To the Graduate Council:

I am submitting herewith a dissertation written by ICK TAE YEOM entitled " Surfactant-Enhanced Solubilization and Biodegradation of Polycyclic Aromatic Hydrocarbons in Coal Tar Contaminated Soil". I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Civil Engineering.

Mriganka M. Ghosh, Major Professor

We have read this dissertation and recommend its acceptance;

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

SURFACTANT-ENHANCED DISSOLUTION AND BIODEGRADATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN COAL TAR CONTAMINATED SOIL

A Dissertation

Presented for the

Doctor of Philosophy

Degree

The University of Tennessee, Knoxville

Icktae Yeom

December, 1995

DEDICATION

This Dissertation is dedicated to my parents

Mr. and Mrs. Wonhak and Kweunok Yeom

who have given me invaluable educational opportunities.

ACKNOWLEDGMENT

I would like to express my gratitude to my major professor, Dr. Mriganka Ghosh for his guidance and encouragement throughout my graduate study at the University of Tennessee, Knoxville. I am also grateful to my committee members, Dr. Chris Cox, Dr. Kevin Robinson, Dr. Bruce Robinson, Dr. Gary Sayler and Dr. Michael Essington for their assistance, input and encouragement through my research. I would like to further extend my gratitude to Dr. Chris Cox for his personal advice and encouragement specially when there seemed to be no end to the tunnel. I wish to express my sincere appreciation to Dr. Gary Sayler and the people at the Center for Environmental Biotechnology for their help, advice and fruitful discussions throughout my stay in the laboratory. In addition, I would like to thank LingLing Chu, Zhou Shi, Wally Hunt and Haejin Woo for their support and friendship. Special thanks is extended to Dr. Raji Ganesh. With sincerity and thoughtfulness, he helped me whenever I was down and we became best of friends.

I acknowledge the financial support received from the U.S. Environmental Protection Agency through Grant No. R819168010.

I would like to thank my family for their support and patience, without which my graduate study would not have been possible. I thank my parents for their constant and dedicated loving support. I am especially indebted to my wife, Seonghee Kong, for her sacrifice and moral support. I also thank my daughter, Hyuna, for the joy and inspiration she has brought to us. Lastly, but most sincerely, I thank God for his guidance and love.

He has walked me through the difficult times of my life with incredible love. Whatever I accomplished belongs to Him.

ABSTRACT

What controls PAH biodegradation in tar-contaminated soils? What role must surfactants play in facilitating bioremediation in such soils? The present research sought answers to these key questions. Thermodynamic equilibria and kinetics of surfactant-PAH interactions in tar-contaminated soils are considered with some rigor in parts two and three of this report. These are brought to fore in part four to gain insight into the limitations and benefits of surfactant-mediated bioremediation of tar-contaminated soils. Five nonionic polyoxyethylene (POE) surfactants and a tar-contaminated soil from a manufactured gas plant (MGP) site were used in this study. Equilibrium distribution of four PAHs, phenanthrene, anthracene, pyrene, and benzo(a)pyrene among soil, water, and micelle phases was determined for given soil-to-surfactant ratios. Up to 30 % of Soxhlet-extractable PAHs could be solubilized in 16 days in completely stirred batch reactors at surfactant loadings of 0.055 g/g soil. Longer periods were required to reach equilibrium at higher surfactant dosages. Surfactants with higher hydrophile-lipophile balance (HLB) produced greater solubilization. Raoult's law satisfactorily described the partitioning of constituent PAHs between the weathered tar and the water. An equilibrium model was developed to predict the solubilization of constituent PAHs for given properties of soil and surfactant. Prediction was satisfactory at relatively low surfactant dosages (< 5.5 g/L). The model overestimated solubilization at higher surfactant dosages. Presumably, thermodynamic equilibrium could not be reached during the duration (380 hours) of the experiments because of mass transfer limitations.

To determine the maximum rates of PAH release achievable under such kinetic limitations, experiments were conducted in the presence of Tenax resin in which organic solutes are known to partition nearly completely. With Tenax in water most constituent PAHs failed to attain equilibrium during the 55-day experiments. However, the release of PAHs significantly increased upon the addition of surfactants. It is postulated that surfactants promote PAH release by two mechanisms: 1) they significantly increase the solubilities of PAHs in micellar solution, and, in so doing they increase the concentration gradient at the tar-water interface; 2) they penetrate and swell the polymeric tar phase and thereby increase matrix diffusivities of PAHs. A modified radial diffusion model was used along with a parametric sensitive analysis to evaluate the relative importance of these mechanisms in surfactant washing of contaminated soils. The matrix diffusivity increased by up to two orders of magnitude in soils washed with 5.5 g/L surfactant solutions. It was concluded that surfactants promote PAH release from contaminated soils mainly by increasing the matrix diffusivities of contaminants; increase in solubility by micellar solubilization plays only a secondary role. Further, the diffusivity enhancement is related to the structure of the surfactant. Surfactants with smaller ethoxylate (polar) head groups and linear alkyl chains performed much better than those with larger head groups and/or branched hydrophobic chains.

Biodegradation of soil-bound PAHs in MGP soil was investigated with and without surfactants. On occasion, soils artificially contaminated with a single PAH were used to develop baseline information on biodegradation employing substrate-specific microbial strains. While surfactants did not affect mineralization of PAHs in soils contaminated for a

short period (2 days), they clearly did so in soils contaminated for longer periods (10 months). Biodegradation of PAHs in the MGP soil appeared to be limited by the slow release of PAHs from soil. With no surfactant added, 40-45 % of phenanthrene was degraded in 98 days while biodegradation of PAHs with more than three aromatic rings was insignificant. Biodegradation of high ring PAHs increased somewhat at supra-CMC dosages. At dosages of 2.5 g/L or higher, both Triton X-100 and Brij 35 resulted in 70-80 % degradation of phenanthrene in 98 days. However, the surfactants themselves were also degraded in the process. In fact, all surfactants except Triton X-100 were completely degraded in 25 days. Biodegradation of PAHs was highest in soil samples washed with the least biodegradable surfactant.

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LIST OF SYMBOLS

$C_{aq,tot}$: total aqueous concentration in surfactant solution, $[M/L^3]$

$C_{aq,i}$: aqueous concentration of compound i in multi-component system, $[M/L^3]$

C_i^L : aqueous solubility of a pure subcooled liquid i, $[M/L^3]$

C_i^S : aqueous solubility of a pure solid i, $[M/L^3]$

C_{mic} : concentration of a compound in micellar pseudophase, $[M/L^3]$

C_{sat} : aqueous solubility of a NAPL constituent, $[M/L^3]$

C_w : solubility of a compound in distilled water, $[M/L^3]$

D_a : Damcohler number, [-]

D_s : diffusivity of a compound in contaminant-soil matrix, $[L^2/T]$

F_{ct} : mass fraction of tar in MGP soil, [M/M]

f^L, f^S : fugacities of a pure compound in subcooled liquid and solid states, respectively, $[M/LT^2]$

f_{oc} : soil organic carbon content, [M/M]

f_{om} : soil organic matter content, [M/M]

k_{bio} : first order biokinetic coefficient, [1/T]

K_d : distribution coefficient between soil and solution, $[L^3/M]$

k_L : mass transfer coefficient, [L/T]

k_La : bulk mass transfer coefficient, [1/T]

K_m : micelle-water partitioning coefficient, $[L^3/M]$

$K_{NAPL-aq}$: NAPL-water partitioning coefficient, $[L^3/M]$

K_{oc} : soil-water partitioning coefficient normalized for soil organic carbon, $[L^3/M]$

K_{ow} : octanol-water partitioning coefficient, [mole/mole]

$K_{soil/tar\text{-}aq,i}$: soil/tar-water partitioning coefficient, [L^3/M]

$K_{soil/tar\text{-}mic,i}$: soil/tar-micelle partitioning coefficient, [M/M]

$K_{soil\text{-}aq}$: soil-water partitioning coefficient, [L^3/M]

$K_{T\text{-}aq}$: Tenax-water partitioning coefficient, [L^3/M]

$[M_{aq}]$, $[M_{mic}]$: mass of a compound in aqueous, micellar pseudophases, respectively, [M]

M_H, M_L : formula weights of the hydrophilic and lypophilic portions of a surfactant molecule, respectively, [M]

M_{mc} : mass of a micelle core, [M]

M_{mic} : mass of a micelle, [M]

M_o : initial mass of a compound in soil phase, [M]

m_s : mass of soil, [M]

M_t : mass of a compound in soil phase at time t, [M]

$[M_{total}]$: total mass of a compound in a system, [M]

MW_{ct} : average molecular weight of coal tar, [M/mole]

MW_i : molecular weight of a compound i, [M/mole]

q^o_{NAPL} : initial concentration of a compound in NAPL phase, [M/M]

$q^o_{soil,i}$: initial concentration of the compound i in soil phase, [M/M]

$q_{soil,i}$: concentration of a compound i in soil phase, [M/M]

$q_{soil/tar,i}$: concentration of i in soil/tar phase, [M/M]

q_{surf} : surfactant concentration in the soil phase, [M/M]

R : radius of soil particle, [L]

SL : surfactant loading per unit mass of soil [M/M]

SL' : mass of micelle applied per unit mass of soil, [M/M]

S_{mic} : concentration of micelle, [M/L^3]

V_{aq} : bulk aqueous volume, [L^3]

V_{mc} : volume of a micelle core, [L^3]

W^o_{NAPL}: initial mass of NAPL per unit volume of water, [M/L^3]

W_{soil} : mass of soil per unit volume of water, [M/L^3]

W_T : mass of Tenax per unit volume of water, [M/L^3]

$x_{ct,i}$: mole fraction of a compound i in coal tar phase, [mole/mole]

X_m, X_a : mole fraction of a compound in micellar and aqueous pseudophases, respectively [mole/mole]

γ_m, γ_a : activity coefficients of a compound in micellar and aqueous pseudophases, respectively, [-]

ρ_{mc} : density of micellar core, [M/L^3]

LIST OF ABBREVIATIONS

CMC : Critical Micelle Concentration

HLB : Hydrophile-Lipophile Balance

HOC : Hydrophobic Organic Compound

MC : Methylene Chloride

MGP : Manufactured Gas Plant

NAPL : Nonaqueous Phase Liquid

PAH : Polycyclic Aromatic Hydrocarbon

POE : Polyoxyethylene (surfactant)

SOM : Soil Organic Matter

PART 1

INTRODUCTION

Contamination of soil and groundwater by polycyclic aromatic hydrocarbons (PAHs) has been a major concern due to their potential carcinogenicity and mutagenicity (McCann and Ames, 1975; Kingsbury *et al.,* 1979). PAHs are nonpolar, neutral, hydrophobic organic molecules comprised of two or more fused benzene rings. They are present at high concentrations in the soils of many industrially contaminated sites including former manufactured gas plant (MGP) sites.

Due to their hydrophobic properties and limited solubilities, PAHs are strongly bound to soil and fairly immobile, but their dissolution is sufficient to contaminate large amount of groundwater over a long period of time (Luthy *et al.*, 1994). Remediation of such sites has been one of the challenging tasks in environmental restoration. The performance of water-based remediation technologies such as pump and treat is limited primarily due to the slow rate of contaminant release from the soil-contaminants matrix (GRI, 1992; Rao and Loehr, 1992; Roy *et al.*, 1995). It appears that contaminants bound to soil are protected from microbial attack and must be released into aqueous phase to be degraded (Alexander, 1981; Ogram *et al.*, 1985). Bioremediation even under ideal environmental conditions has achieved only limited success (Erickson *et al.*, 1993; Wilson and Jones, 1993). Seemingly, the release of PAHs from the soil-contaminant matrix is critical in meeting cleanup goals. Use of surfactant washing has been proposed as a pretreatment for remediating soils contaminated with hydrophobic organic compounds (HOCs). Surfactants can increase the aqueous solubilities of nonaqueous phase liquids (NAPLs) and also promote the release and dissolution of soil-

bound contaminants. In so doing, surfactants may improve the performance of pump and treat and other soil washing operations. By the same token, surfactants may increase the bioavailability of soil-bound HOCs.

Studies so far have shown that surfactants can effectively solubilize HOCs in soil-water systems. For nontoxic surfactants, the micelle-solubilized compounds appear to be eventually biodegraded. However, the effectiveness of surfactants in field applications is still largely unknown. Most of the past studies have focused on the equilibrium distribution of HOCs using laboratory-contaminated soils. Information on the effect of surfactants on the slow release of contaminants from weathered, field contaminated soil is sparse. In particular, effect of surfactant on the diffusional mass transfer within the contaminant-soil matrix has not been addressed though it may control the release of contaminants from soil. Such information is essential for a realistic assessment of benefits of using surfactant in remediating PAH-contaminated sites.

The purpose of this study was to evaluate the effects of nonionic polyoxyethylene surfactants in solubilization and biodegradation of soil-bound PAHs. Both equilibrium and kinetic aspects of solubilization were investigated. Equilibrium solubilization of soil-bound PAHs were studied using two different soils: an artificially contaminated soil and a coal tar contaminated soil from an MGP site. The artificial soil was lightly contaminated with a single PAH and the MGP soil was heavily contaminated with multicomponent coal tar. A model was developed to estimate the extent of PAH release from the soils by

washing the contaminated soils with different amounts of POE surfactants. Kinetic aspects of solubilization were studied only with the MGP soil which exhibited severe mass transfer limitations. The mass transfer rates of PAHs in surfactant solutions were compared with those in the presence of polymeric Tenax-TA adsorbent. The effects of surfactants on the diffusional mass transfer within the soil-tar matrix were evaluated using a modified radial diffusion model.

Biodegradation of soil-bound PAHs were studied using soil-surfactant slurries. Pure cultures were used for the artificially contaminated soil while a natural consortium of microorganisms was used for the MGP soil. Based on the results, the potential factors controlling the efficiency of surfactant-mediated bioremediation were discussed.

The specific objectives of this study were:

- To develop a model for the equilibrium solubilization of PAHs in a single and multicomponent systems;
- To evaluate the effects of surfactants on the matrix diffusion of individual PAHs within the organic phase of MGP soil;
- To determine the effects of surfactants on the biodegradation of soil-bound PAHs; and
- To identify the factors controlling the performance of surfactants in enhancing bioremediation of PAH contaminated soils.

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PART 2

EQUILIBRIUM CONSIDERATIONS IN MICELLAR SOLUBILIZATION OF PAHS FROM COAL TAR CONTAMINATED SOIL

1. INTRODUCTION

Surfactants create a hydrophobic micellar pseudophase in water into which a large amount of HOCs can partition. Thus, they may solubilize soil-bound contaminants, increasing mass transfer of the contaminants from soil to the solution phase. The solubilized contaminants can then be treated by chemical or biological means.

A number of laboratory studies have been performed on surfactant-mediated solubilization of HOCs (Vigon and Rubin, 1989; McDermont *et al.*; Kile and Chiou, 1989). In batch tests, up to 90 % of PAHs could be recovered from soils with moderate f_{oc} (0.9-3.4%) using nonionic polyoxyethylene (POE) surfactants (Liu *et al.*, 1991; Yeom and Ghosh, 1993). One anionic surfactant, sodium dodecyl sulfate (SDS) also showed a similar efficiency in mobilizing phenanthrene and pyrene from similar soils (Jafvert, 1991). The effectiveness of surfactants in mobilizing hydrophobic contaminants was also demonstrated by column studies. Ellis *et al.* (1985) recovered more than 90 % of PCBs, chlorinated phenols, and petroleum hydrocarbons from a soil column by flushing with a 15 g/L surfactant solution. Similar results were reported by Abdul and Gibson (1991); 55 - 85 % of the PCBs was recovered from a soil column after washing with 20 pore volumes of 5-20 g/L solutions of alcohol ethoxylate surfactants.

Based on these results, surfactant treatment of contaminated soils, either by washing or flushing, has been proposed as a promising technique for mobilization of HOCs. However, most studies to date primarily considered solubilization of a single

compound from artificially contaminated soils. Studies on the solubilization of a complex mixture such as coal tar residues in MGP soils are sparse. Extrapolation of results from single component systems to complex, multi-component systems may cause significant errors. For example, the aqueous solubility of PAHs in coal tar is much less than their intrinsic aqueous solubilities (Lee *et al.*, 1992). Solubilization of individual compounds from such mixtures may be much lower than that estimated in single component systems.

Equilibrium aspects of solubilization of PAHs from a weathered MGP soil by nonionic polyoxyethlene (POE) surfactants are examined in this part. Solubilization of a single PAH from an artificially contaminated soil is also determined for comparison. The kinetic limitations to mass transfer of soil-bound contaminants are considered in Part 3. A model is developed to describe the partitioning of individual PAHs between the soil/tar phase, aqueous pseudophase, and micellar pseudophase. Based on the model predictions, estimates are made of the extent of PAH release from the soil at different soil/surfactant ratios.

2. BACKGROUND

The ability of surfactants to increase the solubilities of HOCs and their mobility in the soil environment has been the goal of many studies. In general, studies in the literature have focused on three specific subjects: 1) the micellar behavior of surfactants and the mechanism of solubilization, 2) the solubilization capacities of different types of surfactants for HOCs of environmental concern, and 3) the release of NAPLs from contaminated soils in the presence of surfactants. These subjects are briefly reviewed in this chapter. Finally, the dissolution of coal tar components in water is discussed. Only equilibrium aspects of solubilization are covered in this chapter. The kinetic aspects of PAH release from soil is reviewed in Part 3.

2.1 Mechanism of Solubilization

Surfactants are amphipathic molecules containing both hydrophilic and hydrophobic moieties. While the hydrophilic group has high affinity for polar solvents such as water, the hydrophobic group has little affinity for polar solvents. This unique structure is responsible for the high surface activity of surfactants.

The nonpolar moiety of the surfactant molecule is not compatible with water. Therefore, its presence in the interior of water causes distortion of the ambient water structure, increasing the free energy of the system (Rosen, 1989). Therefore, the removal of the hydrophobic portion of the molecules from its aqueous environment is a thermodynamically favorable process. However, the presence of the hydrophilic group in

the same molecule prevents the surfactant molecule from being expelled completely from the solvent as a separate phase. As a result, surfactant molecules are concentrated at the interface (air-water and/or oil-water) to minimize the free energy of the system with its hydrophilic portion oriented towards the aqueous phase and its hydrophobic portion away from it. Another mechanism to decrease the free energy of the system is the aggregation of surfactant molecules into a cluster in the bulk solution with their hydrophobic groups directed towards interior of the cluster. The hydrophobic groups compose the core of the cluster and are shielded from the surrounding water by the hydrophilic groups. This cluster is called a 'micelle' and the formation of micelle is called 'micellization'. The congregation of surfactant molecules at the interface is favored over micellization at relatively low surfactant concentration. As the surfactant concentration of the solution increases, the interface becomes saturated with surfactant molecules and micellization becomes the dominant mechanism reducing the free energy of the system. The concentration at which micelles first appear is called 'critical micellization concentration' (CMC) and it varies with the structure of a surfactant.

One of the most important consequences of micellization is that micelles are capable of solubilizing organic compounds of limited water solubility. Like the hydrophobic group of surfactant molecule, HOCs are incompatible with water molecules in the aqueous phase due to the strong hydrogen bond between water molecules. Unlike surfactants, HOCs are mostly separated from the solution. As a result, HOCs have very low solubilities in water. Such repulsive interactions between water and HOC is known as the 'hydrophobic effect' (Tanford, 1980). However, the presence of micelles in water

provides a mechanism for HOCs to stay in solution phase without increasing the free energy of the system. Instead of being separated from the solution phase, HOCs can be incorporated into the nonpolar, hydrocarbon-like micellar core. This process is called 'micellar solubilization' or simply 'solubilization' .

In general, solubilization can be defined as 'the preparation of a thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in a given solvent by the introduction of an additional amphiphilic component or components' (Attwood and Florence, 1983). Solubilization is distinguishable from 'emulsification', which is defined as 'dispersion of one liquid in another in the form of droplets' (Becher, 1965). The key difference between solubilization and emulsification is that the solubilized material is considered to be dissolved in the same phase as the solubilizing solution while the emulsified droplet is considered to be a separate phase from the surrounding liquid phase (Attwood and Florence, 1983). As discussed earlier, solubilization is a thermodynamically favored process and the reaction occurs spontaneously. On the other hand, emulsification is thermodynamically unfavorable due to the increase of the interfacial area between the two immiscible liquids. As a result, emulsification occurs only by application of mechanical energy (i.e. shaking) and the emulsion produced is highly unstable thermodynamically.

2.2 Solubilization of HOC in Aqueous System

The hydrophobic groups (-CH_2- chain) in a micelle are generally considered to be disordered, so that the hydrophobic core of a micelle is in effect a small volume of liquid

hydrocarbon. This is different from a large volume of liquid hydrocarbon in that all of the liquid is influenced by the closeness of the liquid to the surface (Valsaraj and Thibodeaux, 1989). However, the freedom of the motion of the hydrophobic group in a micelle is more like to that in a liquid hydrocarbon (Tanford, 1980). Therefore, the micellar solubilization of HOC can be described as the partitioning of HOC between monomer-saturated water and the liquid hydrocarbon of the micellar pseudophase.

At equilibrium, the chemical potential of a solute in the micellar and the aqueous pseudophases (The term 'aqueous pseudophase' denotes the aqueous phase saturated with surfactant monomers) should be equal. Thus :

$$f_o^L \gamma_m X_m = f_o^L \gamma_a X_a \qquad (1)$$

where $f_O{}^L$ is the fugacity at the reference state, γ is the activity coefficient, and X is the mole fraction of the solute. The subscripts *m* and *a* denote the micellar and the aqueous pseudophases, respectively. The ratio of the HOC concentrations in the micellar and aqueous pseudophases is defined as the micelle-water partitioning coefficient, K_m, (Edwards *et al.*, 1991) and is given by:

$$K_m = \frac{X_m}{X_a} = \frac{\gamma_a}{\gamma_m} \qquad (2)$$

The micelle-water partitioning coefficient has been shown to be relatively constant for a given surfactant-solute system over a wide range of concentration above

the CMC and is used to define the solubilizing power of a micelle for a specific HOC (Stearns, 1947; Almgren, 1979; Jafvert, 1991; Edwards *et al.*, 1991). Depending on how the aqueous pseudophase is approximated, two different approaches have been used to determine K_m. Edwards *et al.* (1991) approximated the aqueous pseudophase as the surfactant solution at the CMC, so that X_a in the presence of excess HOC crystals is given by the solubility of HOC at the CMC. On the other hand, Jafvert *et al.* (1994) used distilled water as the reference state for the aqueous pseudophase and X_a in Eq. 2 represents the solubility of a HOC in distilled water. In the first approach, determination of K_m is not always accurate because the measured solubility of a HOC at the CMC often varies significantly. CMC is a range of concentration rather than a fixed value (Rosen, 1989), and the solubility of a HOC varies widely depending on the value of CMC used. Such variabilities can be overcome by using the solubility of a HOC in distilled water that can be accurately measured and is available in the literature. Using distilled water solubility and normalizing X_m for mass units, K_m (L/g) can be expressed as:

$$K_m = \frac{C_{mic}}{C_w S_{mic}} \tag{3}$$

where C_{mic} is the concentration of a HOC in the micellar pseudophase in the presence of excess crystals based on total aqueous volume (g/L) and C_w is the solubility of the HOC in distilled water. S_{mic} is the concentration of surfactant in micellar form (g/L).

The solubilization capacity of a surfactant for a given HOC measured by K_m depends on the characteristics of both the surfactant and the compound solubilized (solubilizate). One of the most important characteristics of surfactants influencing solubilization is the relative size of the hydrophobic and hydrophilic groups of the surfactant molecule. In general, the solubilizing capacity of a surfactant increases with the length of alkyl chain (Klevens, 1950; Ismail *et al.*, 1970) while it decreases with the size of hydrophilic head group (Ismail *et al.*, 1970; Barry and El Enny, 1976). The combined effect has been reported in terms of the relative ratio of polar and nonpolar groups, often represented by the hydrophile-lipophile balance (HLB) (Saito and Shinoda, 1967; Kile and Chiou, 1989; Diallo *et al.*, 1994). The ionic type of the surfactant is also important in solubilization. In general, the order of solubilizing power of a surfactant for HOCs is as follows: nonionics>cationics>anionics (Saito, 1967; Tokiwa, 1968; Liu *et al.*, 1991). Another important factor affecting solubilization is the hydrophobicity of the solubilizate, often measured by the octanol-water partitioning coefficient, K_{OW}. Since the micelle core can be described as a liquid-like hydrocarbon phase, the micelle-water partitioning of a solute can be likened to the partitioning between water and bulk organic solvents such as octanol. A log-linear relationship between K_m and K_{OW} has been reported with the slope close to unity (Valsaraj and Thibodeaux, 1989; Edwards *et al.*, 1991). Other conditions such as temperature and electrolyte concentration are also important and reviewed in detail elsewhere (Attwood and Florence, 1983).

Solubilization of multiple compounds has received little attention. Information on multi-component systems is sparse in the literature, despite the practical importance of such cases. Crooks and Brown (1973) investigated the effect of a second solubilizate on the solubilization capacity of a particular solubilizate. No general pattern was observed; both synergistic and antagonistic effects were observed for co-solubilization of two solubilizates.

2.3 Solubilization of HOC in Soil-Water System

Solubilization of HOCs in soil-water system involves interactions between soil and other phases. In addition to water-micelle partitioning of the HOC, surfactant-soil interaction and soil-water partitioning of the HOC should be considered. When an HOC is present as a NAPL, the solubilization becomes more complex. In this section, the solubilization of a HOC is discussed in terms of its equilibrium partitioning between the different phases of a given system.

Nonionic Surfactant Sorption:

At supra-CMC dosages, sorption of surfactant results in the loss of micelles. Therefore, the sorbed surfactant is not available for solubilization of soil-bound HOC (Yeom and Ghosh, 1993; Edwards *et al.*, 1994a; Sun *et al.*, 1995). On the other hand, the sorbed surfactant acts as an additional sorbent for HOCs, arguably better than the natural soil organic matter (SOM) (Edwards *et al.*, 1994a).

Due to their widespread use and disposal into waste waters and surface waters, anionic surfactants have been used in most studies on surfactant sorption onto soils (Fink *et al.*, 1970; DiToro *et al.*, 1990). Literature on the sorption of nonionic surfactants to soil or sediment is sparse. Most studies with nonionic surfactants deal with adsorption of surfactants on a clean, homogeneous surface such as silica gels or glass beads (Partyka *et al.*, 1984; Levitz and Van Damme, 1986; Michalek *et al.*, 1992). For ethoxylated surfactants, formation of a bilayer at the polar solid-liquid interface is postulated. The number of surfactant molecules adsorbed per unit area has been found to be independent of the overall length of the molecules (Partyka *et al.*, 1984). Such mechanistic descriptions of adsorption in well-characterized media may not be adequate for the surfactant sorption on complex media such as natural soils. Early studies indicated that most of the sorbed surfactant was associated with SOM and that sorption equilibrium was approached relatively rapidly (Valoras *et al.*, 1969; Urano *et al.*, 1984). While Langmuir isotherm well described adsorption of surfactants onto clean and homogeneous solid surfaces such as silica gel (Rosen, 1989), often Freundlich isotherm was found to better describe adsorption onto highly heterogeneous media such as soil humus (Liu *et al.*, 1992; Yeom, 1992; Brownawell *et al.*, 1993).

Surfactant-Enhanced Solubilization of HOC in Soil-Water System:

The solubilization of HOCs by a surfactant in a soil-water system can be viewed as partitioning of the compounds into a multiphase system: soil, aqueous pseudophase, and micellar pseudophase. Air, NAPL, and solid crystals are also phases into which the

HOCs may partition in a contaminated subsurface. At equilibrium, the extent of solubilization in a soil slurry is determined by the distribution of a compound between the soil and/or the NAPL, and the aqueous and micellar pseudophases. The solubilization of HOC in a typical soil-NAPL-water system is illustrated in Figure 1. The solubilization efficiency is given by:

$$\% \ Solubilization = 100 \times \frac{[M_{aq}] + [M_{mic}]}{[M_{total}]} \tag{4}$$

where $[M_{aq}]$ and $[M_{mic}]$ are the mass of HOC in the aqueous and the micellar pseudophases, respectively, and $[M_{total}]$ is the mass of HOC originally present in the soil and/or NAPL phases.

The efficiency of a surfactant in mobilizing a given HOC from soil or NAPL depends on the CMC, the extent of surfactant sorption to soil, and the solubilization capacity (K_m). While the first two parameters control the amount of micelle available for solubilization at a given dosage, the last one represents the solubilization efficiency of a micelle on a mass basis. Of the many commercial surfactants, nonionic polyoxyethylenes (POE) appear to be most effective in solubilizing soil-bound HOCs (Vigon and Rubin, 1989; Liu *et al.*, 1991). They are characterized by low CMC values (Rosen, 1989) and relatively high solubilization capacities (Jafvert *et al.*, 1994). In addition, they cause minimum dispersion of soil colloids and are therefore preferred to other surfactants for *in situ* applications (Abdul *et al.*, 1990).

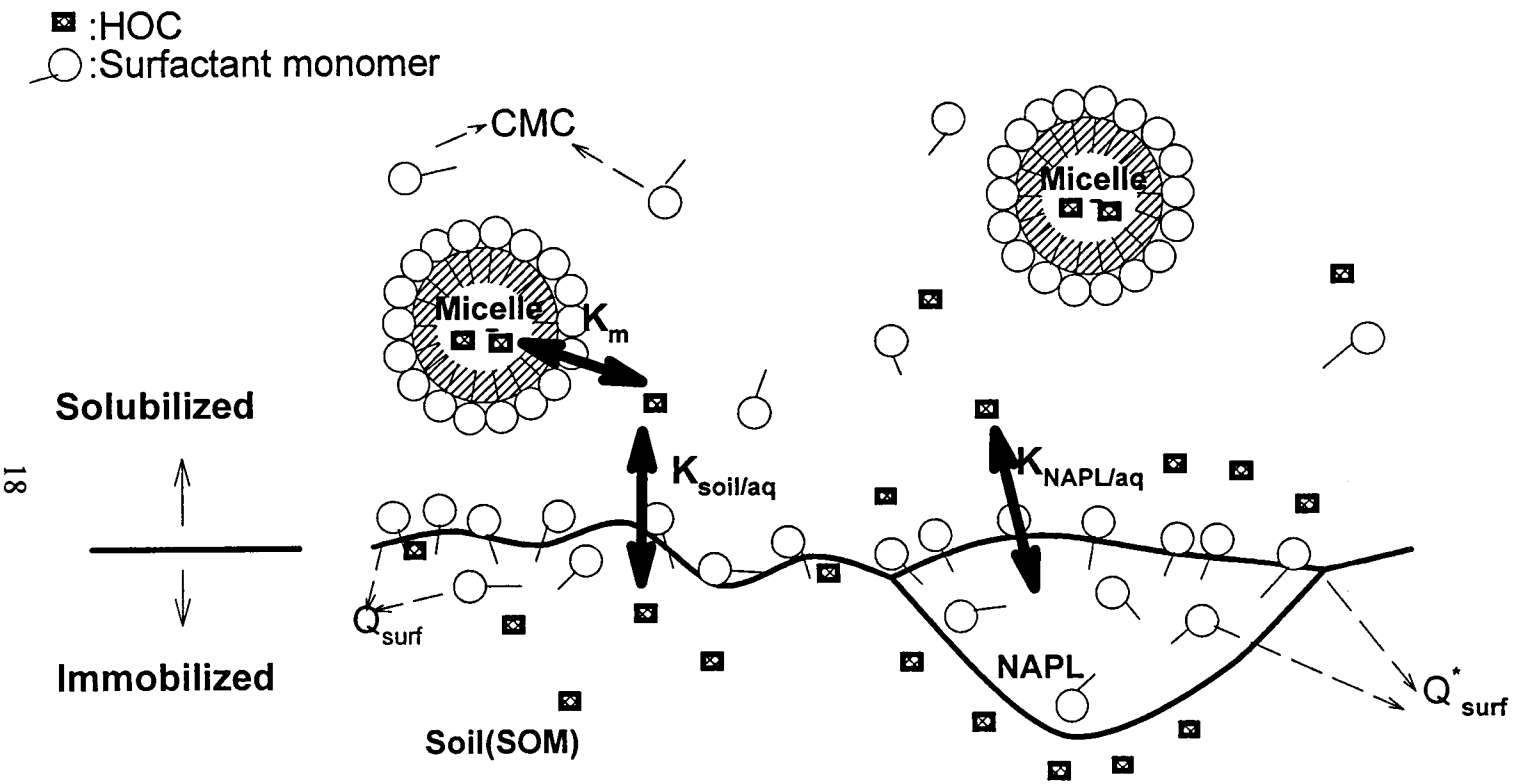


Figure 1. Schematic for solubilizing HOCs in soil-water-NAPL system

Quantitative models of surfactant-enhanced solubilization of HOCs from soil have been developed by including micelle-water partitioning in sorption models (Edwards *et al.*, 1994b; Jafvert, 1991). The primary assumptions in these models are:

- complete reversibility of HOC partitioning between the phases; and
- relatively fast attainment of equilibrium.

