adeel and R.G. Luthy, "Distribution of nonionic surfactant and phenanthrene in a sediment/aqueous system," *Environmental Science and Technology* **28**(8), 1550–1560 (1994).
- [35] S. Ko, M.A. Schlautman and E.R. Carraway, "Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies," *Environmental Science and Technology* **32** (18), 2769–2775 (1998).
- [36] R.P. Schwarzenbach, P.M. Gschwend and D.M. Imboden, *Environmental Organic Chemistry* (John Wiley and Sons, Inc., New York, 1993).
- [37] USEPA, *Test Methods for Evaluating Solid Waste*, Volume 1A: Laboratory Manual, Physical/Chemical Methods, SW-846, 3rd edn (Office of Solid Waste and Emergency Response, Washington, DC, 1986).
- [38] C.T. Jafvert, C. Wei and P.L. Van Hoof, "A quantitative structure-activity relationship for solubilization of nonpolar compounds by nonionic surfactant micelles," In: (D.A. Sabatini, R.C. Knox and J.H. Harwell, eds) *Chapter 3 in Surfactant Enhanced Subsurface Remediation – Emerging Technologies*, ACS Symposium Series 594 (American Chemical Society, Washington, DC, 1995) pp. 24–37.
- [39] J.C. Means, S.G. Wood, J.J. Hassett and W.L. Banwart, "Sorption of polynuclear aromatic hydrocarbons by sediments and soils," *Environmental Science and Technology* **14**(12), 1524–1531 (1980).
- [40] S. Banerjee and S.H. Yalkowski, "Cosolvent-induced solubilization of hydrophobic compounds into water," *Analytical Chemistry* **60**, 2153–2155 (1988).