Edwards *et al.* (1994b) developed a mathematical model to determine the equilibrium distribution of PAH between soil, water, and micelles; percent solubilization was expressed in terms of partitioning coefficients and mass balance equations. Jafvert (1991) proposed a simple equation for the soil-solution distribution coefficient, K_d by expressing it in terms of the experimental correlations for K_{OC}-K_{OW}, and K_m-K_{OW}:

$$K_d = \frac{0.48 K_{oc} f_{oc}}{[1.0 + 0.15 K_{ow} S_{mic}]} \tag{5}$$

where f_{OC} is soil organic carbon content, and K_{OC} is the soil-water partitioning coefficient normalized for f_{OC}.

2.4 Dissolution of PAHs from MGP Soil into Water

Literature on the surfactant solubilization of individual tar constituents in MGP soils is practically nonexistent. After decades of weathering, mostly high molecular weight organic compounds remain in these soils which cannot be extracted or chemically analyzed.

One of the important factors in remediating MGP soils is the dissolution of tar constituents in water. As shown in Figure 1, the NAPL-water partitioning coefficient directly controls the solubility of HOCs in surfactant solutions. Dissolution of coal tar constituents in water is also important in assessing the extent of groundwater contamination and the long term environmental degradation at MGP sites.

Lane and Loehr (1995) proposed two methods to describe the dissolution of PAHs from MGP soils. The first method is based on the application of Raoult's law which states that, in ideal solutions, the concentration of a component in a given phase is proportional to its mole fraction in that phase. In applying Raoult's law to determine the solubility of individual PAHs from multi-component coal tar in the contaminated soil, one must assume that;

- the coal tar is liquid,
- the SOM originally present in the soil is negligible compared to the mass of coal tar in the soil/tar matrix, and
- the activity coefficient of a constituent in the tar phase is uniform

Based on these assumptions, the aqueous concentration of a component i ($C_{aq,i}$) can be expressed as:

$$C_{aq,i} = x_{ct,i} C_i^L \qquad (6)$$

where $x_{ct,i}$ is the mole fraction of compound i in coal tar and C_i^L is the aqueous solubility of the pure subcooled liquid i at the temperature of the solution. Since most pure PAHs are solids at ambient temperatures, C_i^L cannot be measured directly. It can be obtained using the solubility of pure solid PAH (C_i^S) and the fugacity ratio of the pure compound in subcooled liquid and solid states (Prausnitz *et al.*, 1986):

$$C_i^L = C_i^S \left(\frac{f^L}{f^S} \right)_{pure,i} \tag{7}$$

The second method uses partitioning of HOCs between SOM and water (Karickhoff, *et al.*, 1979):

$$K_{soil-aq} = K_{oc} f_{oc} \tag{8}$$

From the definition of $K_{soil-aq}$ ($= q_{soil}/C_{aq}$), $C_{aq,i}$ can be estimated from:

$$C_{aq,i} = \frac{q_{soil,i}}{K_{oc} f_{oc}} \tag{9}$$

where $q_{soil,i}$ is the concentration (mass basis) of i in soil. K_{OC} values for PAHs can be estimated from the corresponding values of K_{OW} (Means *et al.*, 1980) or obtained from available databases (EPA, 1989). As a sorbent for PAHs, the coal tar matrix is quite

different from te organic matter in natural soils; K_{OC} values estimated from SOM may not be appropriate for coal tar.

Raoult's law estimates of constituent solubilities were reasonably good for both free-flowing coal tar and residual coal tar in soil although the variations were a little higher for the latter (Lee *et al.*, 1992a; Lane and Loehr, 1992; Lane and Loehr, 1995). With few exceptions, the agreement between the predicted and measured values were within a factor of 2 for free-flowing coal-tar and within an order of magnitude for residual coal-tar in MGP soils. Raoult's law has also been applied to other organic mixtures such as diesel fuels and gasoline with similar results (Lee *et al.*, 1992b; Cline *et al.*, 1991).

3. MATERIALS

3.1 Soils

Two soils were used in this study: an uncontaminated soil obtained from middle Tennessee and a coal-tar contaminated soil obtained from an MGP site in New York. The Tennessee soil was air-dried and sieved (U.S. Standard #10; 2mm) without pulverization. The organic carbon fraction of the soil (f_{OC}) was determined by the Plant and Soil Sciences Department at the University of Tennessee, Knoxville by combusting the soil in a Leco CR 12 Carbon System. The particle size distribution (PSD) and bulk density of the soil were measured using sieve analysis for the coarse fractions and hydrometer analysis for the fine fractions (Stanley, 1994).

The MGP soil was homogeneously mixed and stored in a refrigerator at 4°C until used. Proper mixing was ensured using a bromide tracer (Sansavrino, 1994). Ten grams of soil was mixed with 20 mL of sodium bromide (NaBr) solution (5 g/L) in a flask. The soil-water mixture was added to about 10 kg of soil and mixed thoroughly. After mixing, randomly collected soil samples (1 g each) were suspended in 5 mL of deionized (DI) water and the aqueous bromide concentration measured using a bromide-specific electrode (Model 94-35, Orion Co.). A variance of 2.67 % was observed in measured values. The soil was air-dried and sieved through U.S. Standard #35 and #200 sieves. The fraction of particles in the size range of 74-500 μm was used in the study. The organic carbon content (f_{OC}) of the soil was determined by combustion with HCl/HF

pretreatment (ASA, 1965) using Leco CR 12 Carbon System (Stanley, 1994). The measured characteristics of the two test soils are summarized in Table 1.

The concentrations of PAHs in the soil were determined by Soxhlet extraction using Soxtec HT 6 system (Itecator Co., Sweden). This unit consists of a separate heating unit, six extraction ports and condensing units. The extraction procedure involved three steps: extraction with boiling methylene chloride (MC), rinsing with fresh MC, and evaporation of the solvent remaining in the extract. First, 1 g of was weighed in a thimble (26x60 mm, Whatman Co.). The thimbles were immersed in 30 mL of boiling MC ($110^{o}C$) for 6 hours. During extraction the evaporated solvent was recycled by the condensing unit. The thimbles were then lifted from the boiling MC and rinsed for an hour with fresh MC recycled from the condensing unit. Finally, solvent recycling was stopped and the solvent remaining in the extract was allowed to evaporate for 3-5 minutes. The extraction time for each step was so selected as to maximize recovery of PAHs from the soil. Preliminary experiments showed that extraction for longer periods increased the loss of relatively volatile PAHs such as naphthalene and its derivatives without significantly increasing the overall recovery. Extraction for too short a period resulted in an incomplete recovery of most PAHs. Using the above extraction protocol, most extractable PAHs could be recovered. Additional recovery by repeated extractions was insignificant. After cooling, the soil extract in the extraction cup was weighed and the mass of the extract determined. The concentrations of individual PAHs in the extract were determined by reconstituting the extract with 10 mL of MC followed by 1: 100

Table 1. Characteristics of soils

Soil	Particle Size Range (μm)	Particle Density (g/mL)	Organic Carbon Content (%)	Organic Matter Content (%)
Natural soil	< 2000	2.45	1.97	NA
MGP soil	74 - 500	1.72	62.0	75.0 %

dilution with methanol (100 μL MC in 5 mL of methanol). The solution was analyzed for PAHs by high performance liquid chromatography (HPLC). The details of HPLC analysis are given in section 4.1.1. Sixteen PAHs were analyzed and their concentrations in the soil are listed in Table 2. While the soil had 75% organic matter by mass, only 1.5 % of this amount was extractable with MC. The sixteen PAHs listed in the table constitute only 35 % of the extract (0.53% of the total organic matter in soil).

3.2 Surfactants

Five nonionic, polyoxyethylene (POE) surfactants: an alkylphenol ethoxylate (Triton X-100), a polyoxyethylene sorbitan monooleate (Tween 80), and three homologs of a linear alcohol ethoxylate (Brij- series), were used in this study. All homologs had a 12-carbon alkyl chain but different numbers of ethoxylate groups. All surfactants, except the alcohol ethoxylate lauryl-10 ether, were obtained from Aldrich Chemical Co. Lauryl 10 ether was purchased from Sigma Chemical Co. Radiolabeled Triton X-100 (phenyl-^{3}H-, specific activity = 2.37 mCi/mg), used for surfactant sorption studies, was purchased from DuPont Co. All surfactants, including the radiolabeled one, were used as received without further purification. The characteristics of the surfactants are summarized in Table 3. The values of CMC were measured using the surface tension method. The procedures for the surface tension method and C MC determination are given in section 4.1.2. The values of HLB given in Table 3 were obtained from the Calbiochem Co. (Calbiochem, 1994)

Table 2. Concentrations of PAHs in MGP soil (q^{o}_{soil})

PAH	q^{o}_{soil} (μg/g)	PAH	q^{o}_{soil} (μg/g)
Naphthalene	2219(±390*)	Pyrene	170 (±12)
2-Bromonaphthalene	256 (±43)	Benzo[*a*]anthracene	67 (±11)
Acenaphthylene	312 (±101)	Chrysene	143 (±8)
Acenaphthene	244 (±84)	Benzo[*b*]fluoranthene	41 (±12)
Fluorene	112 (±7)	Benzo[*a*]pyrene	43 (±6)
Phenanthrene	333 (±19)	Dibenz[*a,h*]anthracene	26 (±9)
Anthracene	106 (±7)	Benzo[*ghi*]perylene	34 (±7)
Fluoranthene	41 (±12)	Indeno[*1,2,3-cd*]pyrene	32 (±4)

*Number within the parenthesis is standard deviation from 7 samples

Table 3. Characteristics of surfactants

Trade Name	Chemical	Structure[a]	CMC(M)	MW	HLB
Triton X-100	POE(10)octylphenol	C_8PE10	$1.7x10^{-4}$	646	13.5
Tween 80	POE(20) sorbitan monooleate	$C_{18}S_6E_{20}$	$1.2x10^{-5}$	1309	15.0
Brij 30	POE(4) lauryl ether	$C_{12}E_4$	$5.5x10^{-5}$	363	9.7
POE(10) lauryl ether	POE(10) lauryl ether	$C_{12}E_{10}$	$1.0x10^{-4}$	626	14.1
Brij 35	POE(23) aluryl ether	$C_{12}E_{23}$	$9.2x10^{-5}$	1198	16.9

[a] C represents alkyl chain length ($-CH_2-$), P represents a phenol ring ($-C_6H_6-$), E represents an ethoxylate group, and S_6 represents a sorbitan ring.

3.3 Polycyclic Aromatic Hydrocarbons (PAHs)

Four PAHs, phenanthrene, anthracene, pyrene, and benzo(a)pyrene, were measured in all solubilization experiments with MGP soil. In some cases, fluorene was also measured. Reagent-grade PAHs were obtained from Sigma Chemical Co. and used without further purification. The properties of these PAHs were summarized in Table 4.

Table 4. Properties of selected PAHs

PAH	Phenanthrene	Anthracene	Pyrene	Benzo(a)pyrene
Molecular Weight[a]	178.2	178.2	202.3	252.3
Melting point (°C)[a]	101	216	149	179
Boiling point (°C)[a]	340	340	360	496
Aqueous solubility (μg/L)[b]	1290	70	140	3.8
Vapor Pressure (mm Hg) (20°C)[b]	6.8×10^{-4}	1.96×10^{-4}	6.85×10^{-7}	5.0×10^{-7}
Log K_{ow}[b]	4.46	4.45	5.32	6.04

[a] Verschueren (1983)

[b] Sims and Overcash (1983)

4. METHODS

This section consists of three parts. The first part describes the analytical techniques used for measuring PAHs and surfactants. The second part describes the experimental methods used to measure the solubilization of soil-bound PAHs in water and surfactant solutions. This part also includes the methods used for surfactant sorption on soil and for artificially contaminating the Tennessee soil. The third part presents the experimental methods used to determine dissolution of pure PAHs in water.

4.1 Analytical Methods

4.1.1 Analysis of PAH

PAHs were analyzed mostly by HPLC. The HPLC system (Waters Co.) used in this study consisted of two HPLC pumps (Model 501), a WISP autosampler (Model 712), a fluorescence detector (Model 420), and a UV detector (Model 486). The pump operation and sample injection were programmed using 'Baseline 810', a computer software supporting the system. A reverse-phase C-18 column (Vydac Co. Model 201TP5μ) was used. This column is useful for separation of complex mixtures of PAHs (Katz and Organ, 1980; Sander and Wise, 1988). PAHs were measured by both UV and fluorescence detectors. UV absorbance was measured at 254 nm. For fluorescence measurement, 254 nm and 360 nm optical filters were used for excitation and emission of light, respectively. A gradient program was developed to optimize the separation of the

many PAHs released from the MGP soil. The gradient program and eluents are listed in Table 5. The program effectively separated 16 PAHs present in standard PAH mixture (PAH Mix, Restek Co.). The chromatogram of the standard 16 PAH mixture is given in Figure 2. A typical chromatogram of components extracted from MGP soil are shown in Figure 3. Sixteen PAHs were identified by comparing their observed retention times with those of the internal standards. The detection limits for PAHs (in μg/L) were: naphthalene (30), acenaphthene (50), fluorene (6), phenanthrene (3), anthracene (1.5), pyrene (10) and benzo[*a*]pyrene (5).

4.1.2 Surfactants

Though several methods were tested for analyzing surfactants, none was found satisfactory for analyzing all five surfactants over the wide concentration range tested. Triton X-100 could be measured by HPLC up to 20 mg/L using a UV detector. However, other surfactants could not be detected by UV or fluorescence detectors.

HPLC Method:

HPLC with a UV or fluorescence detector has been shown to be useful for separation and analysis of benzene-derived surfactants (Huddleston and Nielsen, 1979; Nakae *et al.*, 1980; Linder and Allen,1982). Ahel and Giger (1984, 1985) analyzed alkylphenol ethoxylates (APE) using HPLC by measuring UV absorbance at 277 nm. The reported detection limit was as low as 1 μg/L. Triton X-100, the only test surfactant containing a benzene ring, was measured by HPLC using the same operating conditions

Table 5. HPLC gradient program used for PAHs in MGP soil

Time (minutes)	% Water	% Acetonitrille	Flow rate (mL/min)
0	50	50	1.8
2	50	50	1.8
16	0	100	1.8
24	0	100	1.8
26	50	50	1.8
28	50	50	1.8

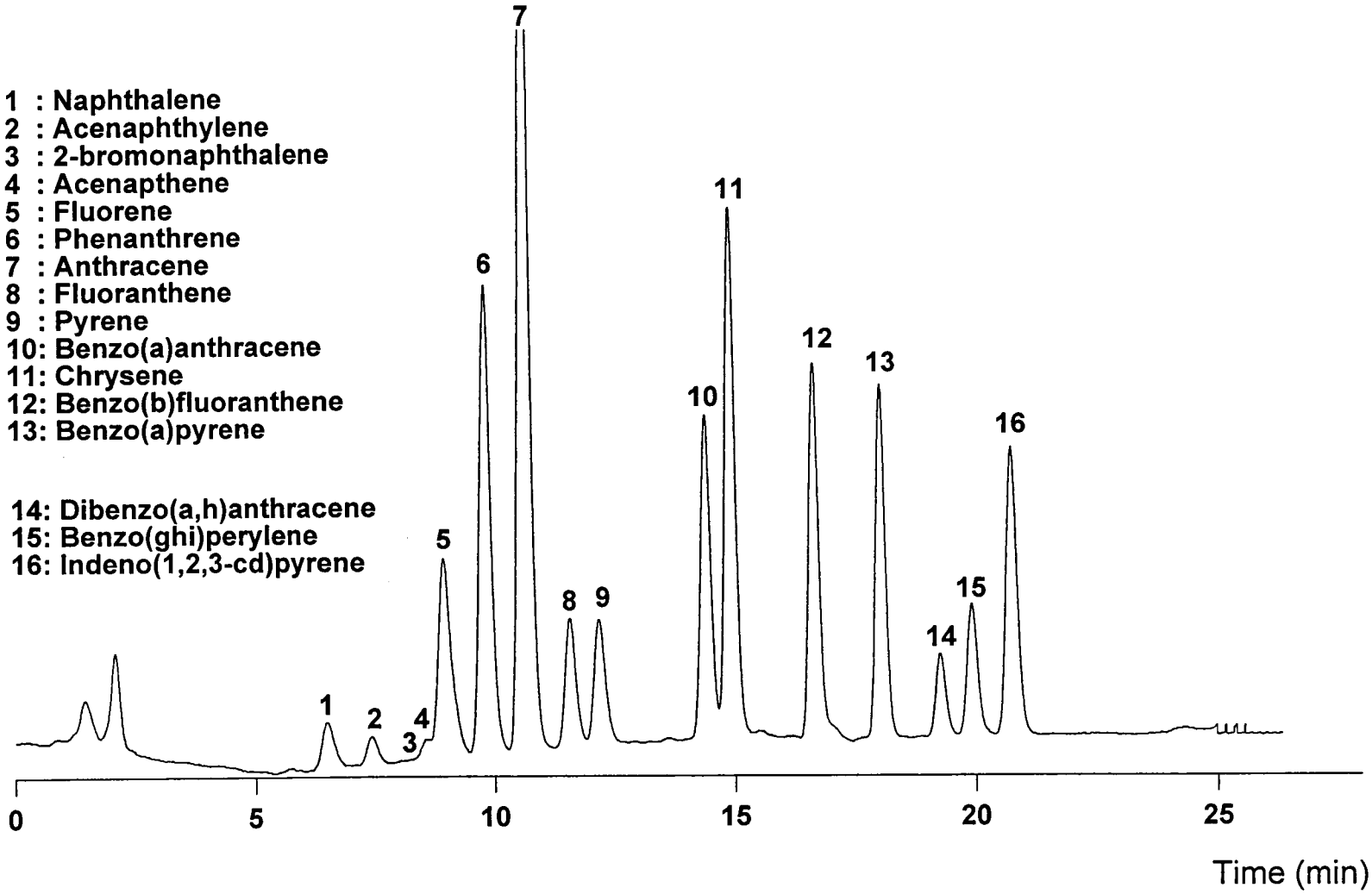


Figure 2. Chromatogram of standard PAH mixture (16PAHs) - UV detector

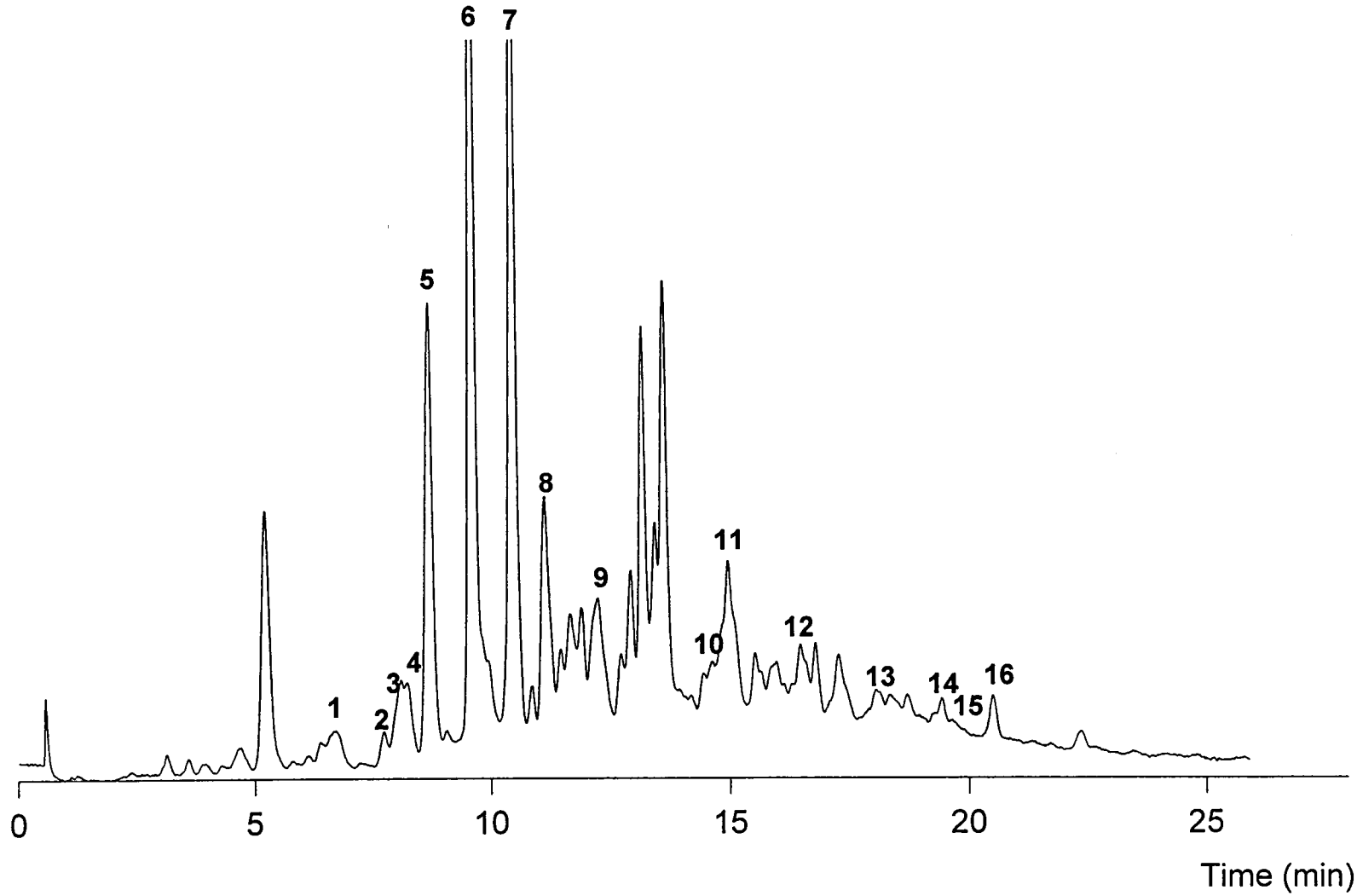


Figure 3. Chromatogram of MGP soil extract: (a) Fluorescence detector

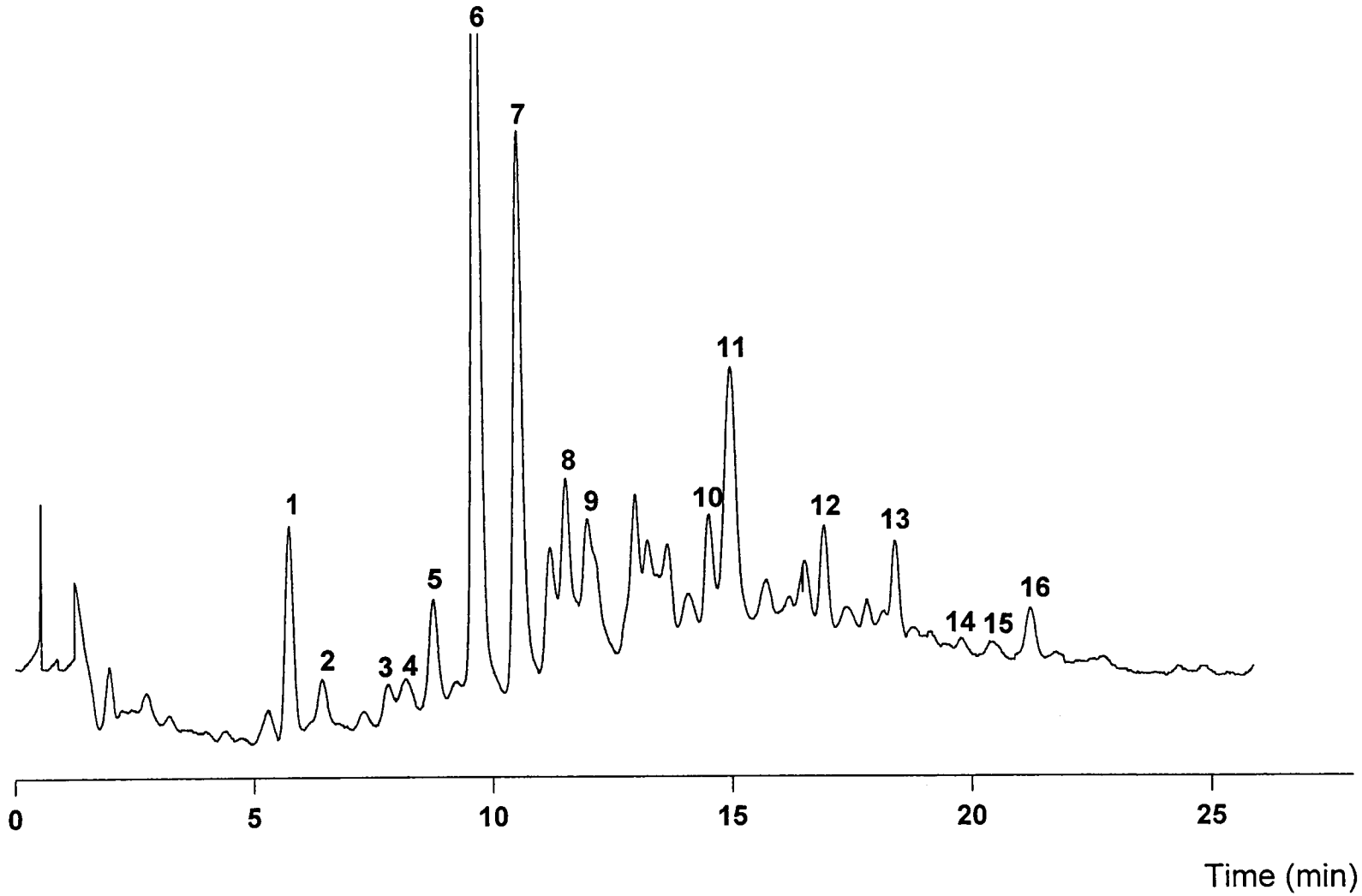


Figure 3. (continued) (b) UV detector

as those used for PAH analysis. Although the UV absorbance of Triton X-100 solution was maximum at 277 nm, a wavelength of 254 nm was used. This allows simultaneous analysis of PAHs and Triton X-100 with little loss of sensitivity. Internal standards were used to plot the calibration curve (Figure 4). Presence of certain PAHs, fluorene in particular, in the leachate of MGP soil caused interference in measuring Triton X-100; the retention times of fluorene and Triton X-100 were about the same. When Triton X-100 was used to solubilize PAHs in MGP soil, the ratio of the area of fluorene peak to that of surfactant peak decreased with increasing concentration of surfactant. Therefore, the HPLC measurement was used only when the concentration of surfactant solution was high enough such that the area of interfering peak was less than 10 % of the area of the surfactant peak.

Surface Tension:

At relatively low concentrations (<0.6 to1.0 g/L), the surface tension method gave reliable estimates of surfactant concentrations. Up to CMC, surface tension decreases log-linearly with increasing concentration due to the congregation of surfactant molecules at the air-water surface (Edwards *et al.*,1991). At CMC, the surface is saturated with surfactant molecules and the formation of surfactant micelles by agglomeration of excess surfactant monomers becomes incipient. Using a log-linear relationship between sub-CMC concentration and surface tension, the aqueous concentration of surfactant can be determined by measuring surface tension. The major limitation of this method is the narrow concentration range in which it can be used. However, with appropriate dilutions,

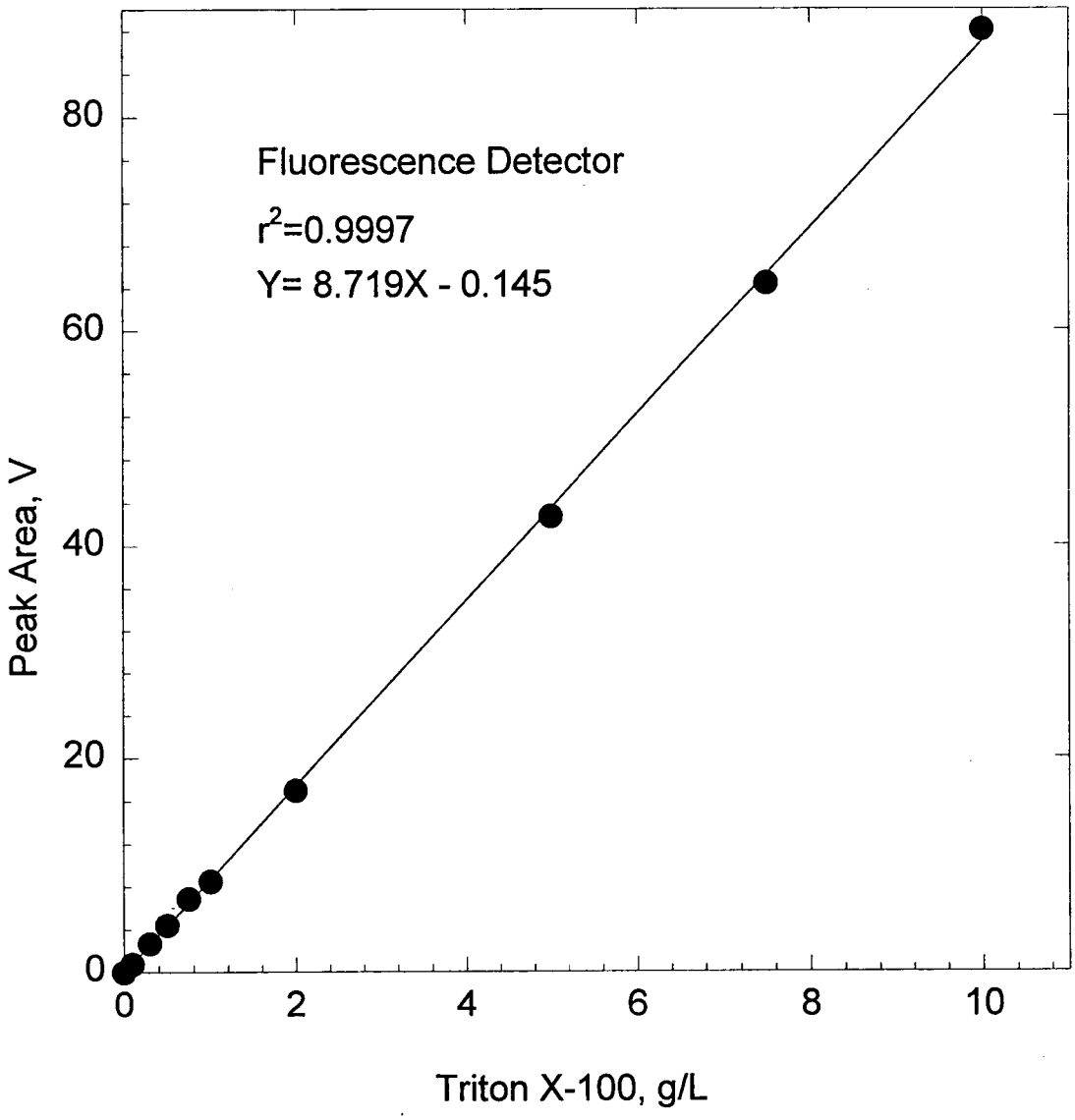


Figure 4. Calibration curve showing peak area of Triton X-100 by fluorescence detector as a function of concentration

concentrations higher than the CMC can be measured, although the accuracy of the measurement may suffer as the required dilution factor becomes large. The standard calibration curve for each surfactant was prepared by measuring the surface tension of surfactant solutions of concentrations of up to three times the CMC. Surfactant solutions were placed in pre-washed 100-mL beakers and allowed to equilibrate for an hour. Although longer equilibration times (5-10 hours) were suggested by some researchers (Kloubek and Neumann, 1969; Heusch, 1972), the change in surface tension after one hour was found to be relatively insignificant. The surface tension was measured at 25°C using a tensiometer (Tensiomat, Model 21, Fisher Co.). This instrument employed a clean platinum-iridium ring that was suspended in the supernatant from a torsion balance, and the force required to pull the ring free from the supernatant was measured in dynes per centimeter (duNouy method). Prior to the measurement, the tensiometer was calibrated at three points by adjusting the arm length of the torsion balance. The measurement was repeated several times until a constant value was obtained. The platinum-iridium ring was cleaned between measurements with acetone and then heated in a gas flame until it glowed red. The measured values of surface tension were plotted against the logarithm of the concentration. The calibration curves for the test surfactants are shown in Figure 5.

Other Methods:

The three alcohol ethoxylate surfactants and Tween 80 do not significantly absorb

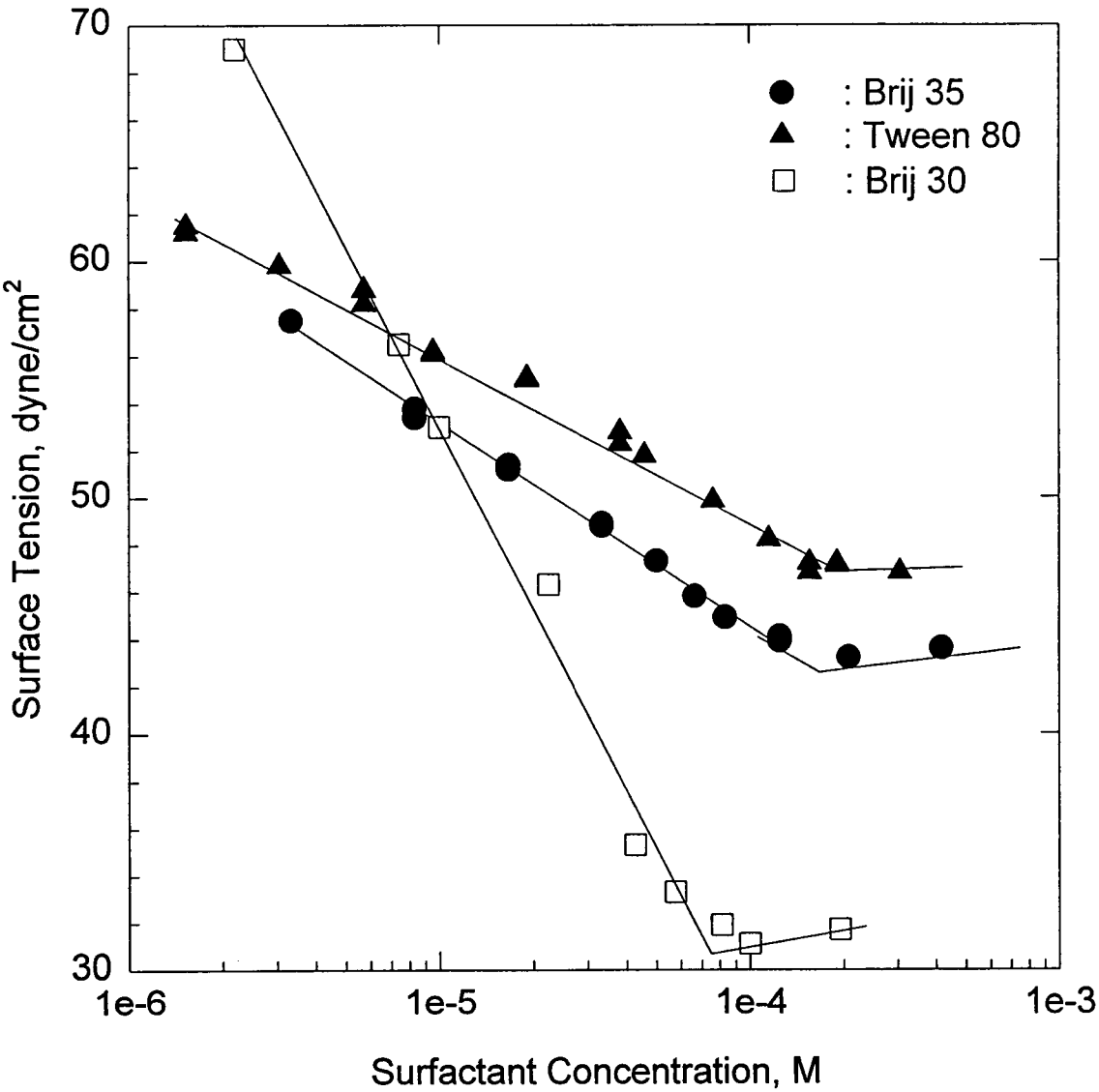


Figure 5. Calibration curves showing surface tension as a function of bulk surfactant concentration

UV-light or fluoresce. Therefore, they could not be analyzed by HPLC. Several methods including CTAS (cobalt thiocyanate active substances) (APHA,AWWA,WPCF, 1989), PPAS (potassium picrate active substances) (Favretto, 1980), and two-phase titration (Tsubouchi et al, 1985; O Connell, 1986) were tested. The two colorimetric methods, CTAS and PPAS, suffered from severe interferences caused by organic matter released from the MGP soil. For example, the concentration of Brij 35 in solution measured by CTAS was higher than initial following sorption on to soil. The two-phase titration method had sensitivity problems due to inaccuracies inherent in the visual inspection of the end point color change. Total organic carbon (TOC) analysis was foiled by the large amounts of organic carbon released from soil.

Derivatization-HPLC:

It appeared that the analysis of surfactants in the MGP soil leachate must be preceded by their separation from the organic milieu. Derivatization-HPLC method, developed by Allen and Linder (1981) and modified by Schmitt *et al.*(1990), accomplishes such separation. In the present study, the derivatization-HPLC method was used for measuring high concentrations (>0.6 g/L) of alcohol ethoxylate homologs and Tween 80. Phenyl isocyanate, a complexant, was used to produce UV-active derivatives upon reaction with the ethoxylate groups. A 2 mL sample was placed in a test tube and the water was evaporated at 80^{o}C. The residue was spiked with 10 μL phenyl isocyanate and 50 μL ethylene dichloride. The tube was mixed by swirling, capped loosely, and

held at 55°C for 45 minutes. The contents of the tube were then dissolved in 250 μL ethylene dichloride. The solution was injected into the HPLC. The surfactant-phenyl isocyanate complex was detected by UV absorbance at 240nm. At concentrations higher than 0.6 g/L, the method produced acceptable results (*s.d.*< 0.04-0.1 g/L). However, at low concentrations (< 0.6 g/L), the peaks were too broad and the accuracy of the measurement decreased, especially for surfactants with a large number of ethoxylate groups such as Brij 35. Therefore, at relatively low concentrations, the values were determined by the surface tension method discussed earlier.

Radiochemical Method :

The concentration of [^{3}H]-Triton X-100 was radiochemically measured in surfactant sorption studies. Triton X-100 solutions with activities of 14,000 to 16,000 dpm/mL were prepared in 0.05 % $HgCl_2$ solution. Solutions of various concentrations were prepared by adding appropriate amounts of nonlabeled Triton X-100 to the [^{3}H]-Triton X-100 solution. The contribution of [^{3}H]-Triton X-100 to the total surfactant concentration was negligible (<3.0 μg/L) compared to the concentration of nonlabeled compound (>10 mg/L). In experiments on surfactant sorption, following mechanical mixing of Triton X-100 with MGP soil suspensions for pre-determined periods, the samples were centrifuged and the surfactant concentration in the supernatant was determined radiochemically. A 0.5 mL aliquot of the supernatant was added to 10 mL of scintillation cocktail (Ready Safe, Beckman Co.), and the radioactivity was measured

in dpm (disintegration per minute) using a liquid scintillation counter (Beckmann Model LS5000TD).

4.2 Micellar Solubilization of Pure PAHs

The solubilization of four individual PAHs, (phenanthrene, anthracene, pyrene, and benzo[*a*]pyrene) by the five test surfactants was determined in single component systems. Concentrated PAH solutions were prepared by dissolving PAH crystals in 10 mL acetone. The concentrations of phenanthrene and pyrene were 100g/L while those of anthracene and benzo[*a*]pyrene were less (25 g/L) due to their limited solubility in acetone. Appropriate volumes of each solution (200 μL of phenanthrene, 50 μL of anthracene, pyrene, or benzo[*a*]pyrene) were added to a series of 8-mL vials. The volume of concentrated PAH solution added to each vial was such that the PAH in each vial was at least 2-3 times the amount that could be solubilized by the highest concentration of surfactants (30 g/L). Having evaporated the acetone, 4 mL of surfactant solution of various concentrations were added to the vials. The volatilization loss of PAH during the evaporation of acetone was inconsequential because the PAH in the vial was much greater than the amount that could be solubilized. Surfactant solutions were prepared in a 0.05% solution of mercuric chloride ($HgCl_2$) in deionized (DI) water to prevent biodegradation surfactant during the experiment. Since accurate weighing of a small amount of surfactant was difficult, stock solutions of high concentrations were prepared. Surfactant solutions of low concentrations were obtained by dilution. The vials were sealed with Teflon-silicone septa and open port screw caps and then were shaken for 5

days in a mechanical shaker (Wheaton Co.). The equilibration time was determined by preliminary studies; the solubilization of phenanthrene in 6 g/L Triton X-100 solution was measured at various time intervals; equilibrium was reached within 2-3 days. An aliquot of the sample was withdrawn into a 5-mL glass syringe and passed through a 0.2 μm aluminum filter (Aerodisc 13, Whatman Co.). A syringe-type, stainless steel filter holder (Whatman Co.) was used to minimize the loss of PAHs due to their adsorption on the filter assembly. The effect of PAH adsorption to the filter assembly was further reduced by discarding the first 2-3 mL of filtrate before collecting HPLC samples. The concentration of solubilized PAH was determined by analyzing the filtrate using HPLC. At low surfactant concentrations (<CMC), the maximum loss of phenanthrene observed was 3-4 %. To prevent cross contamination between samples, the filter unit was flushed with methanol and dried between each filtering operation.

4.3 Sorption of Surfactant

In a series of 30-mL glass centrifuge tubes (Heavy-duty, Corning Co.), 2.5 g of soil and 25 mL of surfactant solution of various concentrations were mechanically mixed for 50 hours. The surfactant solutions were prepared in 0.05% $HgCl_2$ to prevent biodegradation. The soil suspensions were then centrifuged at 8000xg for 40 minutes and the supernatants analyzed for surfactant. Sorption of ^{3}H-Triton X-100 was determined by radiochemical method discussed earlier. Sorption of Triton X-100 was determined as:

$$q_{surf}(g/g) = \left(\frac{S_{surf}}{W_{soil}}\right)\left(1 - \frac{[dpm]_s}{[dpm]_o}\right) \qquad (10)$$

where q_{surf} is the surfactant concentration in the soil, S_{surf} is the concentration of the surfactant solution initially added, and W_{soil} is the concentration of soil. $[dpm]_O$ is the activity of the surfactant solution initially added (dpm/mL) and $[dpm]_S$ is the activity of supernatant after sorption. Background activity (40 dpm) was subtracted from the measured activity.

Also, desorption of surfactant from surfactant-coated soils was measured. After centrifugation of surfactant-coated soil slurries of known composition, the supernatant remaining in the tube was carefully decanted without disturbing the soil pellet. Supernatant remaining in the tube after decanting was determined by subtracting the pre-weighed weight of dry soil plus empty glass from the weight of the tube containing wet soil after decanting of the supernatant. The amount of surfactant remaining in the residual liquid was subtracted from the amount of aqueous surfactant after desorption. The soil pellet in the tube was resuspended with fresh water (0.05% $HgCl_2$) and mixed for 2 days. Following centrifugation, the supernatant was analyzed for radioactivity.

4.4 Solubilization of Phenanthrene from Artificially Contaminated Soil

The Tennessee soil, artificially contaminated as described below, was used for the solubilization experiments. Phenanthrene stock solution consisting of radiolabeled (9-^{14}C) and non-radiolabeled compounds was prepared in 0.05 % $HgCl_2$ solution. The total concentration of phenanthrene was 0.908 mg/L. The phenanthrene solution (25 mL) was added to a series of 30-mL glass centrifuge tubes, each of which contained 2.0 g of natural soil. The tubes were sealed with Teflon-silicone septa and open-port screw

caps, and shaken for 8 days. Following centrifugation at 8000xg for 40 minutes, a 0.5 mL aliquot of the supernatant was collected and analyzed for radioactivity. The phenanthrene sorption density was calculated by the difference between the solution phase activities before and after the sorption experiment. The average sorption density (surface excess) of phenanthrene was found to be 10.7 μg per gm soil. The supernatant was decanted and the remaining soil was used for solubilization experiments.

Solubilization of sorbed phenanthrene was determined by adding 25 mL of Triton X-100 solutions of varying concentrations to the tubes containing the phenanthrene-contaminated soil. After mixing for 24 hours, the suspensions were centrifuged and the supernatants analyzed for radioactivity.

4.5 Solubilization of PAHs from MGP Soil

Surfactant solutions of various concentrations (0.25, 1.1, 6.0, and 30 g/L) were prepared in 0.05 % $HgCl_2$ solution. Four milliliters of the surfactant solutions were added to a series of 8-mL vials each containing 0.4 g of MGP soil. The vials were sealed with Teflon-silicon septa and open port screw caps and shaken by a mechanical shaker. At given time intervals, duplicate samples were removed from the shaker and the suspensions were transferred into 10-mL centrifuge tubes. Following centrifugation at 8000xg for 40 minutes, an aliquot of the supernatant was withdrawn into a 5-mL glass syringe and expressed through 0.2 μm aluminum filter to remove unsettled fine particles. The filtrate was analyzed for PAH.

5. RESULTS AND DISCUSSION

The results of solubilization of crystalline and soil-bound PAHs by surfactants are presented in this section. Solubilization of PAHs from the MGP soil is particularly emphasized because of its practical significance. In presenting results, phenanthrene has been used in most cases as a representative of the suite of PAHs solubilized from the MGP soil. A predictive model to describe the micellar solubilization of soil-bound PAHs is developed by extending the linear partitioning theory.

5.1 Surfactant Solubilization of Crystalline PAHs

Solubilization of four PAHs- phenanthrene, anthracene, pyrene, benzo[*a*]pyrene by surfactant solutions was determined in the presence of excess PAH crystals. Representative results of PAH solubilization are shown in Figure 6. Solubilization linearly increased with surfactant concentration. The slope of the line, mass of PAHs solubilized per unit mass of micelle, represents the solubilization capacity of the surfactant. It is noteworthy that the solubilization capacity of Brij series surfactants decreased with increasing number of ethoxylates. Similar observations were made by others (Tokiwa, 1967; Saito and Shinoda, 1967). The water-micelle partitioning coefficient, K_m, for each PAH-surfactant combination was determined from the slope of the solubilization curve and the aqueous solubility of the PAH (Eq. 3). These are summarized in Table 6. K_m is inversely related to the HLB number of the surfactant. Since HOCs partition into the liquid-like micellar core, the volume of micellar core per

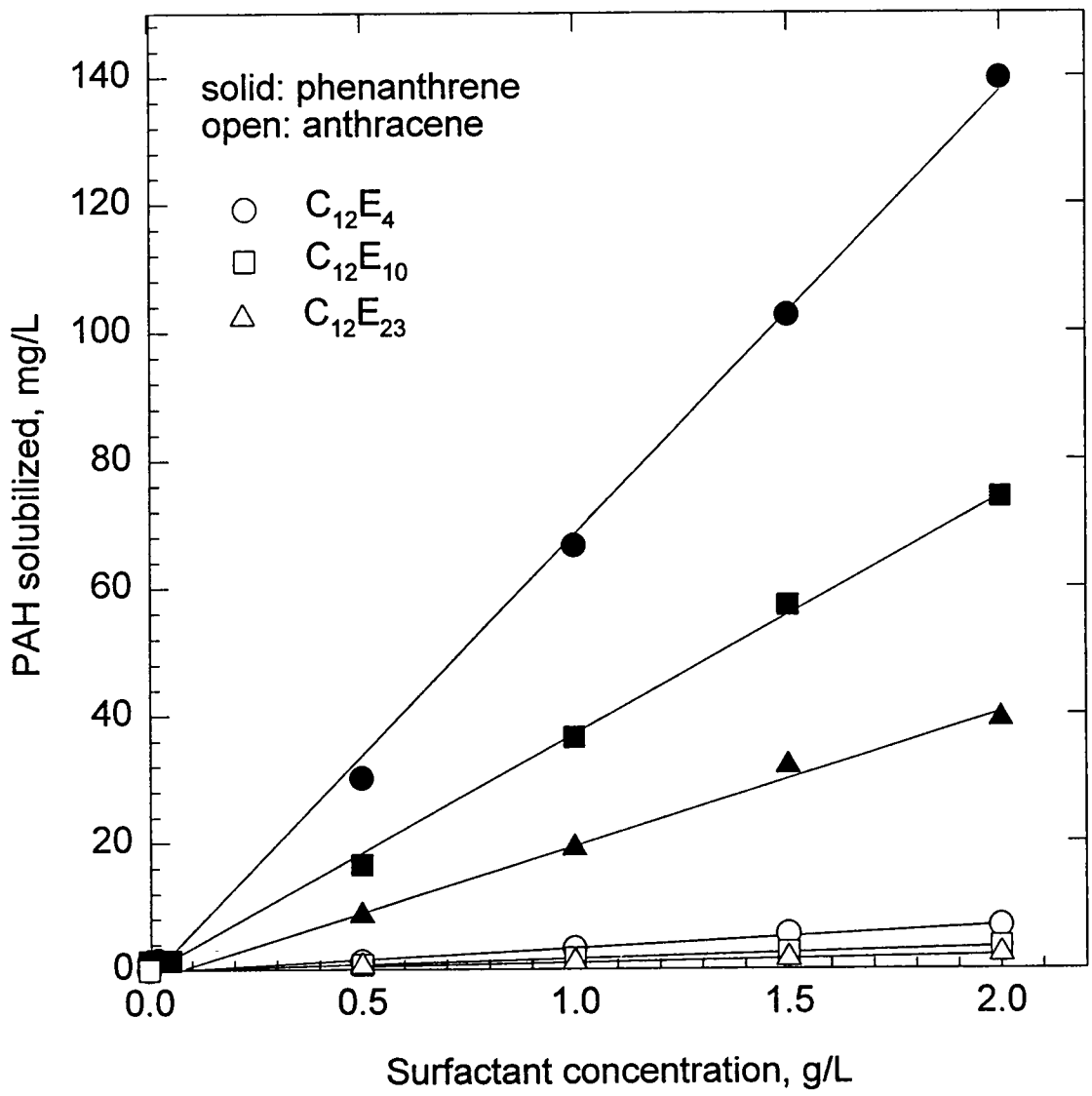


Figure 6. Solubilization of phenanthrene and anthracene by linear alcohol ethoxylate homologs

Table 6. Micelle-water partitioning coefficients of PAHs (K_m (L/g))

	Triton X-100	Tween 80	Brij 30	POE ($C_{12}E_{10}$)	Brij 35
Phenanthrene	23.9	24.3	56.8	28.4	16.0
Anthracene	23.1	19.8	54.0	26.5	15.2
Pyrene	93.3	84.5	213.5	104.5	51.4
Benzo(a)pyrene	1534	1321	2981	1863	955.4

unit mass of micelle should control the solubilization capacity of a surfactant (mass basis). The micelle core volume normalized for mass of micelle (V_{mc}/M_{mic}) is directly related to HLB of the surfactant. The general formula for HLB of nonionic surfactants is given by Rosen (1989):

$$HLB = 20 \times \left(\frac{M_H}{M_H + M_L} \right) \tag{11}$$

where M_H and M_L are the formula weights of the hydrophilic and lipophilic portions of surfactant molecule, respectively. Similarly, HLB can be expressed in terms of the mass fraction of the micellar core (M_{mc}/M_{mic}):

$$HLB = 20 \times \left[1 - \frac{M_{mc}}{M_{mic}} \right] \tag{12}$$

Using the relationship $M_{mc} = \rho_{mc} V_{mc}$, the micellar core volume per unit mass of micelle can be expressed in terms of HLB:

$$\left(\frac{V_{mc}}{M_{mic}} \right) = \left(1 - \frac{HLB}{20} \right) \left(\frac{1}{\rho_{mc}} \right) \tag{13}$$

where ρ_{mc} is the density of the micellar core. The solubility of a HOC in a given volume of micelle also varies with Laplace pressure, the pressure difference across a curved interface due to the surface tension of the solution. However, it has been shown that factors other than the HLB do not account for more than 10 % of variance for most surfactants (Bolden *et al.*, 1983; Valsaraj and Thibodeaux, 1989). The effect of HLB on V_{mc}/M_{mic}, and hence on solubilization capacity, is significant. For example, the ratio of micellar core volumes of Brij 30 and Brij 35 ($V_{mc,30}/V_{mc,35}$) per unit mass of micelle was estimated to be 3.3, assuming ρ_{mc} of the surfactants to be the same. This is close to the ratio of their K_m values, illustrating the dominant effect of HLB on solubilization capacity.

5.2 Surfactant Sorption

Surfactant sorption to soil was conducted mostly with Triton X-100. While radiolabeled Triton X-100 was used for studies with MGP soil, nonlabeled form of the surfactant was used for studies with the Tennessee soil. All other surfactants were used only with the MGP soil, sorption being measured only at concentrations used for soil washing experiments.

Tennessee Soil:

The isotherm for the sorption of Triton X-100 on Tennessee soil is shown in Figure 7. Aqueous surfactant concentrations were measured by both the surface tension

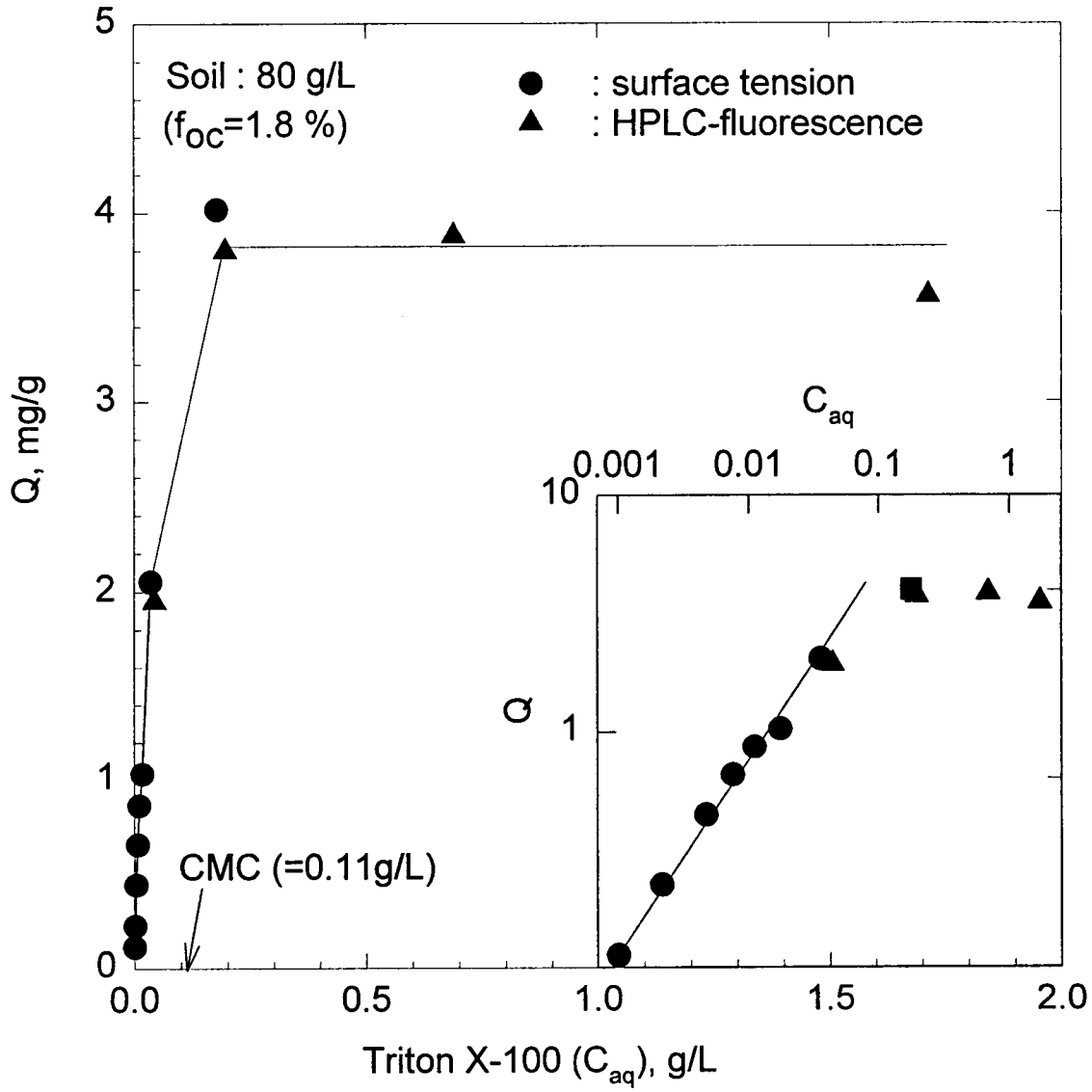


Figure 7. Sorption of Triton X-100 on Tennessee soil

and HPLC (fluorescence) methods at sub-CMC concentrations. Only the HPLC method was used at higher concentrations. Maximum sorption density occurred near the CMC of the surfactant, sorption being well characterized by the Freundlich isotherm (inset). Beyond the CMC, the isotherm yielded a zero slope, uncharacteristic of the Freundlich isotherm. Seemingly, micelles did not sorb well on the mostly hydrophobic soil surface. Similar behavior was observed for the sorption of other alkylphenol ethoxylates to natural soils having moderate f_{OC} (0.9-3.4 %) (Yeom, 1992; Liu *et al.*, 1992). On the contrary, sorption of Triton X-100 on sand with low f_{OC} (0.053%) increased 15-fold at a concentration two orders of magnitude higher than the CMC (Edwards *et al.*, 1994). Increased sorption at supra-CMC levels was attributed to the formation of a bilayer or 'admicelle' on the surface of the relatively polar surface of sand. SOM appears to be the primary sorbent for nonionic surfactants in soils with relatively high organic matter content (Urano *et al.*, 1983, Liu *et al.*, 1992; Yeom, 1992). At supra-CMC concentration of nonionic surfactants, sorption may be hindered by repulsion between the hydrophilic head groups (ethoxylate) of the sorbed and aqueous surfactant molecules.

MGP Soil:

Sorption of surfactant on MGP soil was tested mostly with [^{3}H]-Triton X-100. The soil was equilibrated with surfactant solutions of various concentrations for 50 hours. Sorption densities, Q (mg/g), are shown as a function of aqueous concentration, C_{aq} (g/L), in Figure 8 along with the corresponding Freundlich isotherm (inset). The isotherm is characterized by two linear regions of different slopes, with the discontinuity

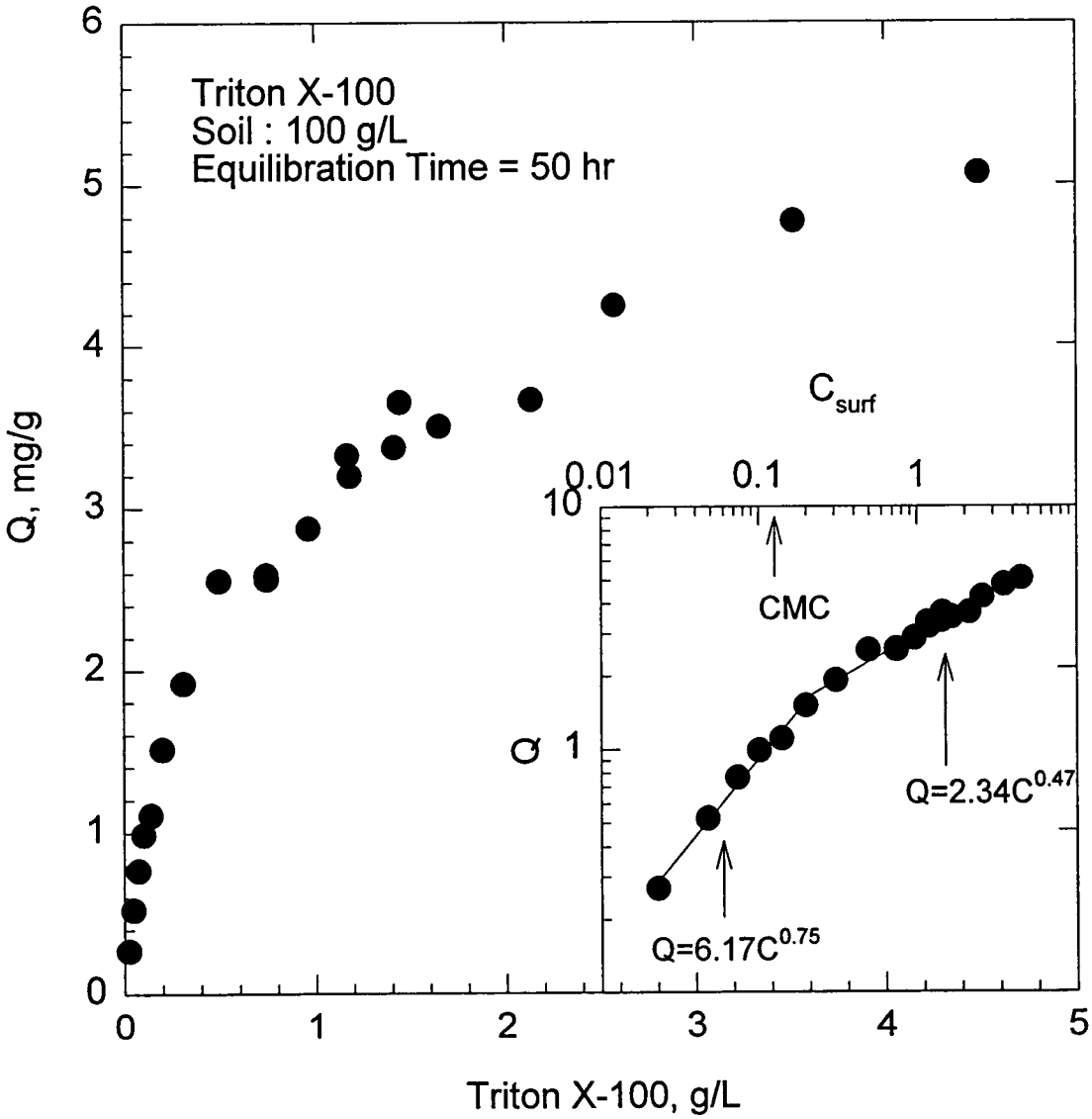


Figure 8. Sorption of Triton X-100 on MGP soil

occurring at about the CMC (0.11 g/L). At the CMC, sorption density is about 1.5 mg/g (2.32×10^{-6} mol/g) while at a surfactant dosage of 5 g/L, the sorption density is 6 mg/g (9.3×10^{-6} mol/g). The mechanism for the additional sorption at surfactant concentrations above the CMC is not clear. Admicelle sorption at supra-CMC may not occur on a highly hydrophobic surface such as the MGP soil. Elucidating the mechanism of surfactant sorption on MGP soil is beyond the scope of this study. However, there is some evidence that sorption is not a simple surficial process. The surfactant molecules may penetrate into the tar phase. These issues are discussed in Part 3 dealing with the kinetics of PAH solubilization.

5.3 Solubilization of PAHs from Artificially Contaminated Soil

Triton X-100 was the only surfactant used in studying PAH-solubilization from the Tennessee soil artificially contaminated with phenanthrene. The contaminated soil had a phenanthrene concentration of 10.7 μg/g at the beginning of solubilization experiments. It was washed with surfactant solutions for 24 hours. The solubilization of phenanthrene as a function of surfactant concentration is shown in Figure 9. Equilibrium was reached within 24 hours regardless of the surfactant concentration (Yeom and Ghosh, 1993). Solubilization of phenanthrene rapidly increased with surfactant concentration once the surfactant dosage exceeded the minimum concentration (≈0.41 g/L) required to satisfy the surfactant demand of the soil plus the CMC of the

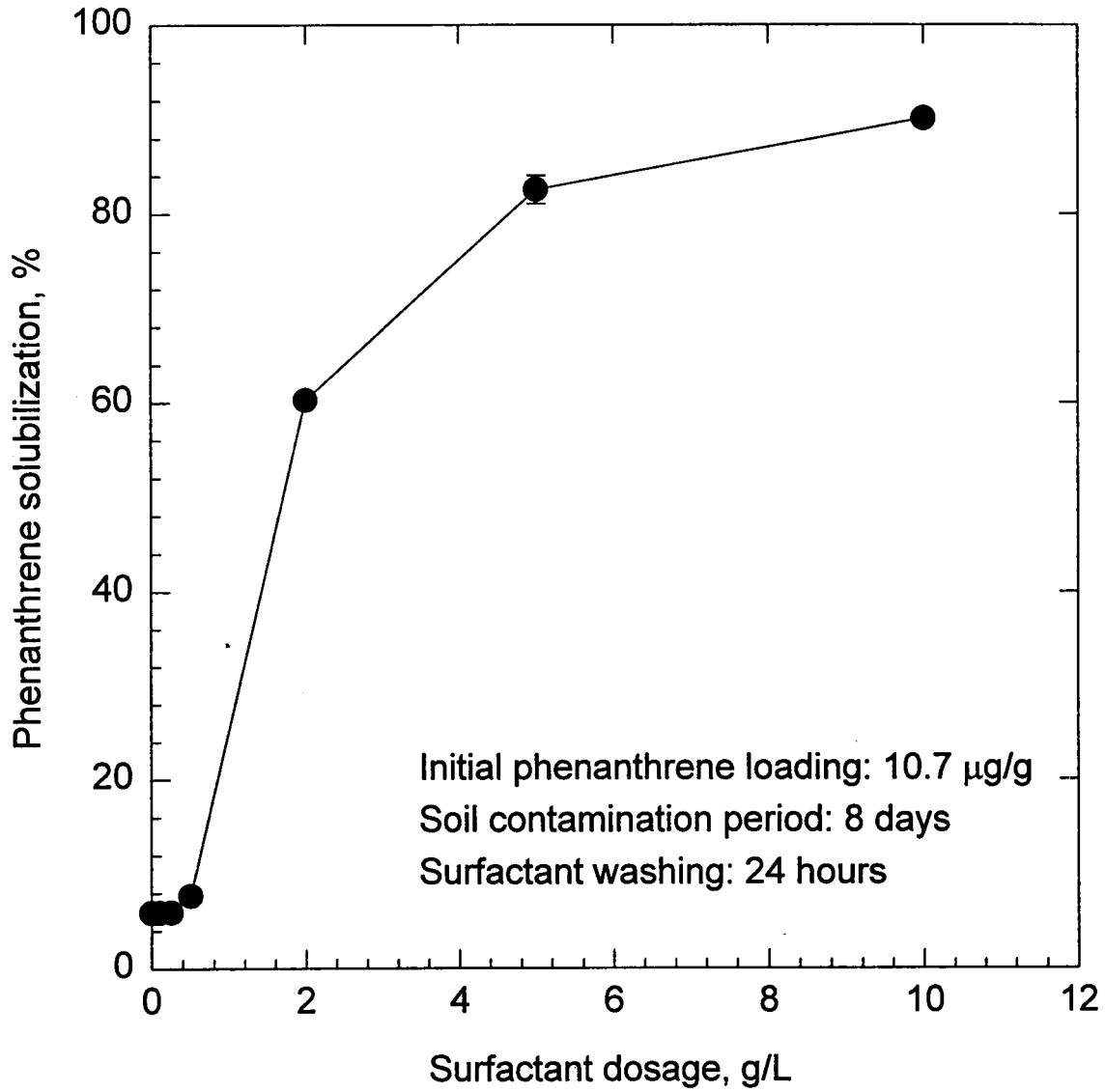


Figure 9. Solubilization of phenanthrene from artificially contaminated Tennessee soil by Triton X-100

surfactant, i.e., ($CMC + q_{surf}$). Up to 90 % solubilization was obtained at a dosage of 10 g/L.

5.4 Solubilization of PAHs from MGP Soil

In general, solubilization of coal tar components in surfactant solution can occur by two mechanisms: emulsification and micelle-solubilization (Rosen, 1989). Emulsification of coal tar, though sparse in the literature, could result in a massive solubilization of coal tar either in the form of submicron particles (microemulsion) or larger particles (macroemulsion). In both cases, the coal tar is solubilized as a bulk phase in the emulsified particle. The extent of emulsification depends on the HLB of the coal tar and that of the surfactant. For best emulsification, the HLB numbers of the NAPL and the surfactant should be the same. In this study, emulsification of the tar was not observed for any surfactants; ultracentrifugation of the supernatant of soil-surfactant solution did not reveal separation of an emulsion phase. The semi-solid tar residue in the MGP soil may not be emulsified by any surfactant. Only micellar solubilization was assumed to contribute to solubility enhancement of the soil-bound PAHs. However, this observation should not be interpreted as the nonoccurrence of emulsification of coal tar. Emulsification may occur with less viscous, small molecular weight coal tar. For example, emulsification of the Soxhlet extract of the MGP soil was observed for at least two surfactants, Tween 80 and Brij 35.

The equilibrium partitioning of PAHs between soil/tar and water occurred in less than 3 hours. Similar observations were made by Lee *et al.*(1992). However, attainment

of equilibrium took much longer in surfactant solutions. Figure 10 shows the solubilization of phenanthrene in the MGP soil by three nonionic surfactants. Release of phenanthrene increased with surfactant concentration but longer time was required to reach equilibrium. At a dosage of 6 g/L, more than 250 hours were required to obtain a relatively constant value of dissolved phenanthrene. And at a dosage of 30 g/L, equilibrium was not reached during the test period (~ 400 hours). The efficiency of different surfactants in solubilizing phenanthrene at a dosage of 5.5 g/L (Brij 30 and $C_{12}E_{10}$) or 6 g/L (other surfactants) are compared in Figure 11. The solubilization efficiency was directly related to the K_m values of the surfactant: Brij 30 > Tween 80 > Triton X-100 > Brij 35. Interestingly, equilibrium was reached relatively fast with Brij 30 and $C_{12}E_{10}$ although more phenanthrene was solubilized by these surfactants. This indicates that the rate of solubilization depends on the characteristics of the surfactants. A detailed discussion of PAH-solubilization rates as affected by different surfactants is presented in Part 3.

In Figure 12, solubilization of different PAHs by 5.5 g/L of Brij 30 solution is compared; phenanthrene was most soluble and benzo[*a*]pyrene was least soluble.

5.5 Development of a Solubilization Model

As shown in Figure 1, solubilization of sorbed PAH or PAH in a NAPL mixture can be described by multiphase partitioning among soil solids, soil water, micelle, NAPL, and soil air. Since PAHs are relatively nonvolatile, partitioning into the air phase

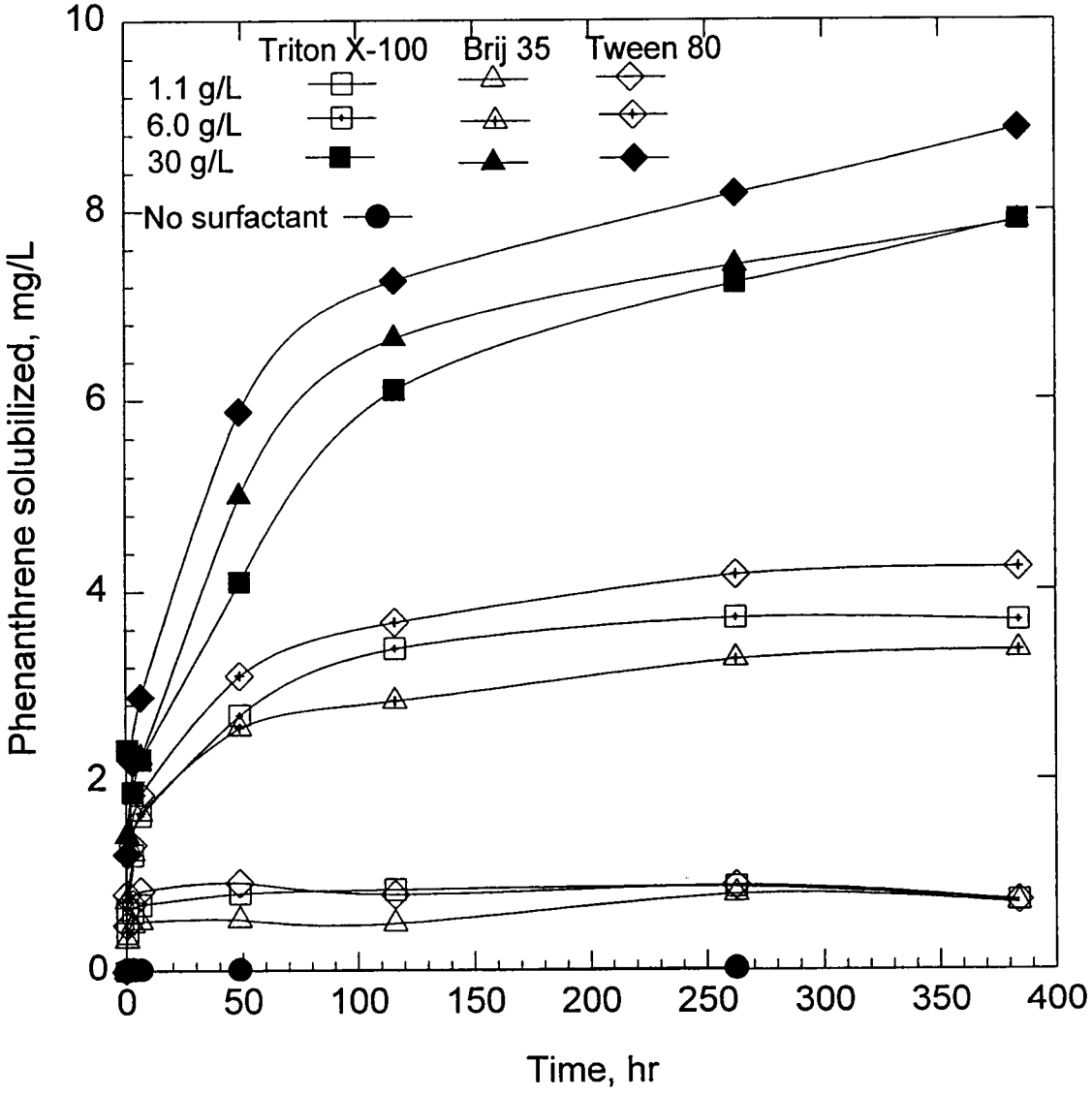


Figure 10. Solubilization of phenanthrene from MGP soil by surfactants

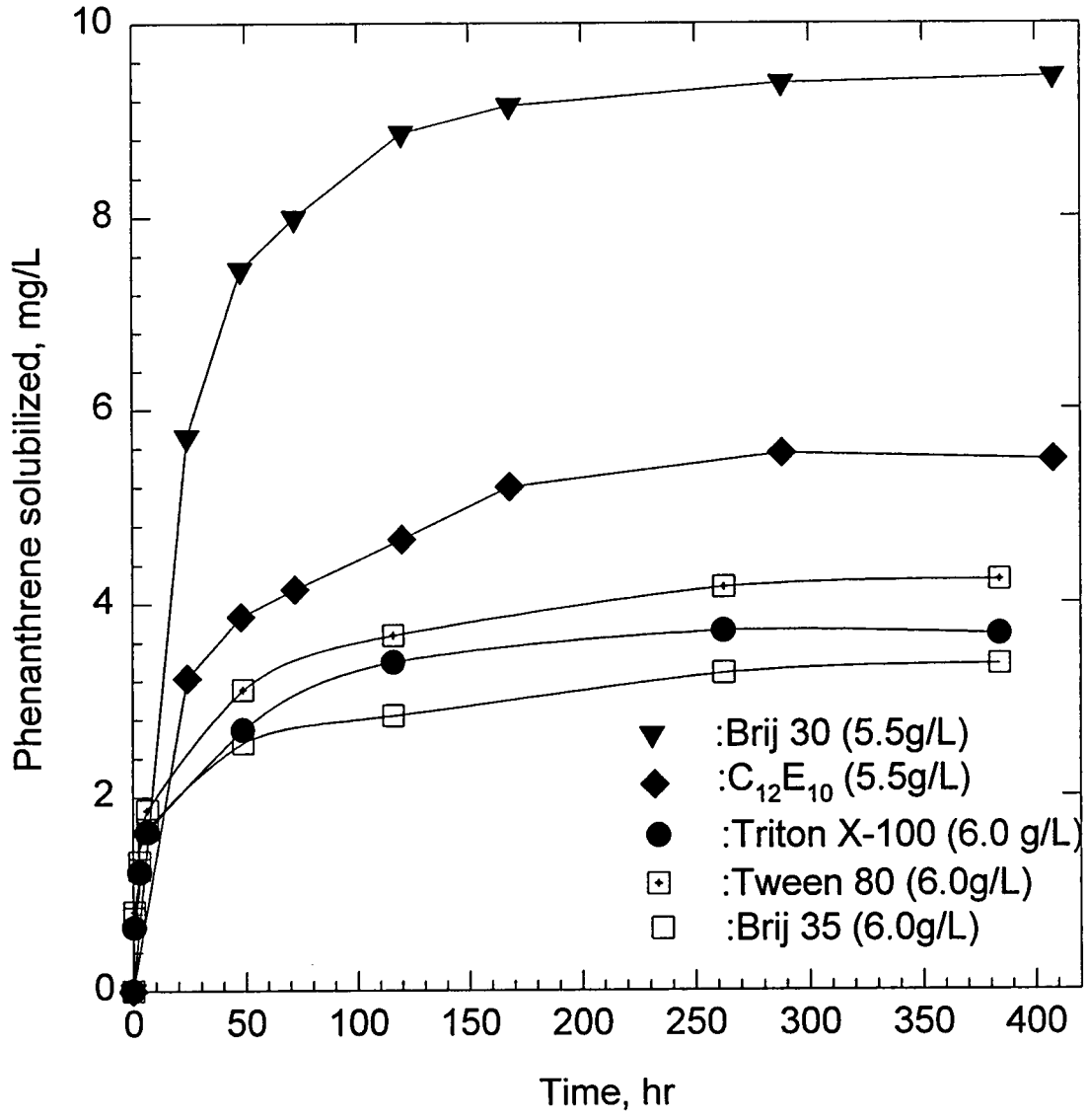


Figure 11. Comparison of phenanthrene solubilization from MGP soil by different surfactants

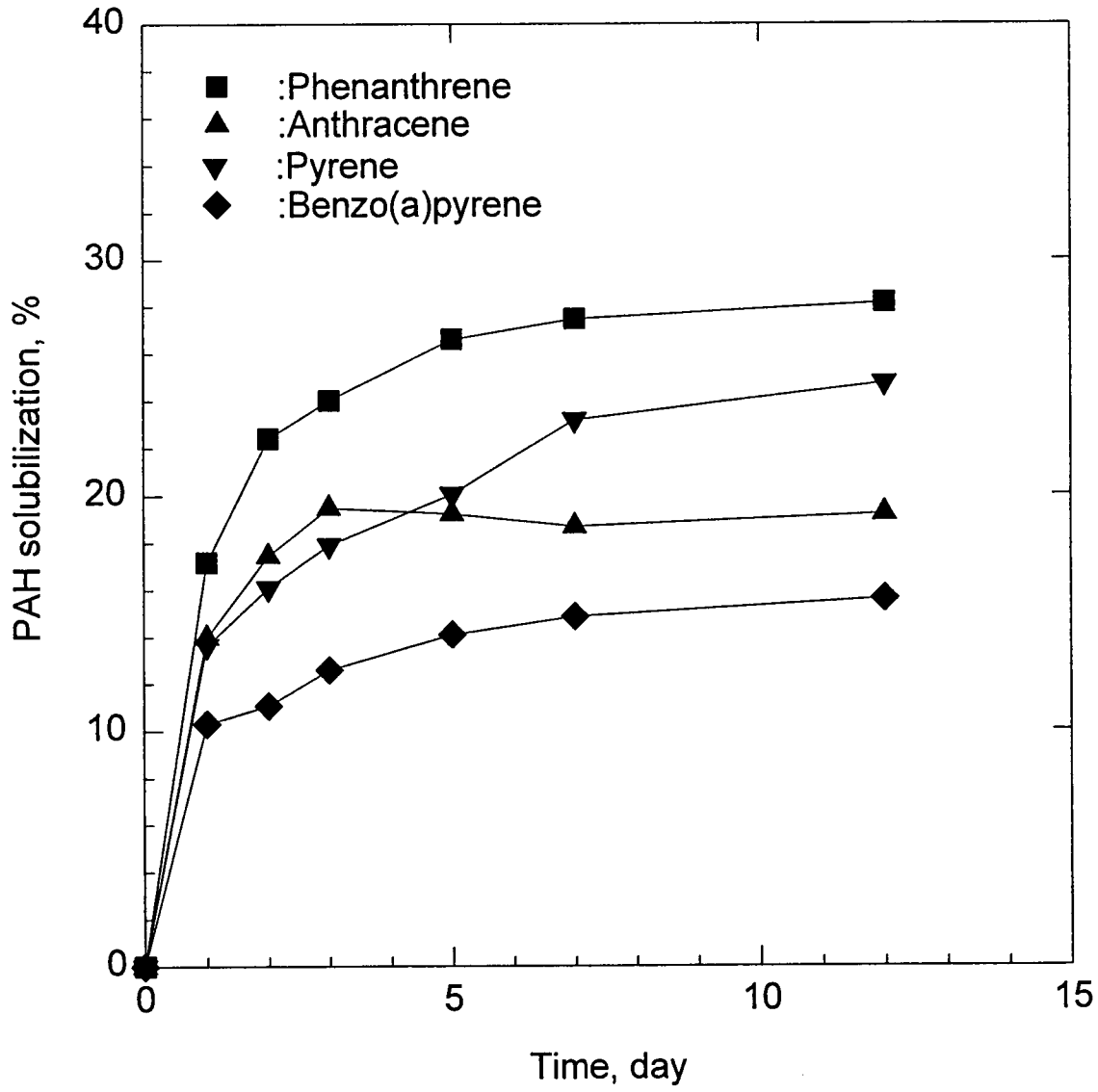


Figure 12. Solubilization of PAHs from MGP soil by 5.5 g/L of Brij 30

is negligible. To determine the equilibrium distribution of a HOC between the remaining four phases, at least three partitioning coefficients must be known. Of the six possible partitions among the four phases, those between water and the other three phases are relatively well understood. These partitioning coefficients can be separately determined. Using these coefficients, the mass balance for a NAPL constituent is given by:

$$q^{o}_{soil} W_{soil} + q^{o}_{NAPL} W^{o}_{NAPL} = C_{aq}\ 1 + K_{soil-aq} W_{soil} + K_{m} S_{mic} + K_{NAPL-aq} W_{NAPL} \qquad (14)$$

where q^{o}_{soil} *and* q^{o}_{NAPL} are the initial concentrations of a HOC in soil and NAPL phases (g/g), respectively. W^{o}_{NAPL} is the initial mass of NAPL per unit volume of water (g/L) and W_{NAPL} is that after solubilization. $K_{soil-aq}$, and $K_{NAPL-aq}$ are the soil-water and NAPL-water partitioning coefficients, respectively. If the NAPL is a single compound, q^{o}_{NAPL} becomes unity and $K_{NAPL-aq}$ is replaced by the aqueous solubility of the compound. If S_{mic} is relatively high, the contribution of aqueous-pseudophase HOC to total dissolved HOC is negligible. From Eqs. 4 and 14, the percent solubilization can be determined as:

$$\%\ Solubilization = \frac{100}{\left[1 + \left(\frac{K_{soil-aq}}{K_{m}}\right)\left(\frac{W_{soil}}{S_{mic}}\right) + \left(\frac{K_{NAPL-aq}}{K_{m}}\right)\left(\frac{W_{NAPL}}{S_{mic}}\right)\right]} \qquad (15)$$

While the ratios of partitioning coefficients, $K_{soil-aq}/K_{m}$ and $K_{NAPL-aq}/K_{m}$, represent the relative affinity of the HOC between micelles and soil (or SOM), and micelles and

NAPL phase, respectively, W_{soil}/S_{mic} and W_{NAPL}/S_{mic} are the mass ratios of soil and NAPL to micelles.

Artificially Contaminated Soil:

Solubilization of phenanthrene from the artificially contaminated soil can be described similarly. In the absence of NAPL phase, Eq. 15 reduces to:

$$\%\ Solubilization = \frac{100}{\left[1+\left(\frac{K_{soil-aq}}{K_m}\right)\left(\frac{W_{soil}}{S_{mic}}\right)\right]} \tag{16}$$

Redefining $K_{soil-aq}/K_m$ as the soil-micelle partitioning coefficient, $K_{soil-mic}$, and rearranging:

$$\%\ Solubilization = 100 \times \left(\frac{SL'}{K_{soil-mic}+SL'}\right) \tag{17}$$

where SL' is the mass of micelle applied per unit mass of the contaminated soil ($=S_{mic}/W_{soil}$). SL' can be obtained from the equation $SL' = SL - CMC/W_{soil} - q_{surf}$ where SL is the surfactant loading per unit mass of soil (g/g). Eqs. 16 and 17 can be used to predict the solubilization of a sorbed PAH from a contaminated soil.

Figure 13 shows a comparison of model prediction of solubilization with experimental data. The value of $K_{soil-aq}$, estimated from the equilibrium sorption of phenanthrene on the natural soil, was 0.239 L/g. The corresponding, derived value of $K_{soil-mic}$ was 0.01 g/g.

MGP Soil:

Solubilization of PAHs from the coal-tar contaminated soil is complicated by the complex nature of the solid-tar mixture. Thermodynamic properties of coal tar are poorly defined. In addition, after decades of weathering, the characteristics of tar change considerably. It is not clear if the tar coating MGP soil should be classified as a solid, a liquid or a mixture thereof.

A semi-empirical model was developed to predict the partitioning of individual PAHs from MGP soil into surfactant solutions. Based on model predictions, estimates are made of the extent of PAH released from soil/tar at different soil: surfactant ratios.

In describing solubilization of PAHs from tar by a surfactant solution, the transfer of a component *i* is envisioned to occur from tar in the soil to water and then to micelle. The mineral fraction of the soil is assumed to be inert. For convenience, the tar-water partitioning coefficient of individual PAHs, K_{tar-aq}, was normalized for the mass of the soil-tar mixture, termed 'soil/tar', consisting of soil mineral and tar ($K_{soil/tar-aq}= K_{tar-aq}/F_{ct}$), F_{ct} being the mass fraction (0.75) of tar in the soil).

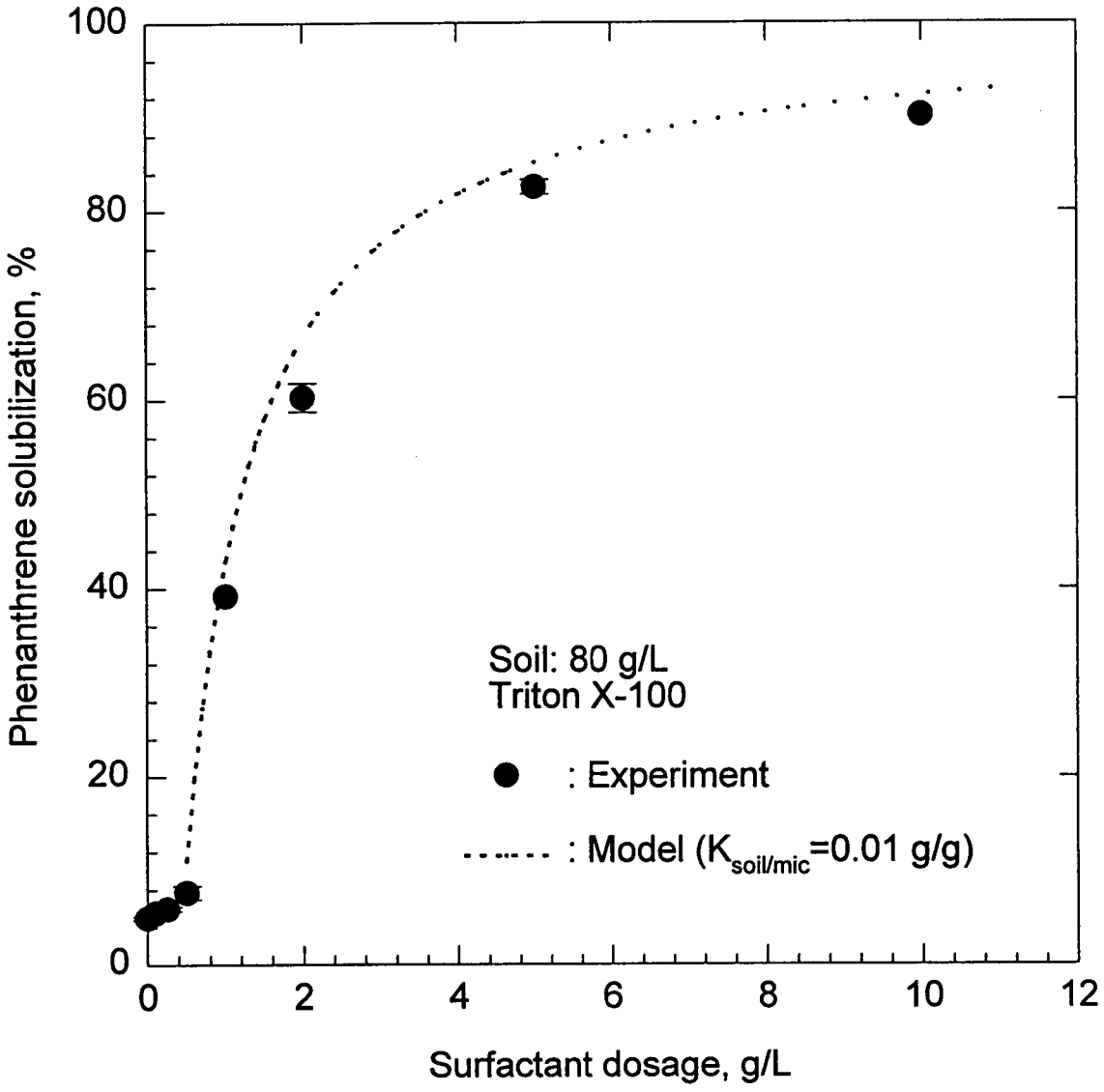


Figure 13. Comparison of model prediction of phenanthrene solubilization from an artificially contaminated soil with measured values

Assuming that the tar mixture behaves ideally, that is Raoult's law is valid, the aqueous solubility of an individual PAH ($C_{aq,i}$) in equilibrium with tar can be estimated using Eqs. 6 and 7. The mole fraction of i in the tar phase can be estimated from its concentration in soil/tar ($q_{soil/tar,i}$, (g/g)):

$$x_{ct,i} = \frac{q_{soil/tar,i} MW_{ct}}{F_{ct} MW_i} \tag{18}$$

where F_{ct} is the mass fraction of tar in soil/tar and MW_{ct} is the average molecular weight of tar. Using Eqs. 6 and 18, an expression for the soil/tar-water partitioning coefficient for i, $K_{soil/tar\text{-}aq,i}$, can be obtained:

$$K_{soil/tar-aq,i} = \frac{q_{soil/tar,i}}{C_{aq,i}} = \frac{F_{ct} MW_i}{C_i^L MW_{ct}} \tag{19}$$

Defining $K_{soil/tar\text{-}aq,i}$ /$K_{m,i}$ as the soil/tar-micelle partitioning coefficient, $K_{soil/tar\text{-}mic,i}$, an equation similar to Eq. 17, can be obtained for the percent solubilization of individual PAHs:

$$\%\ Solubilization = 100 \times \left(\frac{SL'}{K_{soil/tar-mic,i} + SL'} \right) \tag{20}$$

where $K_{soil/tar\text{-}mic,i}$ (g/g) is given by $(MW_i F_{ct})/(C_i^L MW_{ct} K_m)$.

In describing partitioning behavior of individual components in a multi-component system, it was assumed that the activity coefficients in the aqueous, the tar, and the micellar phases were independent of phase composition and that the number of moles of PAHs in the micellar pseudophase was small compared to the number of surfactant molecules in the micelle (molar ratio of solubilizate/surfactant in a micelle≈ 0.03 to 0.06 in this study).

The model allows one to predict the solubilization of PAHs when the amount of individual contaminants and of gross tar sorbed to soil, the average molecular weight of tar, the surfactant loading (SL), the surfactant sorption isotherm, the aqueous solubility of pure subcooled PAH, and the micelle-water partitioning coefficient are known.

Model Verification of Micellar Solubilization:

In applying the model, most thermodynamic data for the constituent PAHs were obtained from published sources or calculated from experimental results. Though the average molecular weight of liquid coal tar can be determined using methods such as vapor phase osmometry, the average molecular weight for the tar-like contaminants in a weathered MGP soil may be extremely difficult to measure. The molecular weight of coal tar has been reported to range from 230 to 1600 (Peters and Luthy, 1994). Since majority of the tar constituents in MGP soil was probably polymerized hydrocarbons insoluble even in methylene chloride, the highest reported values (1600) was selected as

the average molecular weight of tar in the soil/tar matrix. In analyzing the results, no attempt was made to optimize the molecular weight of the coal tar to obtain a better fit of the predictive equations to experimental data.

The aqueous solubility of individual components in liquid-solid mixtures such as coal tar in MGP soils can be described by one of the two limiting cases: the solubility based on Raoult's law (Eq. 6) or the solubility of pure PAH crystals (C_i^S) (Banerjee, 1984). The former typically applies to multi-component single phase liquids and the latter to noninteracting solid phase mixtures. A comparison of experimentally measured values of $C_{aq,i}$ with predicted values using the two limiting cases is given in Figure 14. Clearly, Raoult's law adequately describes $C_{aq,i}$ of PAHs in the MGP soil used in this study. Similar observations are reported by Lane and Loehr (1992). The values of $K_{soil/tar\text{-}aq}$ for each PAH was calculated from Eq. 19. The estimated partitioning coefficients and the parameters used to estimate them are listed in Table 7. A regression analysis of the experimental values of $K_{soil/tar\text{-}aq}$ for PAHs yielded the relationship: $\log K_{soil/tar\text{-}aq} = -0.83 \log C^L - 3.13$ for the untreated MGP soil. The corresponding relationship obtained using Raoult's law (Eq. 2.19) is: $\log K_{soil/tar\text{-}aq} = -\log C^L - 3.30$.

The key parameter in surfactant solubilization of PAHs from MGP soil (Eq. 20) is $K_{soil/tar\text{-}mic}$, the soil/tar-micelle partitioning coefficient. The estimated values of $K_{soil/tar\text{-}mic}$ for four PAHs and all five surfactants are compared with corresponding measured values in Table 8. Overall, the predictions were satisfactory. Also, Figure 15 shows a satisfactory correspondence between the predicted and experimental values of

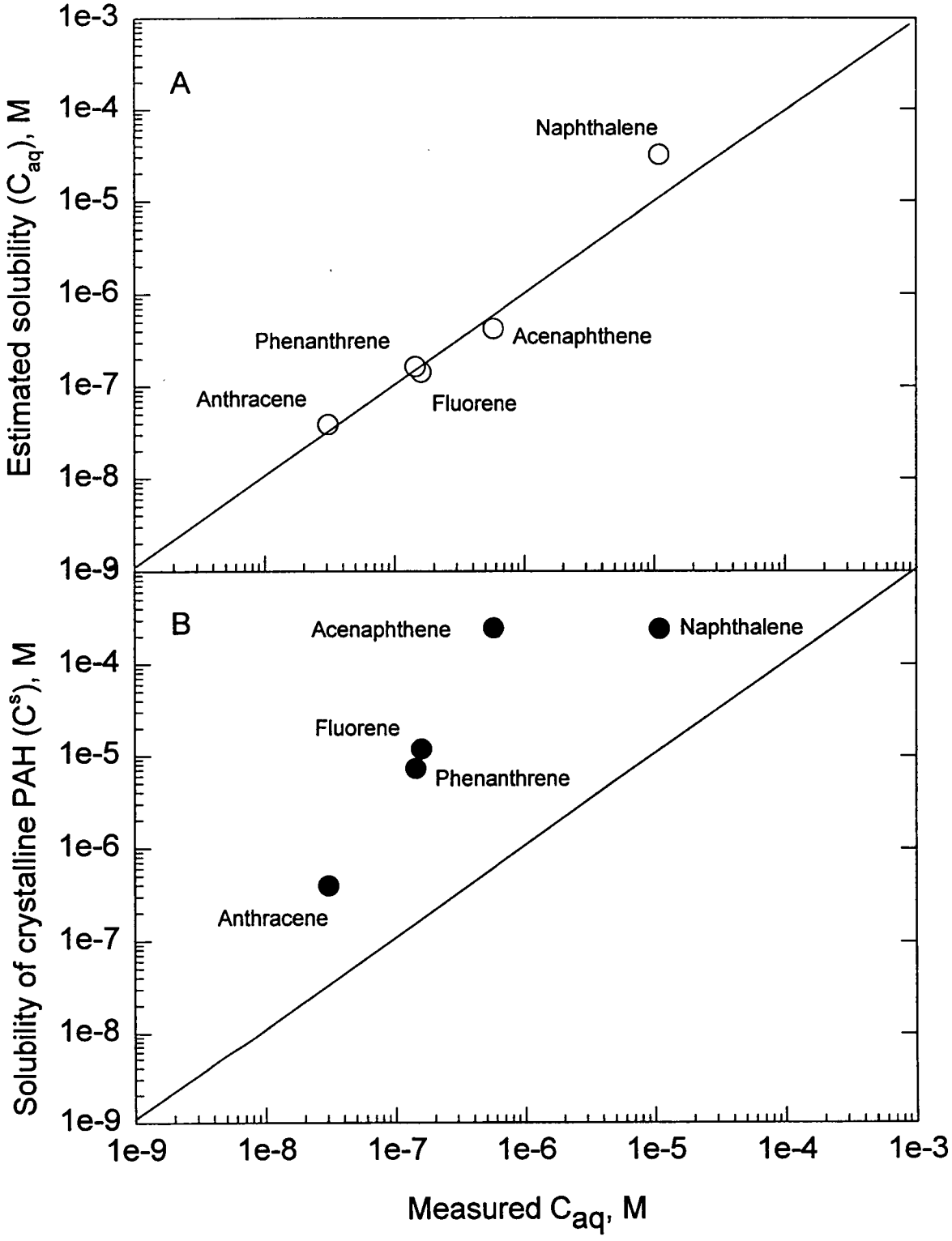


Figure 14. Comparison of measured aqueous solubilities of PAHs from MGP soil with (A) Raoult's law estimates and with (B) solubilities of crystalline PAHs

Table 7. Dissolution of PAHs from MGP soil into water

PAH	C_i^S (M)	(f^L/f^S)	C_i^L (M)	C_{aq}(M)		$K_{soil/tar\text{-}water}$ (L/g)	
				Expt	Est	Expt	Est
Naphthalene	2.42E-4	3.53	8.54E-4	1.10E-5	3.16E-5	1.58	0.55
Acenaphthene	2.47e-5	5.05	1.25E-4	5.75E-7	4.22E-7	2.76	3.75
Fluorene	1.19E-5	7.94	9.46E-5	1.60E-7	1.44E-7	4.21	4.68
Phenanthrene	7.25E-6	5.65	4.10E-5	1.44E-7	1.64E-7	13.0	11.4
Anthracene	3.93E-7	77.5	3.05E-5	3.06E-8	3.88E-8	19.5	15.4
Pyrene	6.93E-7	19.8	1.37E-5	-	2.46E-8	-	34.2
Benzo(a)pyrene	1.51E-8	32.3	4.88E-7	-	1.78E-10	-	960

Table 8. Soil/tar-micelle partitioning coefficients ($K_{soil/tar\text{-}mic}$) for combinations of PAHs and surfactants

PAH	Triton X-100		Brij 35		Tween 80	
	Expt	Est	Expt	Est	Expt	Est
Phenanthrene	0.367±0.04	0.410	0.436±0.06	0.721	0.339±0.03	0.407
Anthracene	0.447±0.03	0.645	0.587±0.09	1.011	0.507±0.03	0.777
Pyrene	0.383±0.07	0.347	0.490±0.10	0.681	0.372±0.05	0.396
Benzo(a)pyrene	0.810±0.04	0.638	1.014±0.24	1.007	0.817±0.17	0.765

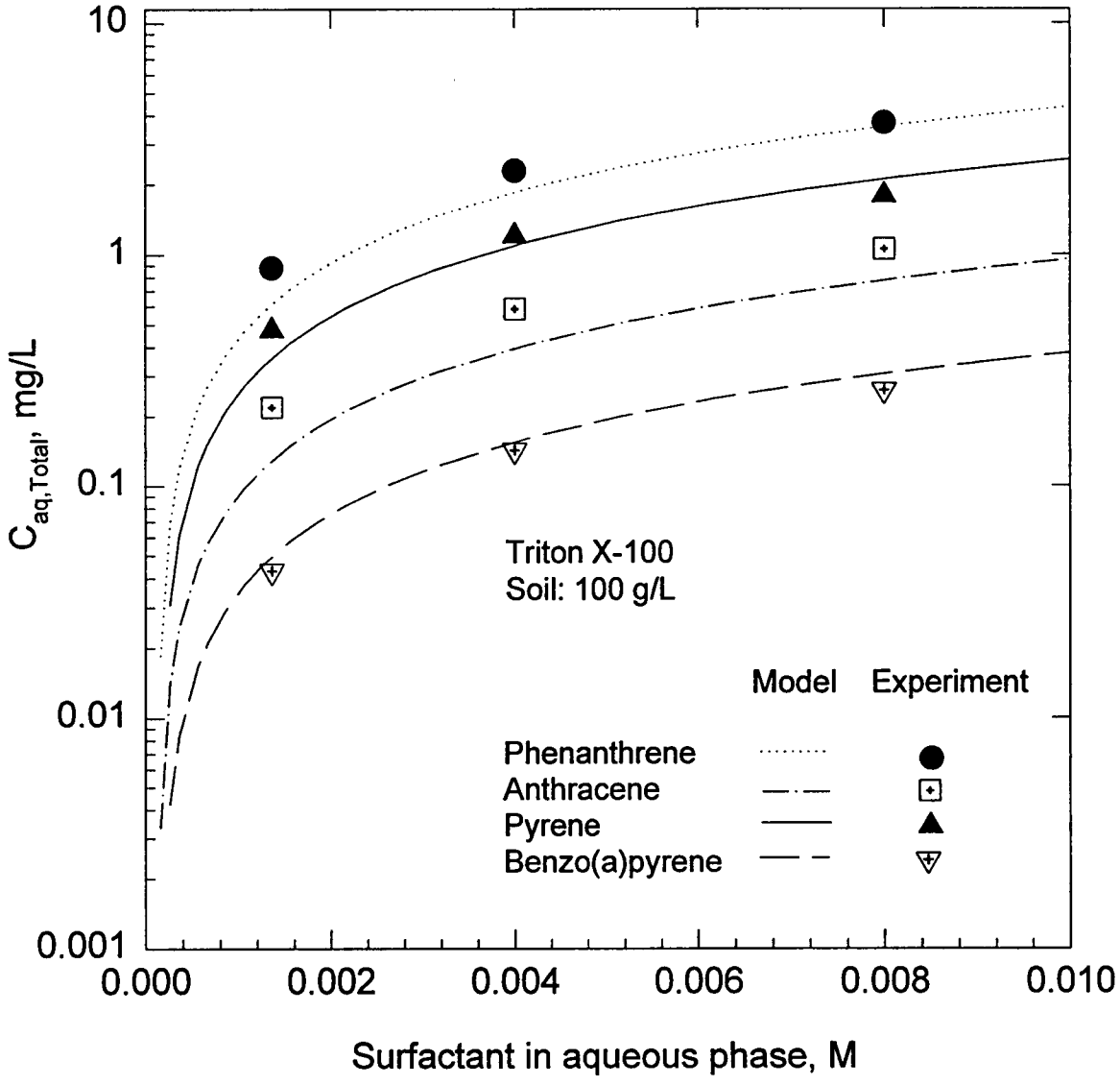


Figure 15. Comparison of predicted solubilization of PAHs from MGP soil by Triton X-100 with measured values

solubilization of all PAHs. For an occasional data point, prediction and experiment were incongruent. Therefore, it is unlikely that the overall accuracy of the estimates would substantially improve if a different value of MW_{ct} were to be selected. The solubilization of anthracene was under predicted, regardless of the type of surfactant used. The sensitivity of the model to MW_{ct} was analyzed for pyrene solubilization by Triton X-100 (Figure 16). No single value of MW_{ct} resulted in accurate prediction of $C_{aq,total}$ over the entire range of data points.

Generally, the model over-predicted solubilization at high surfactant dosages for all PAHs. Nonequilibrium release of PAHs at high surfactant dosages may explain such variances. In addition, the aqueous surfactant concentration may decrease with time due to sorption of surfactant to soil (Figure 5, Part 3). Consequently, solubilization of soil-bound PAH would also decrease.

The predicted release of individual PAHs from the MGP soil at various surfactant loadings (Eq. 20) are compared with experimental values in Figure 17. The value of q_{surf} was determined from Figure 7. At relatively low surfactant dosages, solubilization was observed to increase linearly with dosage, as predicted. Agreement between the model and experimental data was best in this range. As the fractional removal of PAH increased with surfactant dosage, the predictions deviated from measured values. The most plausible explanation for such differences is the nonequilibrium conditions that may exist in solubilization of PAHs at high dosages. To be solubilized, PAHs must be removed from soil/tar. At high surfactant concentrations, PAHs were being removed from deeper areas of the matrix causing significant mass transfer limitations. As shown

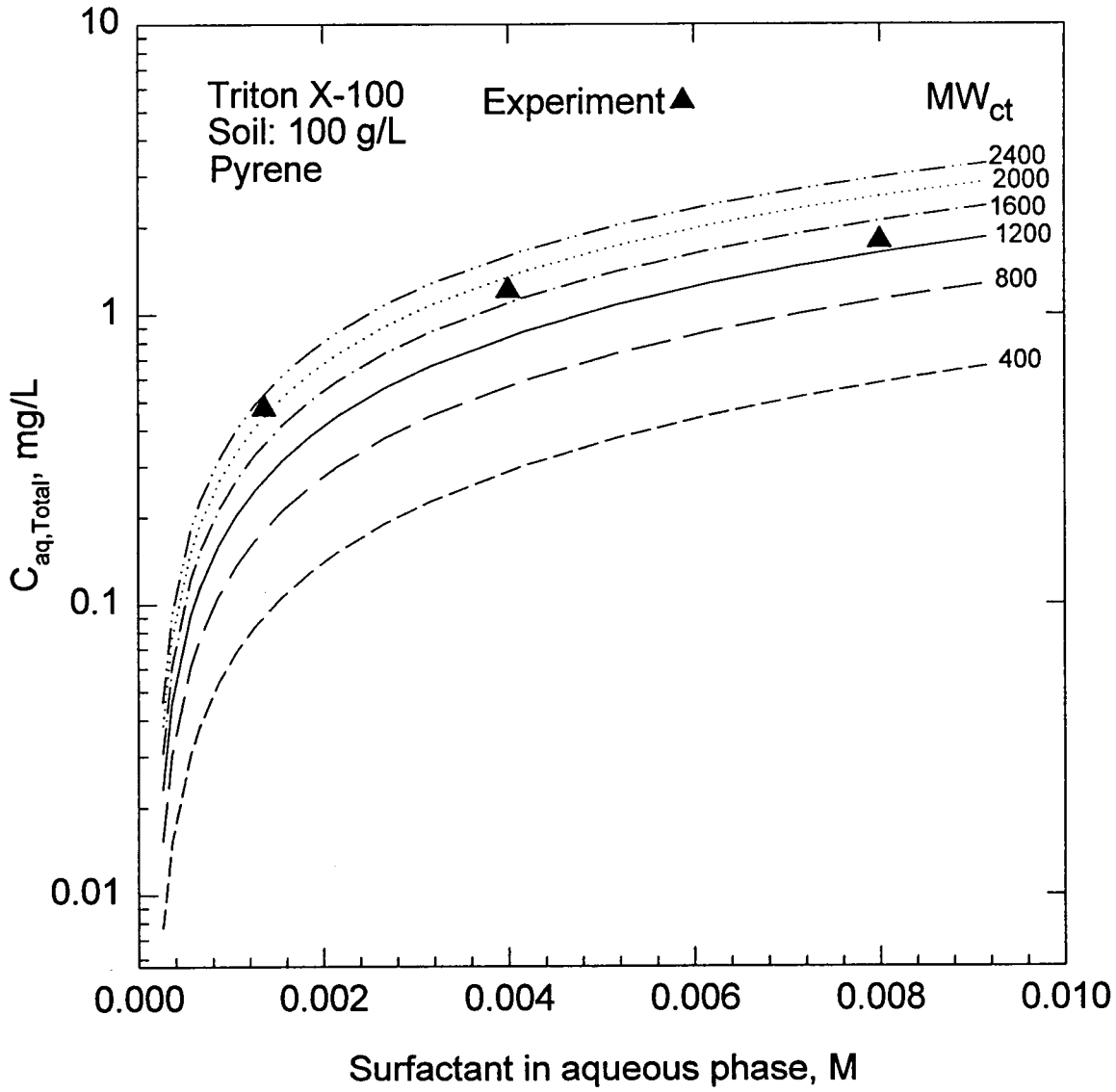


Figure 16. Effect of average molecular weight of coal tar on model prediction of pyrene solubilization from MGP soil

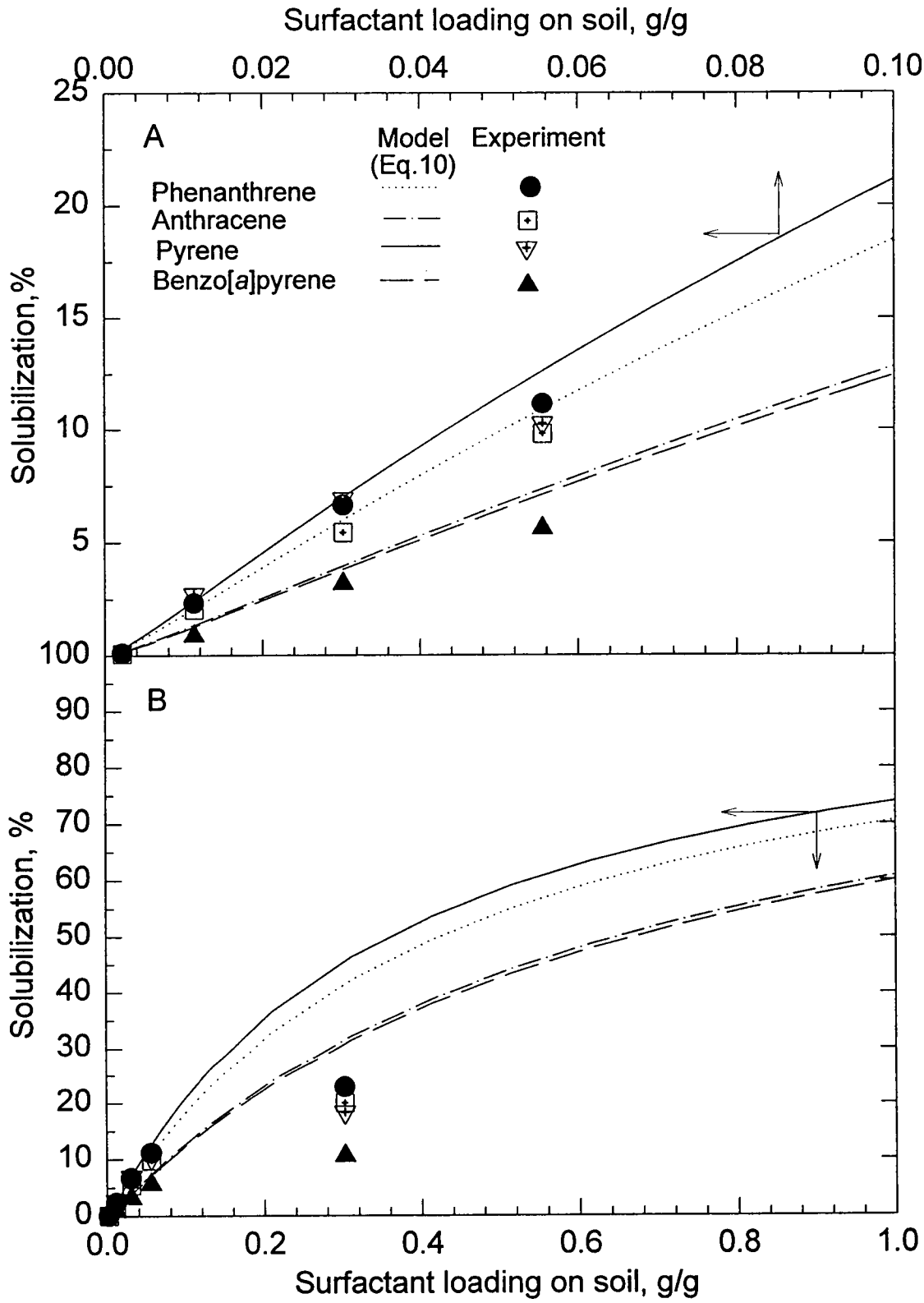


Figure 17. Comparison of predicted solubilization of PAHs from MGP soil at equilibrium with measured values

in Figure 10, at the highest dosage (30 g/L), nonequilibrium effect was manifest. Equilibrium for phenanthrene solubilization was not reached within the experimental period (380 hr).

2.6 SUMMARY

Solubility enhancement of soil-bound PAHs by surfactants was investigated using two soils: an artificially contaminated Tennessee soil and a soil from an MGP site. Five polyoxyethylene (POE) surfactants including three homologs of linear alcohol ethoxylates were used. The capacity of each surfactant to enhance the solubilities of PAHs in water was determined using pure PAH crystals. The solubilization capacity measured as the micelle-water partitioning coefficient, K_m, was correlated with the properties of the surfactants, in particular, the HLB of surfactants. Sorption of surfactants on soils was also measured to determine the micelle concentration in the aqueous phase for a given dosage of surfactant. Sorption of Triton X-100 to the MGP soil increased at supra-CMC dosages; the sorption isotherm at these high dosages distinctly differed from that at sub-CMC dosages. Sorption was described as a partitioning of surfactant molecules between water and the tar phase of the soil rather than an adsorption on the soil/tar surface.

While surfactants were very efficient in solubilizing PAHs from the artificially contaminated soil (f_{oc}=1.8 %), they were much less effective for the heavily contaminated MGP soil. While 90 % of phenanthrene was solubilized from the Tennessee soil at 5 g/L of surfactant, only 20-30 % were removed from the MGP soil at the same dosage. The solubilization efficiency of a surfactant in a soil-water system could be estimated from the soil-micelle partitioning coefficient, $K_{soil\text{-}mic}$, and surfactant:soil

ratio in the system (surfactant loading). $K_{soil\text{-}mic}$ values of 0.01 and 0.55-0.70 were obtained for the natural soil and the MGP soil, respectively. A model describing the partitioning of individual PAHs between tar and soil, and aqueous and micellar pseudophases was developed. The model satisfactorily described solubilization at relatively low surfactant dosages. It over predicted solubilization at very high surfactant dosages. The discrepancies were attributed to the kinetic limitation of PAH mass transfer in the soil/tar matrix. Solubilization of PAHs from MGP soil appears to be a slow rate-limited process and the equilibrium at such high surfactant dosages may not be reached within the practical time limit (months).

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PART 3

KINETIC LIMITATIONS IN MICELLAR SOLUBILIZATION OF PAHS FROM COAL TAR CONTAMINATED SOIL

1. INTRODUCTION

The persistence of toxic hydrophobic organic compounds (HOCs) in soil has been a major impediment to successful remediation of weathered, contaminated soils. Because of their low aqueous solubilities and slow rate of release from soil, pump-and-treat, the most commonly used method for soil remediation, is able to remove only a small fraction of soil-bound contaminants (Haley *et al.*, 1991; DiCesare and Smith, 1994).

Surfactants have been found to enhance the mobility of soil-bound HOCs (Smith *et al.*, 1991; West and Harwell, 1992). By promoting mobilization, surfactants can increase the efficiency of contaminant removal by pump and treat or other soil washing processes (Abdul *et al.*, 1992). Enhanced mobility of a contaminant by surfactant may also increase the availability of the compound for chemical or biological degradation (Aronstein *et al.*, 1991; Bury and Miller, 1992; Aronstein and Peterek, 1995).

To date, studies on mobilization of HOCs by surfactants have mainly focused on equilibrium partitioning of HOCs in artificially contaminated soils. The enhanced mobilization of HOCs is commonly attributed to the increased concentration gradient at the soil-water interface created by the partitioning of aqueous HOCs into the micellar pseudophase. It is assumed that contaminant equilibrium between soil, water, and micelle phases is established rapidly (< 1 day). Such equilibrium partitioning models are able to describe the experimental data fairly well for soils contaminated for brief periods (few days), typical of most laboratory studies with artificially contaminated soils (Edwards *et al.*,

1994; Jafvert, 1991). Successful recovery of HOCs from soils (80 - 90 %) has been postulated based on the results of such controlled studies. Studies with artificially contaminated soils do not provide realistic estimates of the mobilities that can be achieved under field conditions (Pavlostathis and Mathavan, 1992; Connaughton *et al.*, 1993. Remediation of coal tar-contaminated soils commonly found in manufactured gas plant (MGP) sites is mainly limited by slow mass transfer of contaminants (Luthy *et al.*, 1994). It appears that even with surfactant washing mobilization is kinetically limited in these soils (Yeom and Ghosh, 1993; Deitsch and Smith, 1995).

While the solubility enhancement of soil-bound HOCs by surfactants has been extensively studied, little information exists on the effect of surfactant on mass transfer rates. The effects of nonionic POE surfactants on the rates of solubilization of PAHs from a weathered MGP soil is examined in this chapter. Mass transfer rates in surfactant solutions are compared with those in aqueous soil suspensions containing polymeric Tenax-TA adsorbent with no surfactant added. Tenax has a strong affinity for organic solutes. Thus, by maintaining a near-zero aqueous concentration of PAHs, Tenax maximizes the concentration gradient at the soil-water interface and so also the partitioning of PAHs into water. Tenax mediated partitioning can be taken as the reference aqueous solubility of soil-bound contaminants. A modified radial diffusion model was used to evaluate the effects of surfactants on contaminant mass transfer rates in such systems.

2. BACKGROUND

The transfer of soil-bound NAPLs into water have been suggested as the key step in the remediation of weathered MGP soils (Luthy *et al.*, 1994). The steps in the desorption and dissolution of HOCs from contaminated soils and NAPLs are reviewed here. Although such mass transfer may involve many steps, the overall rate is typically controlled by the slowest step. The effects of additives such as surfactant and organic solvent on the rate limiting processes are also discussed.

2.1 Rate-Limited Mass Transfer of HOCs in Soil

In many cases, the desorption of HOCs from contaminated soil is controlled by diffusive mass transfer. Of the many diffusion mechanisms proposed for rate-limited desorption, retarded intraparticle diffusion and intraorganic matter diffusion theories are reviewed in relation to weathering of soils. Possible diffusion-limited dissolution of NAPL is also discussed.

Desorption of HOCs:

Desorption of HOCs from soil has often been considered a two step-process (Brusseau and Rao, 1989): film diffusion at the soil-water interface and diffusion within the sorbent phase, the SOM in particular, the slower of the two steps controlling the overall rate of mass transfer. Although film diffusion may control the initial fast desorption of HOCs

from soil, diffusion within the sorbent region is thought to be responsible for the slow desorption of contaminants from most weathered soils. Of the many mechanisms proposed for mass transfer in the sorbent region, two diffusion processes are commonly used: retarded intraparticle diffusion and intraorganic matter diffusion (Brusseau and Rao, 1989; Brusseau *et al.*, 1991; Ball and Roberts, 1991).

Retarded intraparticle diffusion involves aqueous phase diffusion of a sorbate within soil micropores. Diffusion of sorbate is retarded by instantaneous sorption/desorption at pore walls. Since sorption of HOCs is mostly controlled by SOM, this theory assumes that most SOM reside inside the soil particle. In intraorganic matter diffusion, sorption of HOC is described by diffusion through a three-dimensional matrix of soil humus. Accordingly, initial rapid partitioning of a sorbate into external organic matter surface followed by slow diffusion through organic matrix over a much longer period completes the sorption process. Aging or weathering of contaminant chemicals plays a significant role in such nonequilibrium transport. Both the rate and extent of desorption of HOCs decrease with the weathering period (Pavlostathis and Mathavan, 1992; Hazinger and Alexander, 1995). During aging, the HOCs may diffuse deeper into of the soil humus; the desorption of HOCs is controlled by slow diffusion within the soil organic matter. Alternatively, the chemicals may slowly diffuse into and become entrapped in the soil micropores during aging (Hazinger and Alexander, 1995). Diffusion through the tortuous micropores may cause slow desorption of contaminants observed in aged soils. In either case, the desorption rate would decrease with increased period of aging.

Dissolution of NAPL:

First order mass transfer through the stagnant film at the interface may control the rate of dissolution of NAPLs into water (Hunt *et al.*, 1988; Miller *et al.*, 1990):

$$J = k_L \ C_{Sat} - C_{aq} \qquad (1)$$

where J is the flux, k_L is the mass transfer coefficient, and C_{Sat} is the aqueous solubility of a chemical in the NAPL and C_{aq} is the aqueous concentration of the chemical. In this model, the maximum dissolution rate of NAPL constituents per unit surface area is controlled by their mass transfer coefficients and solubilities (k_L ,C_{sat}). Mass transfer resistance within the NAPL is considered negligible and not addressed in most current models for NAPL dissolution (Borden and Piwoni, 1992; Seagren *et al.*, 1994). However, in a multi-component NAPL, selective dissolution of relatively soluble components for a long period from very viscous NAPLs may result in uneven distribution of constituents in the organic phase. If the diffusion of such compounds in the organic phase is slower than the diffusion through the interfacial hydrodynamic film, organic phase mass transfer may become the rate-limiting step in dissolution. Another form of mass transfer limitation in NAPL dissolution is the possible development of organic film at the NAPL-water interface. Luthy *et al.* (1993), reported the development of an interfacial skin with aging when a drop of free flowing coal tar is exposed to water for a long time (weeks). The film was

suggested as the major mass transfer barrier to dissolution. No information is available on the dissolution kinetics of weathered tar associated with MGP soils.

2.2 Effect of Additives on the Rate of Mass Transfer

To enhance the mass transfer of HOC from soil or NAPLs, solubilizing agents such as water-miscible organic solvents or surfactants are often used. Additives often significantly increase the aqueous solubilities (C_{Sat}) of HOCs and thus increase the dissolution rate of NAPL constituents (Fu and Luthy, 1986; Pennell *et al.*, 1993; Imhoff *et al.*, 1995). Conceivably, the increased concentration gradient at the soil-water interface can, in turn, cause increased desorption of HOCs from the diffusion-limited sorbent matrix. Addition of solubilizing agents may also facilitate the diffusion process by increasing the diffusivity of a solute, as has been observed in studies with organic cosolvents (Nkedi-Kizza *et al.*, 1989; Wood *et al.*, 1990; Brusseau *et al.*, 1991). In these studies, organic matter diffusion was assumed to be the rate limiting process, and the enhanced desorption of HOCs in solvent-water mixtures was attributed to the increased diffusivities of the solutes within the organic matrix of soil. The interactions between soil organic matter and organic solvent are believed to be similar to that observed in polymer-solvent systems. Penetration and swelling of the soil organic matter by organic solvent molecules are the possible mechanisms by which solute diffusivities in a polymer matrix may be increased (Freeman and Cheung, 1981). The effect of surfactant on the diffusional mass transfer has received little attention in spite of its practical importance in surfactant-aided treatment

processes. Only recently, Deitsch and Smith (1995) reported an enhancement of the mass transfer coefficient in the desorption of trichloroethene (TCE) by Triton X-100. It was suggested that increased desorption resulted from the combined effects of an increased concentration gradient and increased intrasorbent diffusivity. It was reasoned that Triton X-100 reduced surface tension between water and SOM and/or expanded the soil organic matrix, thereby reducing tortuosity of the soil.

3. MATERIALS

A coal tar-contaminated soil from an MGP site was used in this study. Five nonionic polyoxyethylene (POE) surfactants, Triton X-100, Tween 80, and three homologs of linear alcohol ethoxylates, $C_{12}E_4$, $C_{12}E_{10}$, and $C_{12}E_{23}$ were used in soil washing experiments. Tritium-labeled Triton X-100 (phenyl-^{3}H-) with a specific activity of 2.37 mCi/mg was used to determine the sorption kinetics of surfactant on the soil. The characteristics of the MGP soil, the concentrations of PAHs in the soil, and the properties of the surfactants are given in Tables 1, 2, and 3 of Part 2, respectively.

Tenax®- TA polymeric beads (20/35 mesh) were obtained from Altech Co. Tenax-TA is a porous polymer made of 2,6-diphenyl-p-phenylene oxide. Due to its exceptionally good adsorption properties and heat resistance, Tenax has been used as both a column packing material for gas chromatography (GC) and an adsorbent for trapping volatile and semi volatile organic compounds. Recently, Tenax was used to study the slow desorption of halogenated aliphatic hydrocarbons (HHCs) in aqueous suspensions of soil (Pignatello, 1990). A similar polymeric resin (XAD-4) has been used to study the desorption of PCBs from sediments (Carroll *et al.*, 1994). Tenax adsorb aqueous HOCs nearly completely from solution and thus help maximize the mass transfer of soil-bound HOCs at the soil-water interface. Tenax is buoyant in water and can be easily removed from the suspension after centrifugation. Reportedly, Tenax-mediated removal of aqueous HOC is superior to that by

gas sparging (Pignatello, 1990). The experimental setup for Tenax-adsorption of HOCs is much simpler than gas sparging. Multiple samples can be studied simultaneously while the soil sample is kept well mixed.

Tenax was preconditioned as follows: It was sequentially washed with acetone and methanol (10 g Tenax/1 L solvent) for a day. At the end of each washing, the beads were dried with nitrogen gas. Finally, they were sieved through a 35 mesh (500 μm) sieve to remove fine beads and stored in a tightly sealed bottle. The properties of Tenax-TA reported by the manufacturer are: specific surface area (35 m^2/g), pore volume (2.4 cc/g), average pore size (200 nm), and density (0.16 g/cc).

4. METHODS

The experimental methods used to measure the mass transfer rate of PAHs from the MGP soil in the presence of Tenax and surfactants are described below. In addition, the method used to determine the kinetics of surfactant sorption to the MGP soil is described.

4.1 Tenax-Mediated Extraction of PAHs from MGP Soil

Partitioning of PAHs into Tenax in a Closed system :

To determine the extent of Tenax-mediated mass transfer of PAHs from the MGP soil, 2.5 g of soil samples were placed in a series of 30-mL glass centrifuge tubes. To each tube were added 25 mL of DI water (0.05 % $HgCl_2$) and 0.2 g of Tenax. The tubes were mixed by a mechanical shaker (Wheaton Co.) at 22 rpm. At given time intervals, a sample tube was removed from the shaker and centrifuged for 40 minutes at 8000xg. It was then filled to the top by adding 2-3 mL of DI water and, the floating Tenax beads were completely raked into a 10-mL conical glass centrifuge tube (Corning Co.) using a spatula without disturbing the soil pellet. The Tenax resin recovered from the tube was washed with DI water (5 mL) by vortexing for 2-3 minutes to remove small soil particles attached to the beads. After washing, the water in the tube was removed by pipeting, and the contaminants sorbed on Tenax were extracted with 5 mL acetone. Having mixed for 1 day, the tubes were centrifuged for 20 minutes at 3000xg. An aliquot of the supernatant was

filtered through 0.2 μm aluminum filter (Whatman Co.) using a stainless steel filter holder. The filtrate was analyzed for PAHs by HPLC.

Tenax-water partitioning coefficients for PAHs were determined after 55 days of mixing using duplicate samples of soil suspensions. PAHs adsorbed on Tenax and that remaining in solution were measured. The aqueous concentrations of high molecular weight (HMW) PAHs (4,5-rings) were below the detection limits of HPLC analysis. To measure the concentrations of these compounds in aqueous solution, 40-mL of the supernatant (20 mL from each of the two samples) was filtered through 0.2 μm filter and equilibrated with 0.02 g of fresh Tenax in a 50-mL glass tube. After mixing for 2 days, Tenax was recovered into a 5-mL conical glass centrifuge tube, and the PAHs adsorbed on Tenax were extracted with 1 mL acetone and analyzed by HPLC.

The Tenax removed for extraction was replaced with fresh Tenax beads. Thus, the mass transfer rate of PAHs was measured under a maximum concentration gradient at the soil/tar-water interface. Two tubes containing soil and Tenax beads were prepared identically as described above. After mixing for 1 day, the tubes were centrifuged for 40 minutes at 8000xg. After carefully recovering the Tenax, the same amounts of fresh Tenax (0.2 g) were added to the tubes and mixed again. The 1 day-mixing cycle was repeated for 12 days. Tenax-sorbed PAHs were extracted with acetone at the end of each 1-day cycle and analyzed.

Extraction of PAHs from Surfactant-Coated Soil:

Surfactant solutions of various concentrations (25 mL) including a control (no surfactant) were added to 30-mL glass centrifuge tubes each containing 2.5 g of the soil. After mixing for two days, the tubes were centrifuged for 40 minutes at 8000xg, and the supernatants were decanted. The soil remaining in the tube was repeatedly washed with 25 mL of DI water until the aqueous concentration of surfactant was 2-3 times lower than the CMC. In a separate experiment, it was shown that, in the absence of repeated washing of excess surfactant, Tenax adsorbed surfactant molecules from supra-CMC solutions and settled with the soil particles, making their separation from the soil suspension difficult. Once the aqueous surfactant concentrations were below CMC, 0.2 g of Tenax was added to the surfactant-amended soil in each tube and the contents mechanically mixed. At given time intervals, the tubes were centrifuged, the Tenax was removed and replaced with the same amount of fresh Tenax. PAHs adsorbed on Tenax so removed were extracted with acetone and analyzed.

4.2 Surfactant Solubilization of PAHs from MGP Soil

The solubilization rate of PAHs from the MGP soil was determined by two sets of batch washing experiments. First, the solubilization of PAH was temporally measured in various surfactant solutions (sec. 4.5, Part2). Second, the soil was repeatedly washed with a known surfactant solution. In a series of 30-mL glass centrifuge tubes, 2.5 g soil and 25 mL of surfactant solutions were mixed. At the end of each 1-day wash cycle, the tubes were

centrifuged and an aliquot of the supernatant was filtered through 0.2 μm filter. The filtrate from duplicate samples were analyzed for PAHs. The remaining supernatant was carefully decanted without disturbing the soil pellet, the same volume of fresh surfactant solution was added to the tube, and the washing cycle was repeated. The PAHs in each wash water sample were determined. The cumulative removal of PAHs by repetitive washing was determined over 10 to 12 wash cycles.

4.3 Kinetics of Surfactant Sorption

Solutions containing 0.75 and 5.5 g/L of radiolabeled Triton X-100 were prepared as described in sec. 4.1, Part 2. In a series of glass centrifuge tubes, 2.5 g of soil and 25 mL of surfactant solutions were mechanically mixed. At given time intervals, duplicate samples of each surfactant solution were removed from the shaker and centrifuged for 40 minutes at 8000xg. The aqueous concentration of Triton X-100 was radiochemically measured as described in sec. 4.1, Part 2. Sorption of Triton X-100 was measured for 56 days. A blank surfactant sample was also run to account for the natural decay of tritium during the adsorption test.

5 RESULTS AND DISCUSSION

5.1 Transport of PAHs from Soil to Water

To determine the mass transfer rates of PAHs from MGP soil, release of individual PAHs from the soil into water was measured in the presence of Tenax. In Figure 1, fractional removal of individual PAHs (M_t/M_0) from soil is plotted as a function of time. Clearly mass transfer of PAHs from soil is a nonequilibrium process. Except for naphthalene, none of the measured PAHs appeared to have reached equilibrium in 55 days. Naphthalene partitioning into Tenax reached a plateau in about 25 days. To estimate the relative attainment of equilibrium for each PAH, their release under equilibrium conditions was estimated using the soil/tar-water partitioning coefficients, $K_{soil/tar\text{-}aq}$, and Tenax-water partitioning coefficients, $K_{T\text{-}aq}$. The values of $K_{T\text{-}aq}$ were measured separately and are given in Table 1. The values of $K_{soil/tar\text{-}aq}$ were obtained from Table 7 of Part 2. The fractional removal of PAH can be estimated from the equilibrium distribution between soil/tar and Tenax as shown below:

$$\left(\frac{M_t}{M_0}\right) = \frac{1}{1+\left(\frac{K_{soil/tar-aq}}{K_{T-aq}}\right)\left(\frac{W_{soil}}{W_T}\right)} \qquad (2)$$

where $W_{soil,}$ and W_T are, respectively, the concentrations of soil and Tenax added (g/L). The estimated values of M_t/M_O at equilibrium are shown in Table 1. The release of

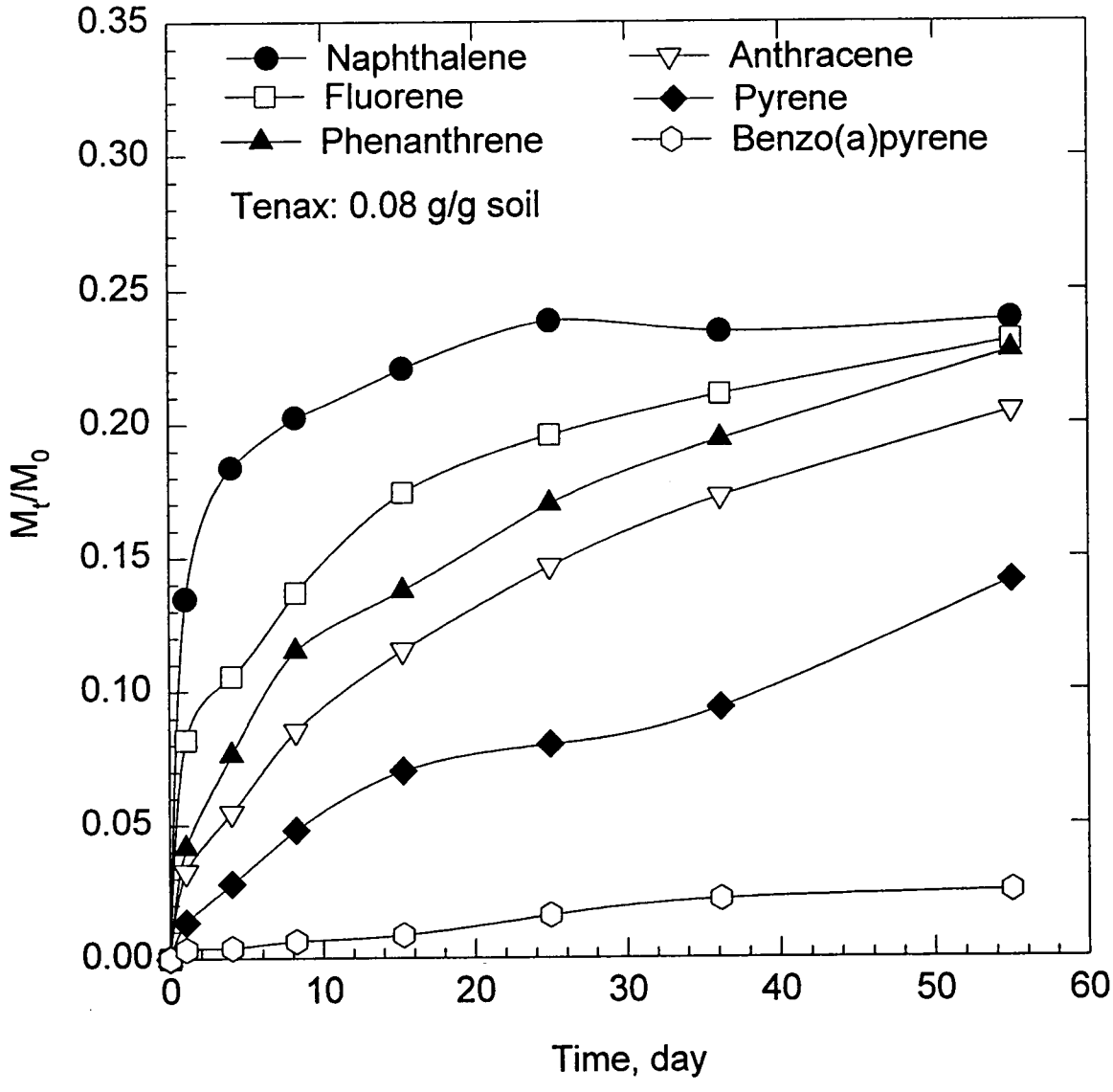


Figure 1. Fractional removal of PAHs from MGP soil in the presence of Tenax

Table 1. Tenax-water partitioning coefficients ($K_{T\text{-}aq}$) and estimated equilibrium values (M_t/M_o) of PAHs

PAHs	$K_{T\text{-}aq}$ (L/g)	(M_t/M_o)
Naphthalene	45.1	0.27
Fluorene	131.8	0.58
Phenanthrene	270.0	0.68
Anthracene	259.5	0.57
Pyrene	1325	0.75

naphthalene after 25 days was close to its predicted equilibrium value (26.5 %). However, release of other PAHs, even after 55 days, were much less than the predicted equilibrium values. For example, fluorene release was less than a half of the equilibrium value (58 %), and phenanthrene release was only one-third of the equilibrium value (68 %). Only 2.6% of benzo[*a*]pyrene partitioned into Tenax in 55 days.

The mass transfer of individual PAHs from MGP soil in the presence of Tenax involves at least three steps: (1) tar phase matrix diffusion of PAH molecules, (2) mass transfer at the soil/tar-water interface, and (3) partitioning into Tenax. Given that partitioning of PAHs into Tenax is relatively fast (Pignatello, 1990), step 1 and/or step 2 must be rate-limiting.

The interfacial mass transfer of a PAH (step 2) can be described by Eq. 1. Since the surface area of the MGP soil particles is unknown, Eq.1 can be rewritten using a lumped parameter to include the mass transfer coefficient, k_L (LT^{-1}) and the specific surface area, a (L^3/L^2):

$$\frac{dC_{aq}}{dt} = k_L a\, C_{sat} - C_{aq} \qquad (3)$$

Mass transfer coefficient for the dissolution of PAHs from coal tar are sparse in the literature. Recently, Ramaswami *et al.*, (1994) reported k_La values of 500- 2500/day for the

dissolution of naphthalene from coal tar with varying periods of aging in water. For comparison, the measured naphthalene removal from the MGP soil (Figure 1) was fitted to the mass transfer model. To include partitioning of aqueous PAHs into Tenax, Eq. 3 was modified to:

$$(K_{T-aq}W_T)\frac{dC_{aq}}{dt} = k_L a\, C_{sat} - C_{aq} \tag{4}$$

The aqueous solubility of PAH in the MGP tar (C_{sat}) can be determined using Raoult's law (Eq. 6, Part 2). However, the value of C_{sat} changes during dissolution because its mole fraction changes. The solubility of a compound, *i*, can be given by:

$$C_{sat,i} = C^{o}_{sat,i} - (x^{o}_{ct,i} - x_{ct,i})C^{L}_{i} \tag{5}$$

where the superscript '*o*' denote initial conditions. The moles of *i* removed from the soil during dissolution are equivalent to the mass adsorbed to Tenax plus the mass in aqueous phase. This is given by:

$$\left(\frac{F_{ct}MW_i}{MW_{ct}}\right)(x^{o}_{ct,i} - x_{ct,i}) = 1 + K_{T-aq,i}W_T\left(\frac{C_{aq}}{W_{soil}}\right) \tag{6}$$

From Eqs. 5 and 6, $C_{sat,i}$ can be estimated as a function of $C_{aq,i}$.

The measured naphthalene dissolution in the presence of Tenax was fitted to the mass transfer model (Eq.4) using Sigmaplot curve fitter (Jandel Co. ver. 2.01). A value of 166/day was obtained for the lumped mass transfer coefficient, $k_L a$, with a coefficient of variation of 32.5 (CV%=100× (std. err./parameter value)) which is significantly lower than the values reported by Ramaswami *et al.* (1994) for soils with a particle size (237 μm) similar to those used in this study. Further, the model resulted in a poor fit of data for higher-ring PAHs. Matrix diffusion of a PAH in the tar phase appears to be the most likely rate-limiting step; given the high organic content (f_{OM} = 0.75) of the MGP soil, intra-organic matter matrix diffusion is more likely to occur than intrapore diffusion.

The majority of the organic matter in the MGP soil was not soluble in boiling methylene chloride. Lighter PAHs mixed with the insoluble asphaltene fraction in fresh coal tar might have been preferentially dissolved into ground water during weathering processes. The remaining higher molecular compounds might have formed a semi-solid polymer-like mixture, in which resistance to PAH diffusion was significantly increased. As a result, further dissolution of PAHs trapped in the matrix may be kinetically limited. This scenario is supported by the much lower fraction of smaller PAHs typically found in weathered MGP soils than in liquid coal tars (Lane and Leohr, 1992; Peters and Luthy, 1993). The fraction of naphthalene, fluorene, phenanthrene, and anthracene together was only 0.37% of the organic matter in the MGP soil used in this study compared with 6.3 % found in a liquid coal tar (Peters and Luthy, 1993). Later in the chapter, a matrix diffusion

model has been shown to describe well the release of constituent PAHs from the test MGP soil.

5.2 Effect of Surfactant on the Release of PAHs from MGP Soil

Solubilization of four individual PAHs, phenanthrene, anthracene, pyrene, and benzo[*a*]pyrene from the MGP soil by surfactants was determined using both single and multiple washing experiments. In single washing, the release of PAHs from the soil into surfactant solutions was measured as a function of time. In Figure 2, the release of phenanthrene from soil using surfactants and Tenax are compared. Among the surfactants used, Brij 30 ($C_{12}E_4$) was the most efficient, and Brij 35 ($C_{12}E_{23}$) was the least efficient. However, regardless of the surfactant used, partitioning equilibrium of phenanthrene in surfactant solutions was reached faster than in the presence of Tenax. While phenanthrene solubilization for all five surfactants reached maximum values in 5 to 10 days, the partitioning into Tenax continued to increase even after 55 days. Similar trends were observed for anthracene, pyrene, and benzo(a)pyrene.

In Figure 3, solubilization of phenanthrene by repetitive surfactant washing is compared with phenanthrene partitioning into Tenax. After 12 washing cycles, more than 90 % of phenanthrene was removed from the soil by 5.5 g/L Brij 30 solution compared to only 20 % removal in the presence of Tenax-TA. Solubilization of phenanthrene by different surfactants varied widely. At the end of the experiments, the test soils were dried in a desiccator and the PAHs remaining on them were measured. The mass balance for

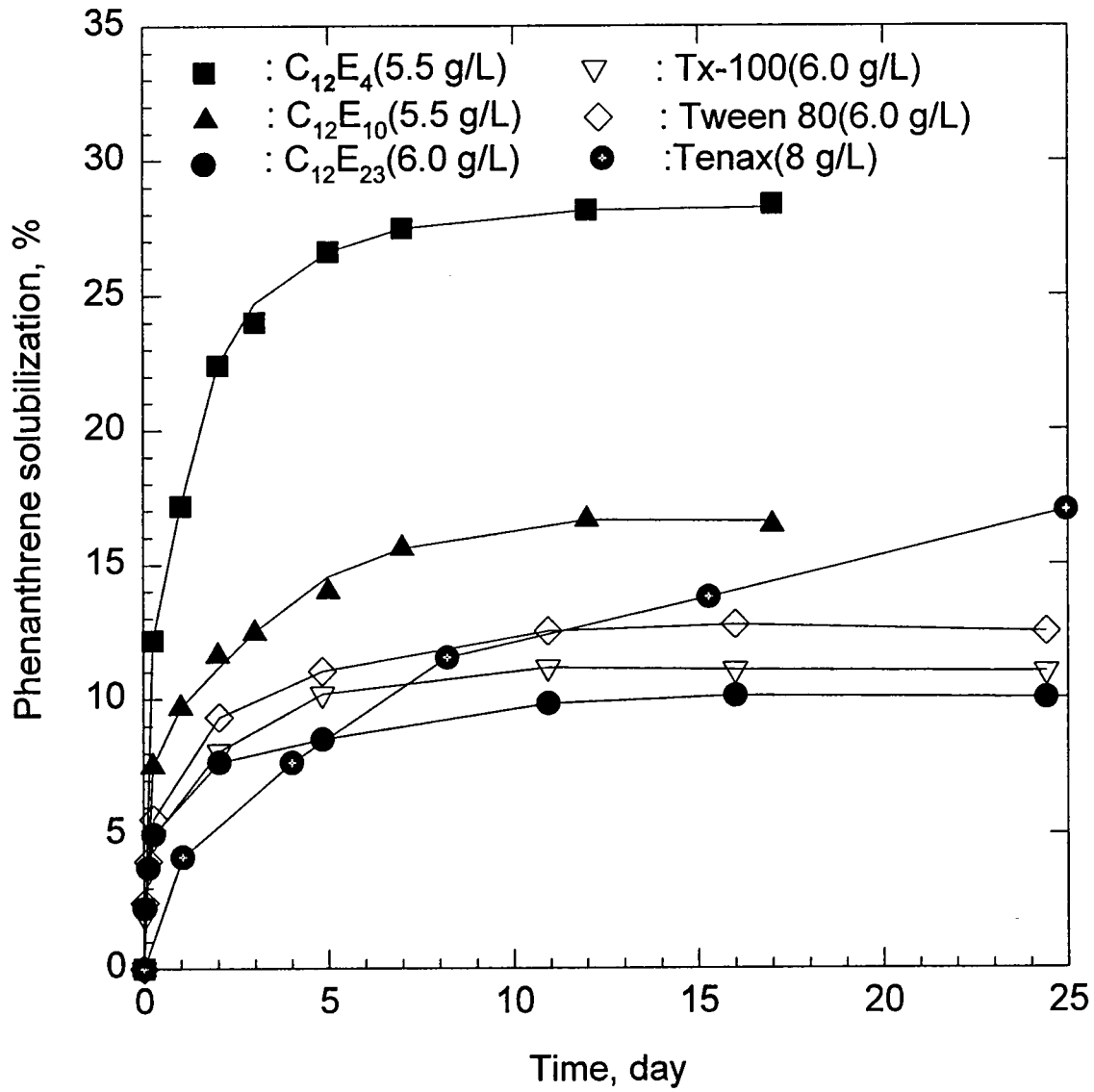


Figure 2. Release of phenanthrene from MGP soil in the presence of surfactants and Tenax

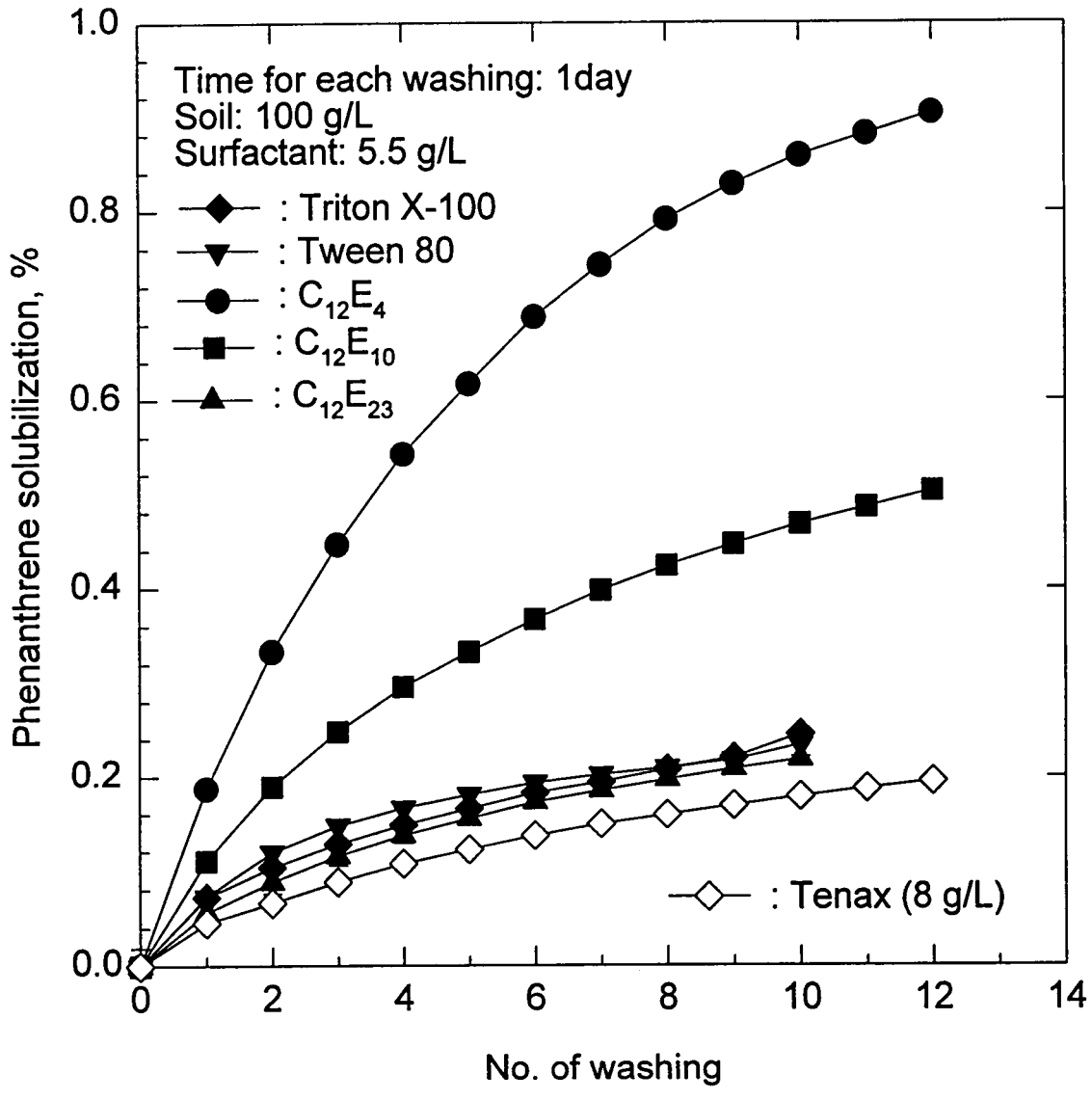


Figure 3. Solubilization of phenanthrene from MGP soil by repetitive washing with surfactant solutions and Tenax

phenanthrene yielded 107±3%, 101±3%, 94±4%, 103±5%, 92±5%, and 93±8% for $C_{12}E_4$, $C_{12}E_{10}$, $C_{12}E_{23}$, Triton X-100, Tween 80, and Tenax, respectively. Solubilization of different PAHs by Brij30 are compared in Figure 4. Solubilization by the surfactant appears to be inversely related to the number of rings in the PAH molecule.

If matrix diffusion within the tar phase limits solubilization of constituent PAHs, surfactants must enhance mass transfer by increasing the matrix diffusion of PAHs. The two possible mechanisms by which surfactants can enhance the matrix diffusion are described below. First, solubility enhancement in surfactant solution can facilitate matrix diffusion by increasing the concentration gradient. The enhanced solubility of a PAH increases the maximum rate of interfacial mass transfer ($k_L a C_{sat}$), and creates a larger concentration gradient facilitating diffusion within the tar matrix. Second, surfactants may increase the diffusivity of PAH in the tar matrix by changing the physical properties of the medium. Surfactant molecules may penetrate into the organic matrix of the MGP soil, swell the medium, and create more space for PAH diffusion. In this hypothesis, the residual tar in the MGP soil is assumed to be a polymer-like, three-dimensional, flexible mesh. This is similar to the mechanism proposed for organic extraction of HOCs from sediment (Freeman and Cheung, 1981). The enhanced extraction of di(2-ethylhexyl) phthalate (DEHP) from a natural sediment by organic solvent was attributed to enhanced diffusivity caused by swelling of the humin-kerogen pore structure. The different extraction efficiency of different solvents were correlated to the ability of each solvent to swell the organic matrix in the sediment, measured by swelling of a reference polymeric gel.

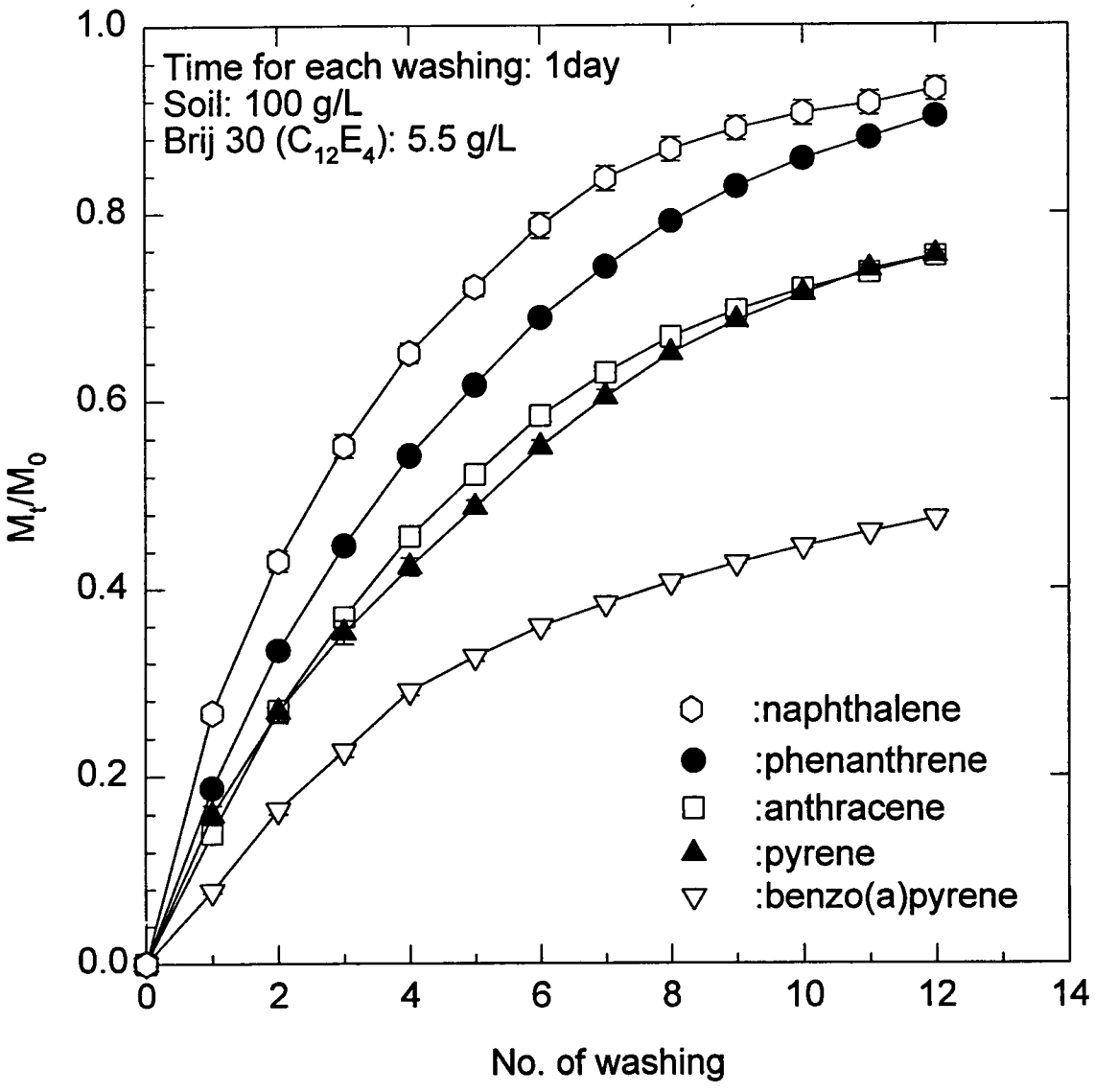


Figure 4. Fractional release of PAHs from MGP soil by repetitive washing with Brij 30 solution

Similarly, a polymer swelling theory has been used to explain the increased intrasorbent diffusion of HOCs by cosolvency of the solution (Nkedi-Kizza *et al.*,1989; Brusseau *et al.*, 1991). Although there is no report on the swelling of weathered coal tar by surfactants, the alkyl chains of the surfactant molecules sorbed to the tar matrix may act like an organic solvent.

Surfactant penetration (or diffusion) into organic matrix in the MGP soil is consistent with the observed nonequilibrium sorption behavior of a surfactant (Figure 5). Clearly, sorption of Triton X-100 to the MGP soil is a nonequilibrium process. Even after 56 days, the sorption increased for both surfactant dosages, 0.75 and 5.5 g/L. Desorption of surfactant was measured by washing the soils obtained from the sorption experiments with DI water for 2 days. Sorption of Triton X-100 was reversible, but the desorption rate was much slower (Figure 6).

5.3 Role of Surfactant in Enhancing Matrix Diffusion

To test the role of sorbed surfactant in mass transfer of PAH from MGP soil, PAHs were extracted with Tenax from soils amended with different surfactants. The soil was equilibrated with surfactant solutions for 2 days, then, repeatedly washed with DI water (each for 1 day) until the aqueous surfactant concentration was at least 2-3 times lower than its CMC. Thereafter, Tenax was added and the suspensions were mechanically mixed. At given time intervals, Tenax was withdrawn and replaced with an equivalent amount of fresh

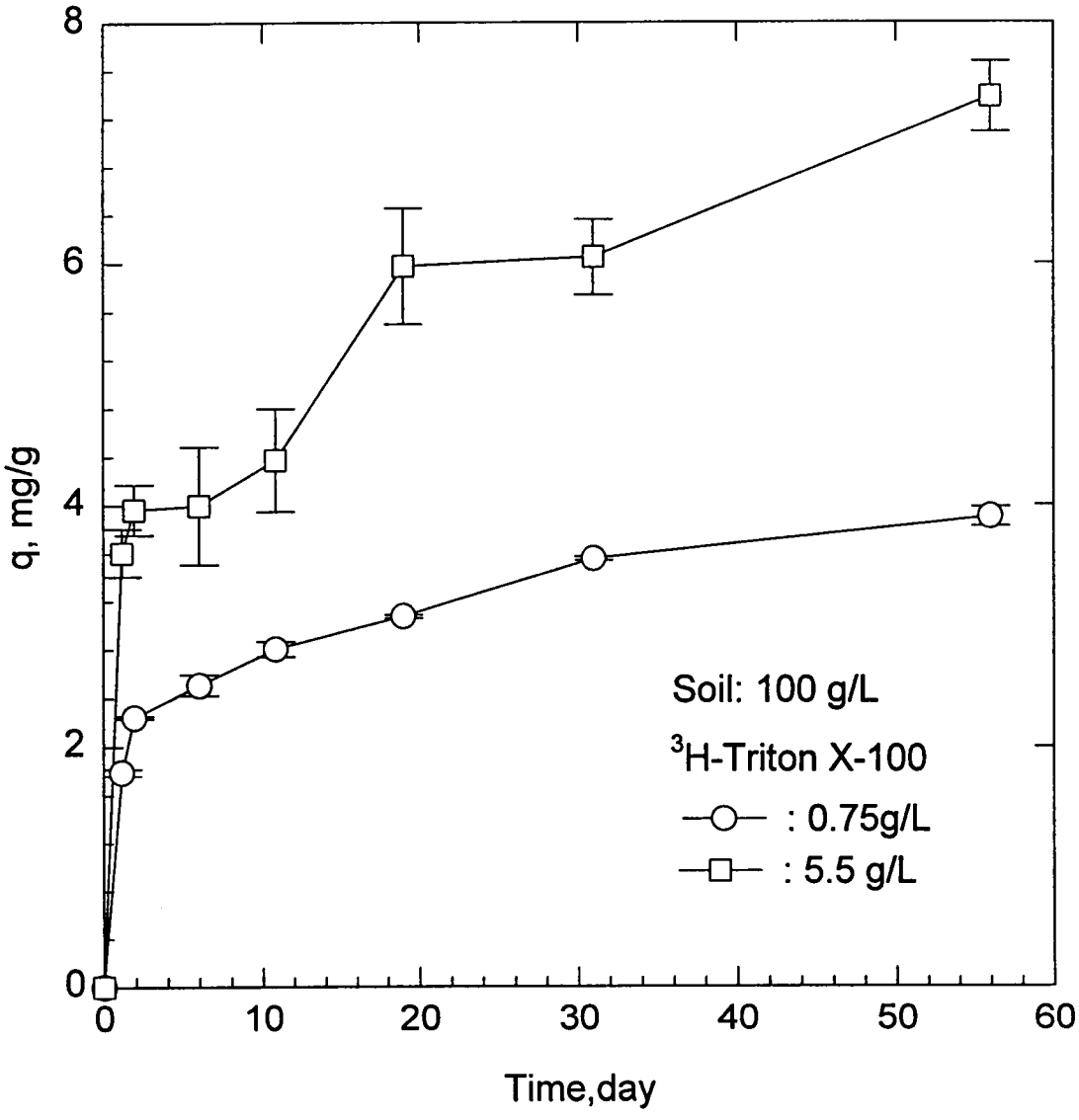


Figure 5. Sorption of Triton X-100 on MGP soil as a function of time

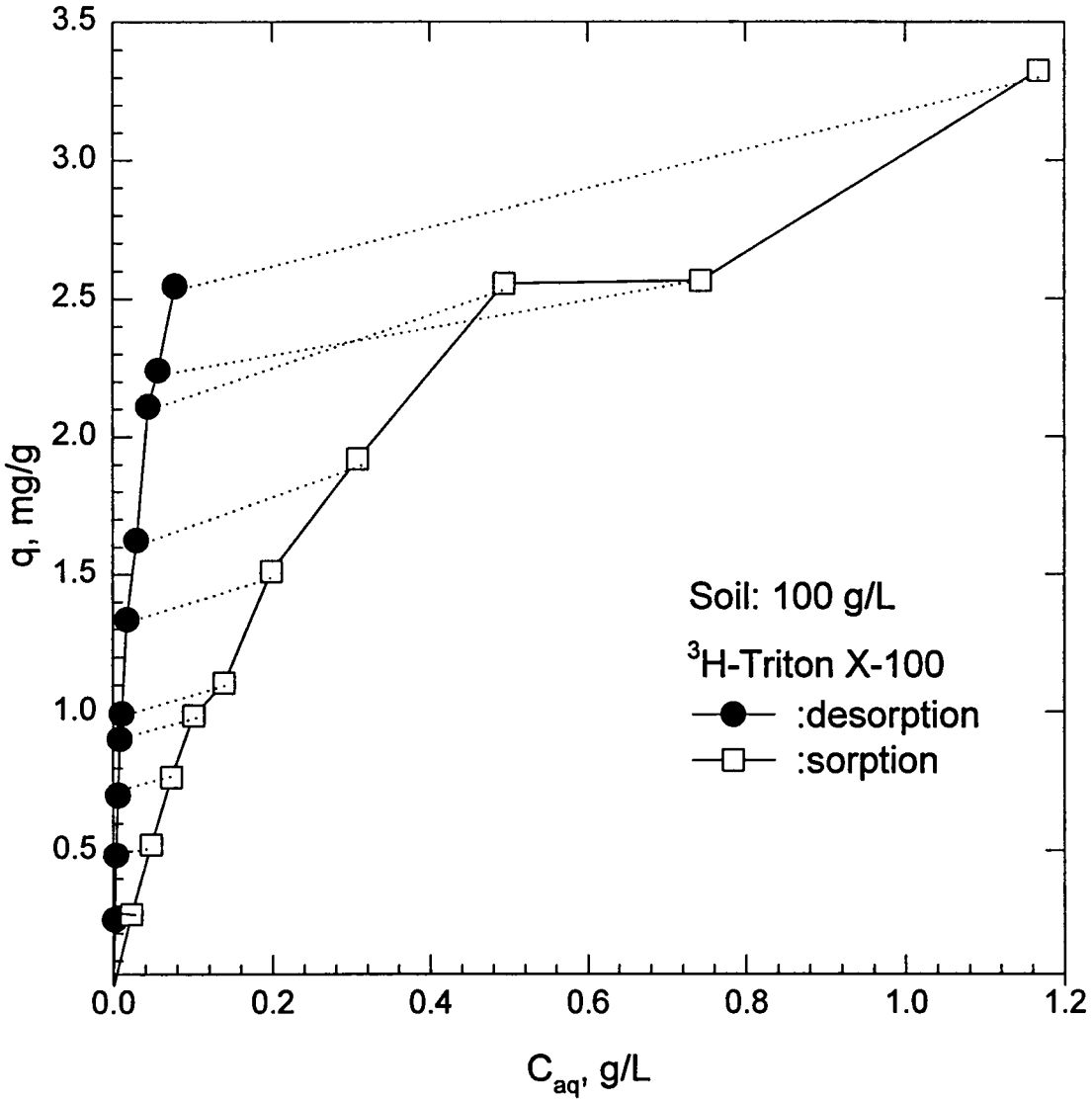


Figure 6. Sorption/desorption hysteresis of Triton X-100 on MGP soil after 2-day equlibration

Tenax. The PAHs adsorbed on the withdrawn beads were measured. Figure 7 shows the removal of phenanthrene from surfactant-treated soils. Since certain amounts of PAHs were removed from the soil during surfactant sorption (before adding Tenax), the initial PAH concentrations in the soils treated with surfactants were less than the concentrations in the untreated soil. However, the rate of phenanthrene removal from surfactant-treated soil was faster than that from the untreated soil, indicating faster mass transfer of phenanthrene from surfactant-treated soils. Phenanthrene removal from the soil treated with 5.5 g/L Brij 30 was 25 % in 12 days while only 12 % was removed from the untreated soil in the same time period. Brij 30 exhibited the largest increase in phenanthrene removal. Extent of removal of phenanthrene is directly related to the dosage of surfactant as indicated by the results of soils treated with two dosages of Triton X-100. Similar data were obtained for other PAHs. Since there were no micelles in the aqueous phase, the enhanced mass transfer was most likely caused by the sorbed surfactant. Interestingly, the initial sorption density of Brij 30 in the soil (18.7 mg/g) was greater than those of Brij 35 and Triton X-100 (3.5 and 4.9 mg/g, respectively) indicating a crude correspondence of the amount of surfactant sorbed to the mass transfer enhancement. Most of the mass transfer enhancement occurred within a day following the addition of Tenax. The sharp decline in the rate of mass transfer after 3-4 days could not be explained immediately. One possible explanation is the removal of sorbed surfactant molecules by Tenax. Although surfactant desorption was not significant after 2-3 washing (1 day) with DI water (C_{surf} <CMC), the preferential adsorption

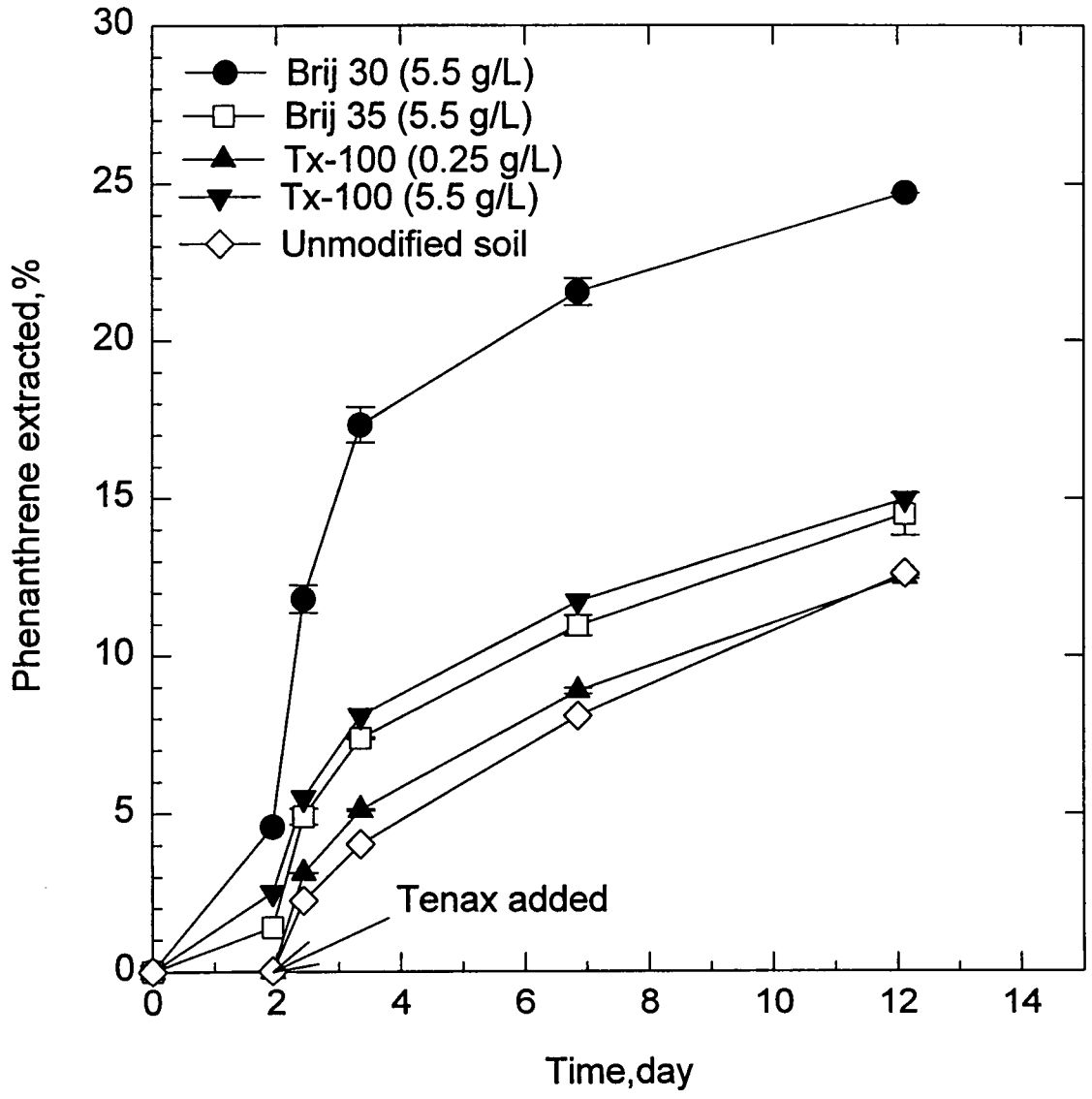


Figure 7. Phenanthrene removal by Tenax from surfactant-treated MGP soil

of aqueous surfactant molecules to a sorbent with high affinity such as Tenax may facilitate desorption.

5.4 Modeling Kinetics of Solubilization

Diffusion within the weathered soil-tar matrix is the most likely rate-limiting step in dissolving soil-bound PAHs from MGP soil in water or surfactant solutions. PAH molecules within the polymeric matrix of tar must reach the tar-water interface by diffusion. Surfactant may enhance the diffusive process in two ways: 1) increase concentration gradient in the matrix by micellar solubilization at the tar-water interface, and 2) increase matrix diffusivity by penetration into and swelling of the tar matrix. To test this hypothesis, an existing radial diffusion model (Wu and Gschwend, 1986; Ball and Roberts, 1991) was modified by including partitioning of aqueous solutes into micelles or Tenax.

The total mass balance for individual PAHs in batch-type surfactant washing is given by:

$$V_{aq}\left(\frac{\partial C_{aq}}{\partial t}\right)\left(1+K_m S_{mic}\right)+m_s\left(\frac{\partial \bar{S}}{\partial t}\right)=0 \qquad (7)$$

where V_{aq} is the bulk aqueous volume, m_S is the mass of soil. The average concentration of HOC within the soil particles, $\bar{S}$, is given by:

$$\bar{S} = \frac{3}{R^3} \int_0^R S r^2 dr \tag{8}$$

where R is the particle radius, S is the sorbed phase concentration. According to Fick's second law of diffusion:

$$\frac{\partial S}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial S}{\partial r} \right) \tag{9}$$

subject to the boundary conditions:

$$S = \left(\frac{K_{soil/tar-aq}}{1 + K_m S_{mic}} \right) C_{aq} \qquad \text{at } r=R, \text{ and}$$

$$\frac{\partial S}{\partial r} = 0 \qquad \text{at } r=0$$

where D_S is the sorbent phase diffusivity (cm^2/sec). Eqs. 8 and 9 were solved numerically using Simpson's Rule and Crank-Nicolson finite-difference approximation, respectively. The program was originally used to model the release of PAHs from MGP soil by gas purging (Cox *et al.*, 1994). The algorithm was designed to accommodate various boundary conditions such as closed batch system, multiple batch washing, and biodegradation. In the model, the particle radius, R, was used as the characteristic length of diffusion assuming the

soil/tar to be a random mixture of tar (75%) and solid minerals (25%). The mean diffusional radius R was incorporated into a lump fitting parameter, D_S/R^2. Purportedly, the present model was not designed to accurately estimate matrix (sorbent phase) diffusivities, D_S, of the constituent PAHs. Assuming that the change in R caused by surfactant is small, the relative changes of matrix diffusivity may be determined from the changes in D_S/R^2 values. The values of K_m and $K_{soil/tar\text{-}aq}$ are listed in Tables 6 and 7 of Part 2, respectively.

5.5 Model Verification

In Figure 8, solubilization of phenanthrene by multiple washing with Brij series homologs (5.5 g/L) is compared with the partitioning of phenanthrene into Tenax. The values of D_S/R^2, the lump fitting parameter, were determined from the best model fit of experimental data shown by solid lines. The effect of surfactant on D_s is clear. Relative to Tenax, surfactant increased of D_S/R^2 of phenanthrene by up to two orders of magnitude. In fact, the increase in D_S/R^2 would be still greater if the radius of soil particle were to increase due to swelling of the organic matrix. Similar effects were observed with other PAHs such as anthracene, pyrene, and benzo[*a*]pyrene. Table 2 shows a comparison of D_S/R^2 values for various PAH-surfactant combinations. Although the diffusivity parameter D_S/R^2 increased for all surfactants used, the amount of increase varied widely with surfactants. The following general observations can be made correlating surfactant characteristics with matrix diffusivity:

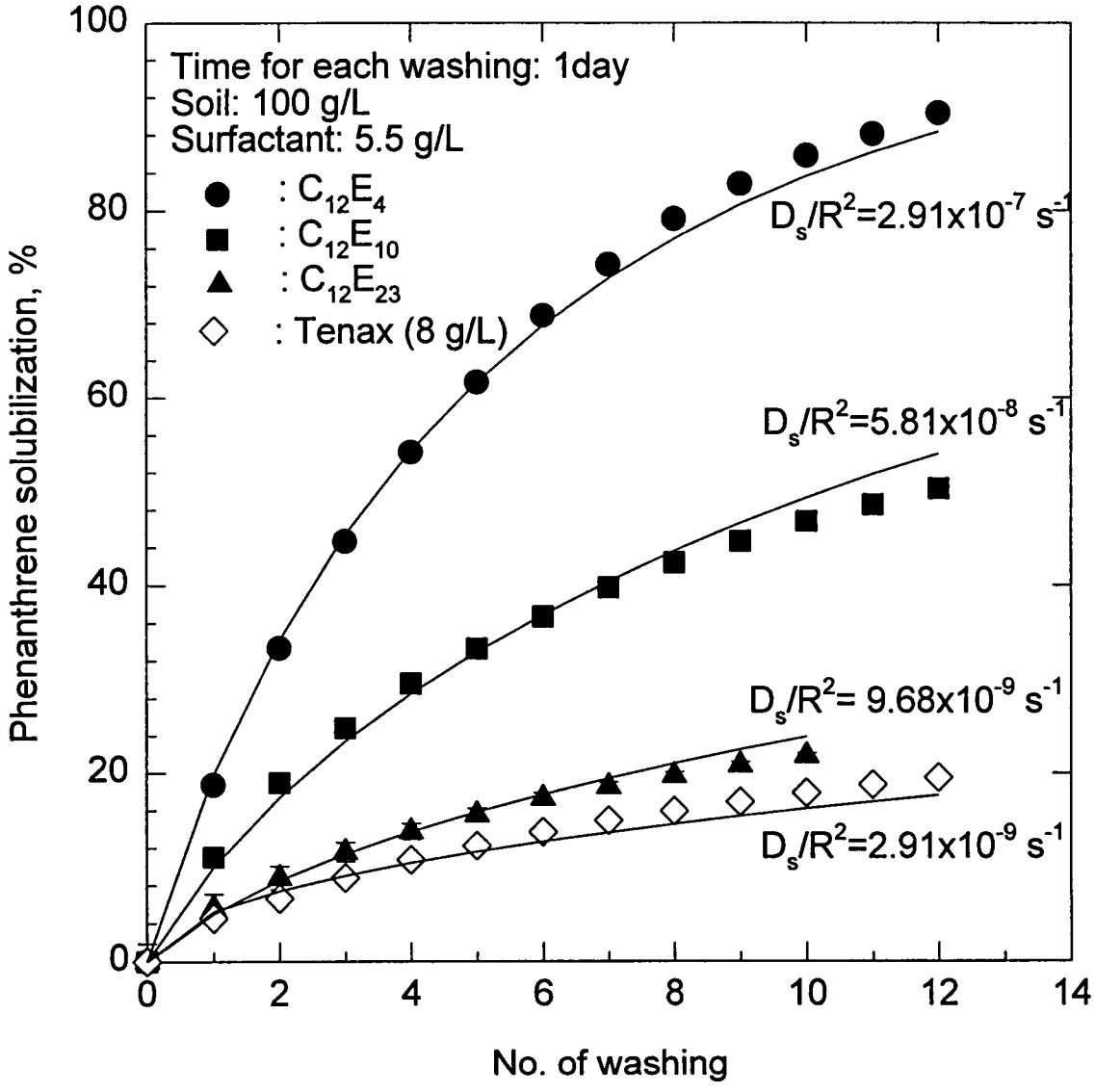


Figure 8. Estimating diffusivity parameter D_s/R^2 for phenanthrene mass transfer by surfactants and Tenax using a radial diffusion model

Table 2. Values of D_s/R^2 (s^{-1}) for various surfactant-PAH and Tenax-PAH combinations

PAH	$C_{12}E_4$ (Brij 30)	$C_{12}E_{10}$	$C_{12}E_{23}$ (Brij 35)	Triton X-100	Tween 80	Tenax
Phenanthrene	2.91×10^{-7}	5.81×10^{-8}	9.68×10^{-9}	4.84×10^{-9}	6.09×10^{-9}	2.91×10^{-9}
Anthracene	2.51×10^{-7}	1.89×10^{-8}	7.55×10^{-9}	2.96×10^{-9}	4.21×10^{-9}	1.89×10^{-9}
Pyrene	1.25×10^{-7}	2.27×10^{-8}	3.40×10^{-9}	1.01×10^{-9}	1.83×10^{-9}	4.50×10^{-10}
Benzo[*a*]pyrene	4.44×10^{-8}	7.87×10^{-9}	1.21×10^{-9}	5.40×10^{-10}	7.40×10^{-10}	6.46×10^{-11}

- the extent of enhancement of diffusivity is inversely proportional to the number of ethoxylate groups in the surfactant molecule or its HLB;
- surfactants with straight alkyl chains ($C_{12}E_{10}$; MW= 626) increase diffusivity more than those with branched chains (Triton X-100; MW=646).

These observations are consistent with the hypothesis that upon sorption to SOM, surfactant molecules penetrate and swell the soil-tar matrix. Penetration of surfactant through a hydrophobic matrix such as soil/tar would be retarded by large hydrophilic groups or branched structure of the surfactant molecules.

The relative importance of the two mechanisms in surfactant washing, micelle solubilization and enhancement of D_S, can be best demonstrated by comparing the model analysis of phenanthrene removal from soil in the presence of Brij 30 and Tenax (Figure 8). The $K_{T\text{-}aq}$ for phenanthrene was 270 L/g while the K_m for Brij 30 was only 56.8 L/g. Given that these two partitioning coefficients are analogous, it can be inferred that the partitioning capacity of 8 g/L Tenax was more than seven times than that of 5.5 g/L Brij 30. Nevertheless, phenanthrene partitioned much more into Brij 30 than into Tenax, indicating that the rate of mass transfer in the surfactant solution was mainly enhanced by increased diffusivity rather than the increased concentration gradient at the interface. In fact, if the diffusivity of PAHs were low as observed for the MGP soil, the effect of K_m on dissolution rate would be small. This is illustrated in Figure 9 by a sensitivity analysis of the model for K_m and D_S/R^2. Values of K_m in the range of 20-500 L/g and two extreme values of D_S/R^2, $2.91\text{x}10^{-9}$ s^{-1} and $2.91\text{x}10^{-7}$ s^{-1}, were used. The mass transfer of phenanthrene

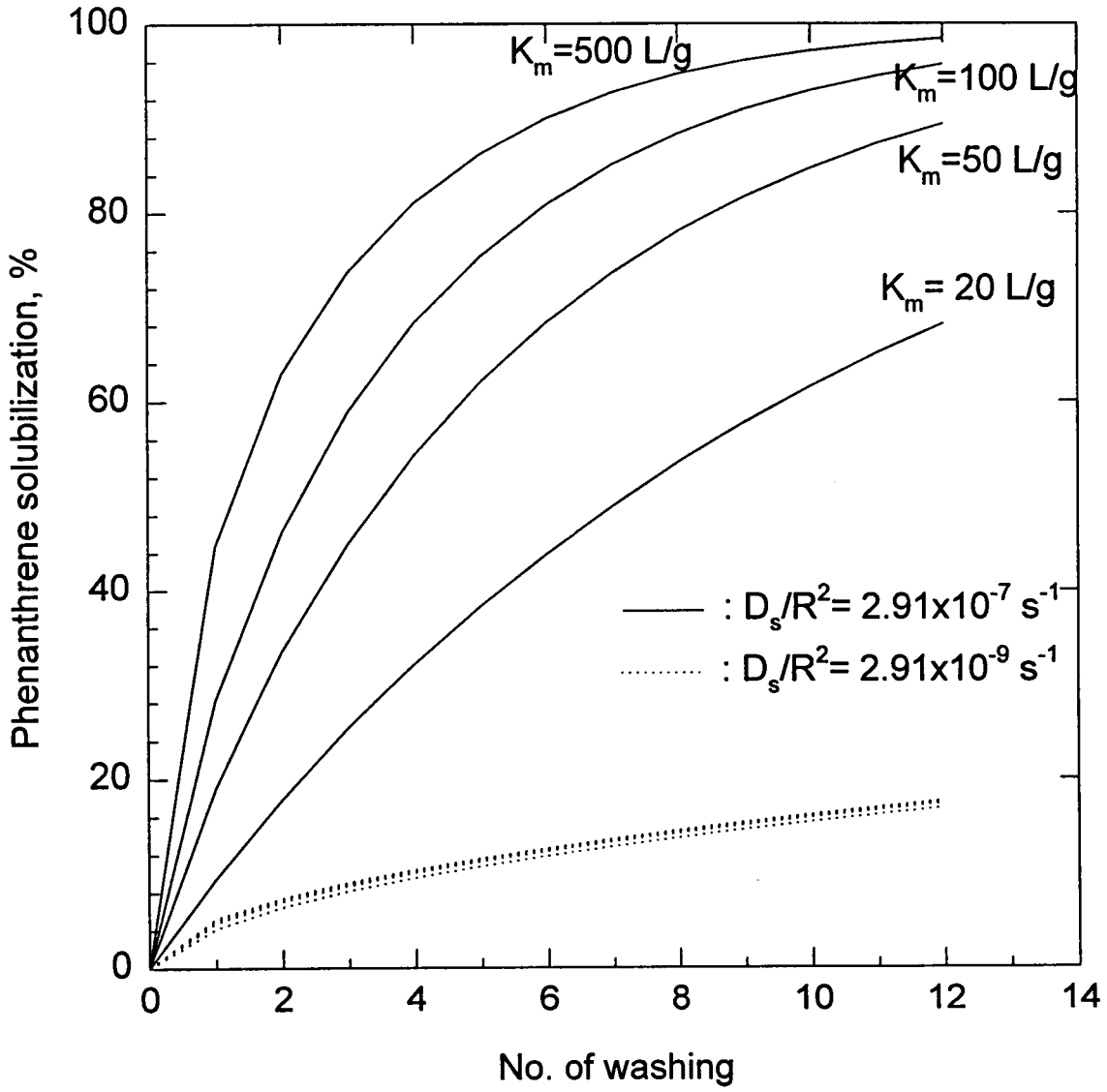


Figure 9. Sensitivity analysis of model for K_m and D_s/R^2

corresponding to $D_s/R^2 = 2.91 \times 10^{-7}$ s^{-1} was sensitive to K_m: 65 % at K_m=20 L/g and 98 % at K_m=500 L/g. For the same values of K_m, there was no discernible effect on solubilization for $D_s/R^2 = 2.91 \times 10^{-9}$ s^{-1} (Tenax). In other words, if mass transfer of HOCs from soil into water is limited by slow diffusion in the sorbent matrix, the increased concentration gradient caused by surfactant has a minimal effect on mass transfer.

In general, micellar solubilization is important only when the release of contaminant is mostly limited by the interfacial mass transfer. For example, dissolution of NAPLs is often limited by the mass transfer at the NAPL-water interface. The presence of micelles can enhance the dissolution by increasing the solubility of NAPL in aqueous phase (C_{sat} in Eq. 2). However, in most weathered contaminated soils, the mass transfer of soil-bound compounds is limited by slow diffusion. In such cases, the success of surfactant treatment is determined by the extent of diffusivity enhancement accomplished.

5. SUMMARY

The effects of nonionic polyoxyethylene (POE) surfactants on the solubilization of PAHs from a weathered coal tar-contaminated soil was investigated. Time-varying partitioning of PAHs to a polymeric adsorbent, Tenax-TA, was also measured. Because of the large partitioning coefficient for organic solutes, Tenax continuously removed aqueous PAHs, maximizing their mass transfer at the soil/tar-water interface. The dissolution of PAHs from the MGP soil into water exhibited a nonequilibrium behavior. Matrix diffusion within the weathered soil/tar matrix is proposed to be the most likely rate-limiting in releasing PAHs into water. Surfactants significantly enhanced the rate of PAH dissolution, the rate being dependent upon the structure of the surfactant. It is postulated that the enhancement of PAH dissolution by surfactants occurs by two mechanisms: 1) increased concentration gradient at the soil/tar-water interface due to partitioning of aqueous PAHs into the micellar pseudophase; 2) sorption and penetration of surfactant molecules causing swelling of soil-tar matrix and increasing matrix diffusivities of PAHs. The role of sorbed surfactant molecules was tested by measuring the partitioning of PAHs from the surfactant-treated soil into Tenax. Even without micelles in the aqueous phase, the release of PAHs from the surfactant-treated soils was faster than that from the untreated soil. A modified radial diffusion model was used to evaluate the relative importance of the two mechanisms in surfactant washing of contaminated soils. The estimated diffusivities of PAHs in the soil/tar matrix in surfactant solutions were up to two orders of magnitude higher than that

without surfactant. Based on the model analysis, it was concluded that surfactant-enhanced mass transfer of PAHs from MGP soil occurs mainly by increased matrix diffusivities while increase in solubility by partitioning of PAHs into the micellar pseudophase plays only a minor role.

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PART 4

EFFECTS OF SURFACTANTS ON BIODEGRADATION OF PAHS IN COAL TAR CONTAMINATED SOIL

1. INTRODUCTION

Bioremediation appears to be a promising technology for cleaning up of sites contaminated with hazardous wastes. It has several advantages over thermal and other physicochemical methods. It neither alters the intrinsic soil properties nor does it involve transport of contaminants off site, especially when applied *in situ*. However, bioremediation has not been extensively field-tested to warrant its wide scale use. Several issues remain unresolved in using bioremediation, bioavailability of soil-bound contaminants and delivery of necessary nutrients in *in situ* applications among them, not to mention the slow rates at which many recalcitrant organic contaminants, such as PAHs and PCBs, are biodegraded. High molecular weight (MW) PAHs are relatively stable in soils and difficult to biodegrade (Heitkamp and Cerniglia, 1987; Sims *et al.*, 1988).

One of the major factors limiting the success of bioremediation of PAH-contaminated soils, *in situ* or *ex situ*, is the slow release of contaminants into the aqueous phase. The slow release of PAHs is primarily due to the low aqueous solubilities of the compounds and/or their slow diffusion through the contaminated soil. Addition of surfactants, synthetic or biologically produced, has been proposed to facilitate the release of PAHs thus enhancing the overall performance of bioremediation (Oberbremer et al., 1990; Aronstein and Alexander, 1991; Abdul *et al.*, 1992). Surfactants have been shown to enhance the desorption or dissolution of sparingly soluble compounds such as PAHs by increasing their solubilities in the aqueous phase. Micelle-incorporated PAHs appear

to be biodegradable unless the surfactant is toxic (Liu *et al.*, 1995; Volkering *et al.*, 1995). Many nonionic polyethoxylated surfactants were shown to be non-toxic to PAH-degrading microorganisms even at concentrations above their CMC values (Bury and Miller, 1993; Ghosh *et al.*, 1994; Thiem, 1994; Köhler *et al.*, 1994). However, the usefulness of surfactant in enhancing bioremediation of contaminated sites is still largely unknown. While the literature is replete with bioremediation studies of artificially contaminated soils using pure bacterial cultures, data on surfactant-mediated bioremediation of contaminated field soils are sparse. Availability of surfactant-solubilized PAHs for degradation by indigenous microbial consortia and the toxicity of surfactants themselves have not been studied in depth. Further, sufficiency of nutrients for bioremediating field soils and cometabolism of surfactants themselves during bioremediation have also not been satisfactorily addressed.

The purpose of this study is to determine the effects of nonionic polyoxyethylene (POEs) on the biodegradation of soil-bound PAHs. Two different types of soils, laboratory-contaminated soil and a contaminated field soil from an MGP site were used. While pure cultures were used for the laboratory-contaminated soils, an enriched mixed culture was used for the MGP soil. The observed effects of surfactant on bioremediation are explained in terms of contaminant biodegradation rate relative to the rate of release of contaminants from soil, and biodegradation of the surfactants themselves. The factors limiting surfactant-mediated bioremediation of MGP soils are also discussed.

2. BACKGROUND

To bioremediate PAH-contaminated soils, requisite degradative genes must be expressed in the microbial community, and usually they are. No less important are the nutrients and terminal electron acceptors (TEAs), such as oxygen, nitrates, and hydrogen peroxide, that must not be in short supply. In addition, soil-bound compounds are usually protected from biodegradation (Alexander, 1981; Ogram et al., 1985). The target compounds must be transported from the soil to water where they dissolve and become available for biodegradation.

2.1 Bioremediation of PAH-Contaminated Soils

Microbial Degradation of PAHs:

PAHs are biodegraded in one of two ways, either they are utilized as the sole source of carbon and energy or they are cometabolized. In the latter, an enzyme produced for degradation of a certain growth-supporting compound also degrades a PAH that is not essential for growth (Heitkamp and Cerniglia, 1988). The capability of a variety of naturally occurring microorganisms to completely mineralize 2 or 3 ring PAHs have been demonstrated by a number of researchers (Cerniglia, 1984; Cerniglia and Heitkamp, 1989). Reportedly, these low MW PAHs can be used as the sole carbon and energy source by many naturally-occurring bacteria. PAHs with four or more rings are less

soluble, more stable and therefore more recalcitrant. Bacterial mineralization of these PAHs generally occurs by cometabolism (Heitkamp and Cerniglia, 1988; Muller et al., 1989). In general, biodegradation of high MW PAHs in contaminated soils occurs at a rate much slower than that for low MW PAHs. Under laboratory conditions, biodegradation of most four and five-ring PAHs exhibited half-lives of more than 200 days while half-lives for 2- and 3-ring PAHs were 16 and 134 days, respectively (Sims et al., 1988).

Treatment Studies :

Studies on bioremediation of contaminated soils have been conducted for three different treatment scenarios: *in situ* treatment, on site treatment, and treatment in *ex situ* bioreactors (Wilson and Jones, 1993). In *in situ* treatment, the contaminated soil is treated in place and it essentially remains undisturbed. In on site treatment, waste material is applied to the soil as a slurry and the area is managed by fertilization, irrigation, and nutrient addition. In bioreactor treatment the contaminated soil is excavated and transported to the reactor site. Despite occasional accounts of success reported in the literature, particularly in removing 2-and 3-ring PAHs (April *et al.*, 1990; Morgan and Whatkinson, 1990), *in situ* treatment has generally been ineffective for the bioremediation of most contaminated soils in a reasonable time frame (Wilson and Jones, 1993). Maximum removal of low-MW PAHs was achieved in bioreactors where good mixing of soil and nutrient could be ensured (Rittman and Johnson, 1989; Muller *et al.*,

1991). Biodegradation of high MW PAHs has been unsatisfactory even in carefully controlled bioreactors.

Often lack of an acclimated microbial population becomes a significant limitation in PAH biodegradation. Reportedly, mineralization of PAHs significantly increased at a site when microorganisms isolated from the contaminated soil were cultured separately and reapplied to the soil (Grosser *et al.*, 1991). Also, application of acclimated microorganisms isolated from one soil to another enhanced the mineralization of hydrocarbons in the latter soil (Vecchioli *et al.*, 1990). Other factors promoting bioremediation include supply of oxygen or other terminal electron acceptors, nutrients, and maintaining optimal environmental conditions such as optimal temperature and pH. Soil may be pulverized before treatment and mixed well during treatment. These conditions are best accomplished in a bioreactor.

Under identical experimental conditions, the efficiency of bioremediation can vary from 0 to 70 % or more (Weissenfels *et al.*, 1990). Such extreme variations in performance cannot be explained by factors that usually control bioremediation. While a bioreactor treating an MGP soil showed insignificant removal of PAHs , it removed more than 80% of PAHs with four or less number of rings from a wood-impregnation plant waste (Weissenfels *et al.*, 1990; Erickson *et al.*, 1993). The type and composition of a contaminant mixture as well as site-specific factors appear to control the performance of bioreactors.

Bioremediation of PAHs in MGP soils offers many technological challenges.

In laboratory studies, a range of 2- to 6-ring PAHs extracted from an MGP soil could be biodegraded (Sherman *et al.*, 1988). However, biodegradation of PAHs trapped in the soil-tar matrix was much less efficient and less predictable (Erickson *et al.*, 1993; Smith and Weightman, 1988). Fresh PAHs added to the tar-contaminated soil were degraded readily indicating that toxicity did not limit biodegradation. Limited availability of PAHs strongly bound to the soil appear to limit biodegradation (Erickson *et al.*, 1993; Luthy *et al.*, 1994). Cushy and Morgan (1990) reported a rapid, initial removal of contaminants from soil in slurry bioreactors followed by a much slower rate of removal. The two-phase removal was attributed to mass transfer limitations. The end of the initial period was designated as the treatment end point. Eighty to ninety five percent of the total PAHs was removed in six weeks, but less than 50% of the high MW PAHs was removed. Biodegradation of PAHs in free-flowing liquid coal tar occurs much faster than that of PAHs in weathered tar-contaminated soils (Luthy *et al.*, 1994).

2.2 Effect of Surfactants on Biodegradation of HOCs

Both enhancement and suppression of substrate utilization and cell growth have been ascribed to surfactant addition to biological systems (Guerin and Jones, 1988; Rittman and Johnson, 1989; Aronstein *et al.*, 1991; Laha and Luthy, 1992; Bury and Miller, 1993; Tiehm, 1994; Volkering *et al.*, 1995). However, the experimental conditions such as the surfactant dosage, presence of alternate substrates, and presence of soil, varied widely in different studies making a direct comparison of results all but

impossible. An important consideration in applying surfactants to biological systems is the possible toxicity of these chemicals to degradative microorganisms. Inhibitory effects of surfactants at supra-CMC dosages have been reported in the literature (Aronstein *et al,* 1991; Laha and Luthy, 1992; Tiehm, 1994). However, in the main, surfactants were not found to be toxic to cells even at concentrations much higher than their CMC values (~100xCMC). Toxicity appeared to be microorganism specific.

Studies where no toxicity of surfactants was observed can be divided into two groups. In the first group, excess HOC was present as a separate phase, either as crystals or as NAPL. With a few exceptions, surfactants enhanced overall biodegradation in these studies (Guerin and Jones, 1988; Bury and Miller, 1993; Efroymson and Alexander, 1991; Köhler *et al.*, 1994; Tiehm, 1994; Volkering *et al.*, 1995). In most cases, the enhancement was attributed to either increased solubilization of HOCs by surfactant micelles or to an increased interfacial area of the HOCs, either as crystals or NAPLs. Enhanced biodegradation of liquid hydrocarbons and oils using emulsifiers has also been observed (Whitworth *et al.*, 1973; Roy *et al.*, 1979; Liu, 1980; Reddy *et al.*, 1982; Rittman and Johnson, 1989 Goswami and Singh, 1991;). Emulsifiers produce microdroplets of hydrocarbons. The large HOC-water interfacial area so created greatly increases the dissolution of HOC substrates and is believed to cause enhanced biodegradation.

The second group of studies involves the biodegradation of soil-sorbed HOCs in the presence of surfactants. Aronstein and Alexander (1992) showed that

mineralization of phenanthrene and biphenyls in soil slurries was enhanced at sub-CMC dosages of ethoxylated alcohols. Similarly, Jahan and Maier (1994) observed small enhancement of phenanthrene mineralization at low surfactant dosages. However, very few studies attempted to evaluate biodegradation of soil-bound HOCs at of supra-CMC dosages of surfactants.

One of the debated issues in surfactant-mediated biodegradation is the bioavailability of HOCs incorporated into surfactant micelles. Recent studies focused on two aspects of micelle-incorporated HOCs: whether they are completely biodegradable and if so, how they are transferred into the cell. Studies have shown that HOCs in micellar solutions of nonionic POEs are completely degraded at moderate surfactant dosages (< 10 g/L) (Ghosh *et al.*, 1994; Thiem, 1994; Liu *et al.*, 1995). Only a few studies addressed the mechanistic aspects of biodegradation of micelle-incorporated compounds. Volkering *et al.*, (1995) reported that biological activity in surfactant solutions was controlled only by the concentration of HOCs in the aqueous phase and not the total soluble HOC concentration. They contend that HOCs in the micellar phase merely serves as a reservoir that may replenish HOCs in the aqueous phase as they become depleted due to biodegradation. The micellar solubilization of HOCs is a dynamic process. The rate at which organic solutes enter a micelle is limited by their diffusion rates in water ($k \gg 5 \times 10^{9}\ s^{-1}$). The residence time of a solute within a micelle is 10^{-6} to 10^{-10} s (Waggoner *et al.*, 1968; Oakes, 1972; Almgren *et al.*, 1979; Hunter, 1987). In such dynamic systems, transport of substrate between micelle and water is not

likely to limit biodegradation. The relative distribution of a substrate between the two phases may remain constant during biodegradation as alluded to by Liu *et al.*(1995). They reported that in the presence of a limited amount of naphthalene crystals, the increased micelle-solubilized naphthalene concentration failed to increase the rate of mineralization. Though the total soluble naphthalene concentration increased, naphthalene in the aqueous phase did not. In fact, it decreased somewhat. The modest reduction of naphthalene in the aqueous phase did not significantly affect the extent of mineralization achieved.

3 MATERIALS

Two soils were used in this study. An artificially contaminated soil was used for mineralization experiments with pure cultures while a coal tar-contaminated MGP soil was used for experiments with mixed cultures obtained from the MGP soil itself. The characteristics of the two soils are given in Part 2. Only Triton X-100 was used for mineralization experiments with the artificially contaminated soil. Four surfactants, Triton X-100, Brij 30, Brij 35, and Tween 80, were used for biodegradation studies with the MGP soil. Radiolabeled PAHs, 9-^{14}C-phenanthrene, 1-^{14}C- naphthalene with specific activities of 13.1 mCi/mmol and 10.3 mCi/mmol, respectively, were used for mineralization experiments.

3.1 Pure Cultures of PAH-Degrading Microorganisms

Pseudomonas fluorescens DFC 50 and *Acidivorax delafieldii* were used, respectively, for the mineralization of naphthalene and phenanthrene in the artificially contaminated soils. The former was obtained from the Center for Environmental Biotechnology at the University of Tennessee and used for degradation of naphthalene used as the sole source of carbon and energy. *Acidovorax delafieldii*, capable of using phenanthrene as the sole carbon and energy source, was isolated from a creosote-contaminated soil in Tennessee . One hundred milliliters of the enrichment medium contained 1 g of soil, 0.1 g of phenanthrene, and a minimal salts medium (MSM)

composed of 4.0 g of $NaNO_3$, 1.5 g of KH_2PO_4, 0.5 g of Na_2HPO_4, 0.2 g of $MgSO_4 \cdot 7H_2O$, 0.01 g of $CaCl_2 \cdot 2H_2O$, and 0.005 g of $FeCl_3$ per liter of DI water with pH adjusted to 7.0. Prior to isolation of the bacterium, the cultures were allowed to grow for about 2 weeks at 30°C in mechanically shaken culture flasks. A portion of the fluid was transferred to sterile media containing 0.1 g/L of phenanthrene and shaken for a week. This procedure was repeated twice. Finally, the enriched culture was streaked on yeast-extract-peptone-glucose (YEPG) plates. After incubation for 2 days, the plates were sprayed with phenanthrene solution in 20 g/L acetone using a spraying unit (Chromist, Gelman Co.). The colonies that formed zones of clearance were streaked on another YEPG plate. After incubation, the cells grown on the plates were collected and stored in 10 % glycerol solution at -80°C. The isolated bacterium was identified as *Acidovorax delafieldii* based on the fatty acid analysis conducted by Microcheck. Inc.

3.2 Mixed Culture

An enriched mixed culture capable of degrading various PAHs was prepared using a mixture of an MGP soil and a creosote-contaminated soil. The enrichment medium contained 1 g of each of the two soils, 100 mL of MSM and a mixture of about 0.1 g each of naphthalene, acenaphthene, fluorene, phenanthrene, fluoranthene, salicylic acid, succinic acid, and 0.01 g of benzo(a)pyrene. After being shaken for 2 weeks, 10 mL of the fluid was transferred to another enrichment medium and shaken for an additional 2 weeks. The soil particles were allowed to settle and 10 mL of the

supernatant were transferred to a medium containing 10 g of MGP soil in 100 mL of MSM. After mixing for 1 week, the soil suspension was used as a seed for biodegradation experiments.

The ability of the mixed culture to degrade PAHs was assayed using ^{14}C-labeled PAHs. Radiolabeled PAH solutions prepared in 10 mL of MSM were added to 22-mL vials containing 0.4 g of the MGP soil. Upon inoculation with the mixed culture, the production of $^{14}CO_2$ was monitored (see sec. 5.4.1). Within a week, $^{14}CO_2$ production was observed for naphthalene (1-^{14}C), phenanthrene (9-^{14}C), anthracene (U-^{14}C), and pyrene (4,5,9,10-^{14}C), indicating mineralization of these compounds. The culture grown on benzo(a) pyrene (7-^{14}C) did not exhibit production of $^{14}CO_2$ even after 4 weeks.

4 METHODS

4.1 Mineralization of Naphthalene in Surfactant Solution

Mineralization of naphthalene in surfactant solutions was measured by trapping $^{14}CO_2$ in NaOH solution. Naphthalene solutions containing a mixture of radiolabeled and nonlabeled compounds with a total activity of 20,000-30,000 dpm/mL were prepared in MSM. The concentration of radiolabeled compound was determined from the specific activity of solution using the conversion factor, 2.22×10^6 dpm/μCi (56.0 ng/10,000 dpm). The final concentration in solution was obtained by adding labeled and unlabeled naphthalene concentrations. One hundred milliliters of the naphthalene solution was added to a series of 250-mL bottles containing varying amounts of surfactant. The naphthalene-surfactant solution (10 mL) was added to 22- mL vials and inoculated with *P. fluorescens* DFC 50. Glass tubes containing 0.5 mL of 0.5N NaOH solution were placed in the vials to trap CO_2. The vials were capped with Teflon-silicone septa and open-port screw caps and shaken at 140 rpm at 30°C. At given time intervals, the trapping solution was removed using 1-mL syringe and replaced with fresh NaOH. The solution collected in the syringe was added to a 20-mL vial containing 10 mL of scintillation cocktail (Ready-Safe, Beckman Co.). After mixing vigorously, the samples were stored overnight and the radioactivity was determined by liquid scintillation counting (LS5000TD, Beckman Co).

The inocula for the experiments were prepared by growing the cells in MSM

containing 50 mg/L of PAH. Cultures from the early stationary phase, as determined by OD_{600} were passed through a glass frit to remove the remaining crystals , and then the cell suspension was centrifuged at 9600xg for 40 minutes. The cell pellets were washed with MSM and centrifuged again. The process was repeated 2-3 times. The inoculum density was so chosen as to yield an initial cell concentration of about $5x10^6$-10^7 cells/mL.

4.2 Mineralization of PAHs in Soil-Water System

Mineralization of sorbed PAHs was determined using the natural soils artificially contaminated with naphthalene and phenanthrene as described in Part 2, 4.4. The contaminated soil pellets were resuspended in 25 mL of surfactant solutions prepared in MSM. The suspensions were transferred to 50-mL vials and inoculated with bacteria. A glass tube containing 1 mL of NaOH solution was placed inside the vial to capture $^{14}CO_2$. Mineralization of soil-bound PAHs was measured by monitoring the activity of the NaOH solution. To estimate the effect of sorption on the mineralization of PAHs, mineralization was measured in samples containing only PAH and MSM. The total amount of PAH (nonlabeled and labeled) in the solution was equivalent to the amount present in samples containing the contaminated soil.

4.3 Biodegradation of PAHs in MGP Soil

Biodegradation of PAHs in MGP soil was determined in batch experiments with and without surfactant. In 250-mL Erlenmeyer flasks, 10 g of the soil and 100 mL

of surfactant-MSM (or MSM only) were inoculated with the mixed culture and thoroughly mixed. The initial total cell density was 8.5 $x10^5$ cells/mL determined by plate count including an indigenous population of $5x10^5$ cells per g of soil in suspension.

Of these, $1.7x10^5$ cells/mL were phenanthrene degraders. The concentrations of surfactants used in different batch tests were: 0, 0.25, 0.75, 2.5,5,10 g/L. Abiotic controls, prepared similarly, contained 0.05% $HgCl_2$. The flasks were capped with heavy-duty aluminum foil and incubated at 30°C in a shaker (Enviro-Shaker 3597, Lab-Line Instruments). At varying time intervals, aliquots of the soil suspensions were collected and filtered through 0.2 μm aluminum filter. The filtrates were analyzed for PAHs. Less frequently, approximately 1 g of soil was taken from each flask using a wide-mouth pipette (10-mL) and transferred into a 25-mL glass centrifuge tube. Following centrifugation at 8000xg for 40 minutes, the soil pellets were transferred into weighing boats and dried in a desiccator for a day. The PAH concentrations in the soil were determined as described in Part 2, sec. 3.1. All biodegradation tests were duplicated.

5 RESULTS AND DISCUSSION

5.1 Mineralization of Naphthalene in Surfactant Solution

To determine the effect of surfactant on the bioavailability of dissolved PAH, mineralization of naphthalene in surfactant solutions was measured using *P. fluorescens* DFC-50. Different distributions of naphthalene between the aqueous and micellar phases were obtained by varying the surfactant concentration while the total dissolved concentration of naphthalene was held constant at 27.8 mg/L. Mineralization was measured by the $^{14}CO_2$ evolved (Figure 1). At relatively low surfactant dosages (<0.73 g/L), mineralization of naphthalene was not affected by surfactant. However, at higher dosages (2-10 g/L), initial mineralization was slower relative to that with no surfactant. At a high dosage of 30 g/L, there was no mineralization. At this dosage, almost all of the naphthalene was micellar, not to mention that surfactant might have caused cellular damage. With the exception of the 30 g/L dosage, maximum mineralization occurred in 25 hours regardless of the surfactant dosage. No significant degradation of Triton X-100 was observed in the present study.

The initial naphthalene concentration in aqueous phase decreased with surfactant dosage due to partitioning into micellar phase. From the definition of micelle-water partitioning coefficient, K_m, (Eq.3, Part 2) , aqueous naphthalene concentration can be estimated by:

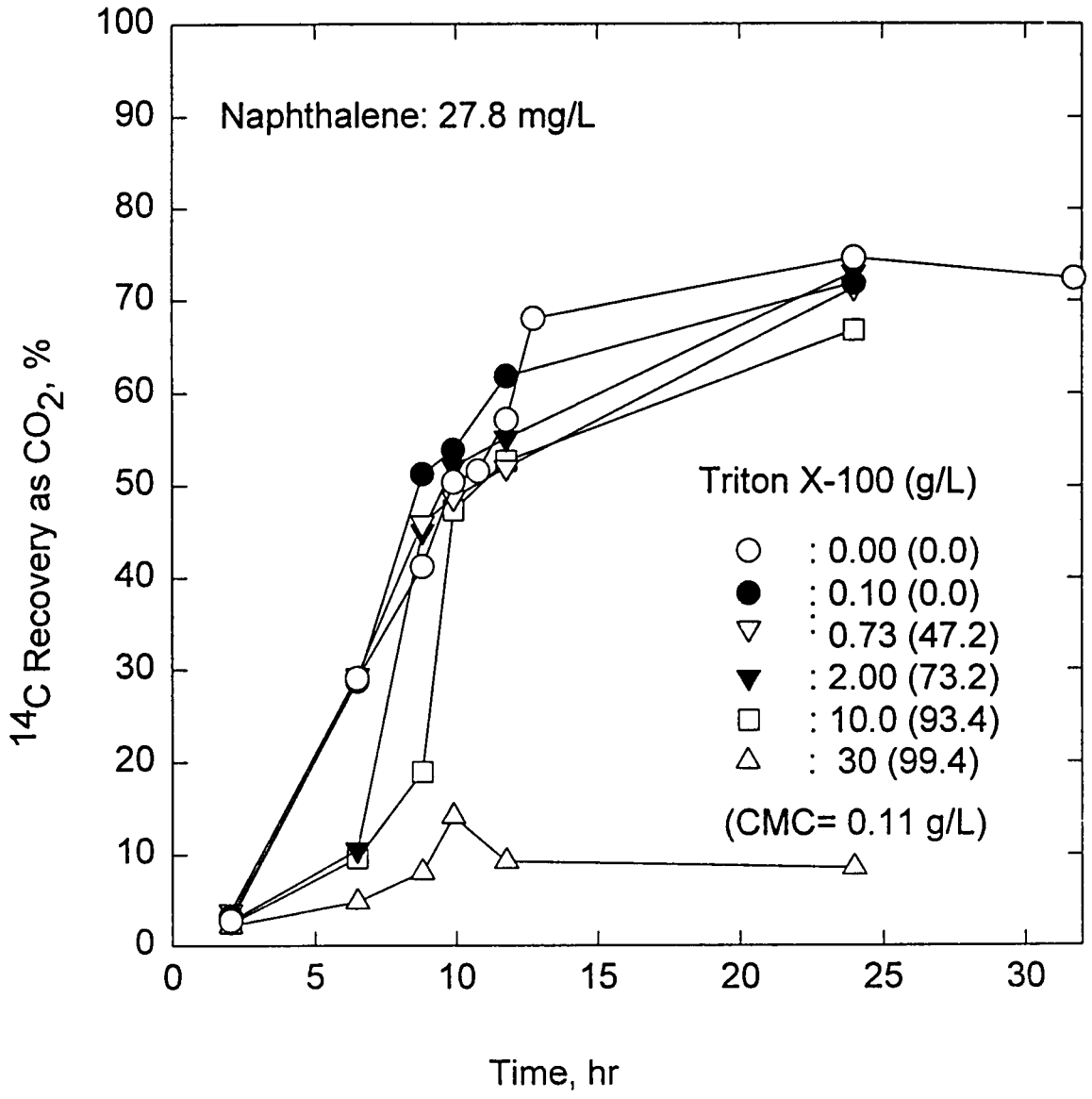


Figure 1. Mineralization of naphthalene by *P. fluorescens* (DFC50) in the presence of Triton X-100 (numbers in parenthesis represents percent naphthalene micellized)

$$C_{aq} = \frac{C_{aq,tot}}{(1 + K_m S_{mic})} \quad (1)$$

The calculated values are given in the parenthesis in Figure 1. The decrease of initial mineralization at high surfactant dosages (2-10 g/L) could be due to the decreased naphthalene concentration in the aqueous phase assuming only free aqueous naphthalene is available for biodegradation.. This is consistent with the recent literature on the bioavailability of PAHs in surfactant solutions (Liu *et al.*, 1995; Volkering *et al.*, 1995). The substrate must be present in the aqueous phase to be degraded, the rate of degradation being controlled by aqueous PAH concentration (Volkering *et al.*, 1995). Since equilibration of naphthalene between the aqueous and micellar phases is relatively fast, eventually all naphthalene should be degraded. In essence, micelles simply serve as a pool for substrates for degradative bacteria to draw upon, as the substrate in the aqueous phase is depleted.

5.2 Effect of Surfactant on Mineralization of PAH in Soil-Water System

Effect of surfactant on the mineralization of PAH sorbed to soil was determined using Triton X-100 and soils artificially contaminated with naphthalene and phenanthrene. Figures 2 and 3, respectively, show the mineralization of sorbed naphthalene and phenanthrene in Triton X-100 solution. Triton X-100 did not significantly enhance mineralization of PAHs at both dosages. At best, 5-10 % enhancement was observed in about 15 hours. If desorption of PAH from the soil is not

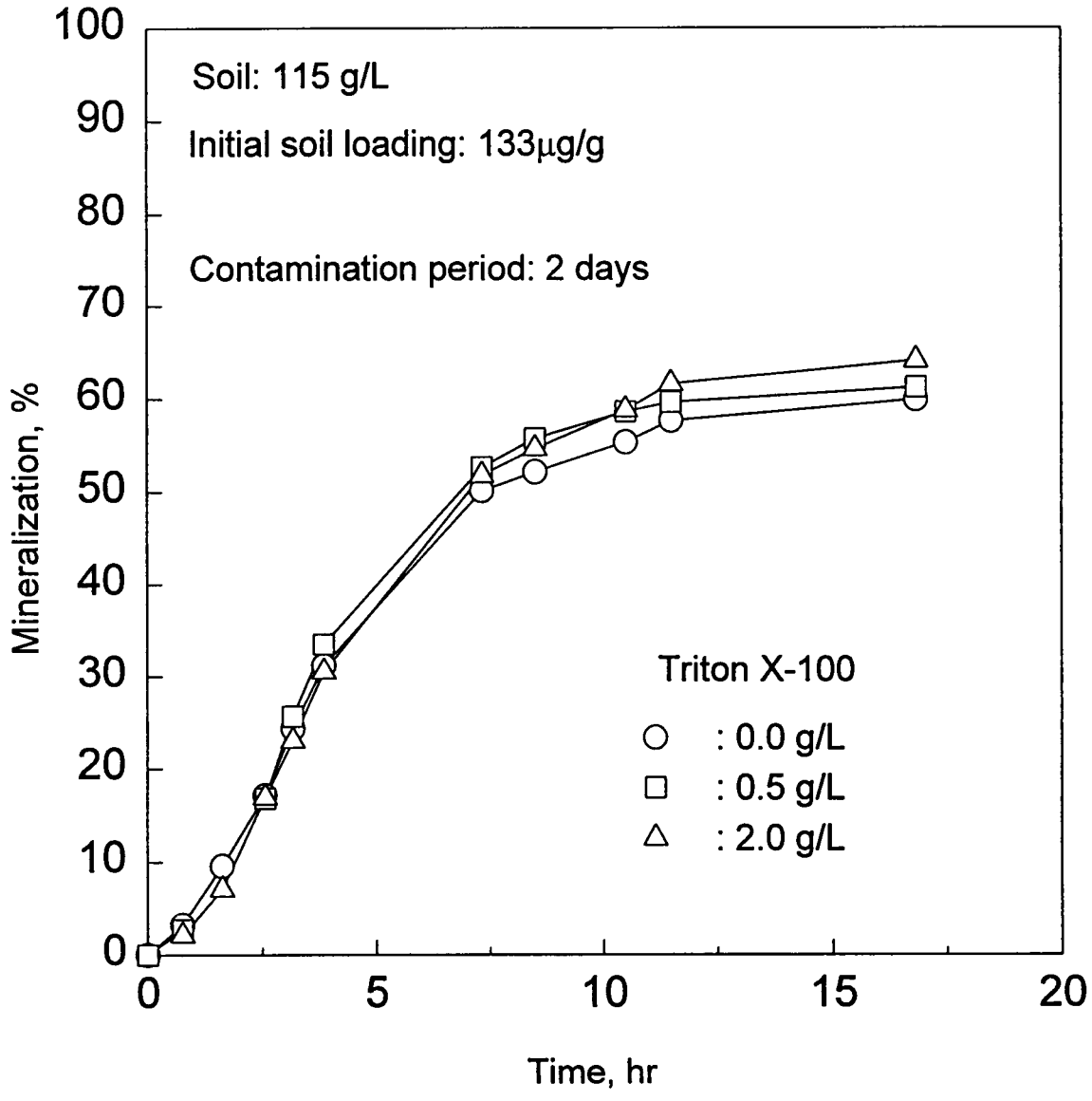


Figure 2. Mineralization of soil-bound naphthalene in the presence of Triton X-100

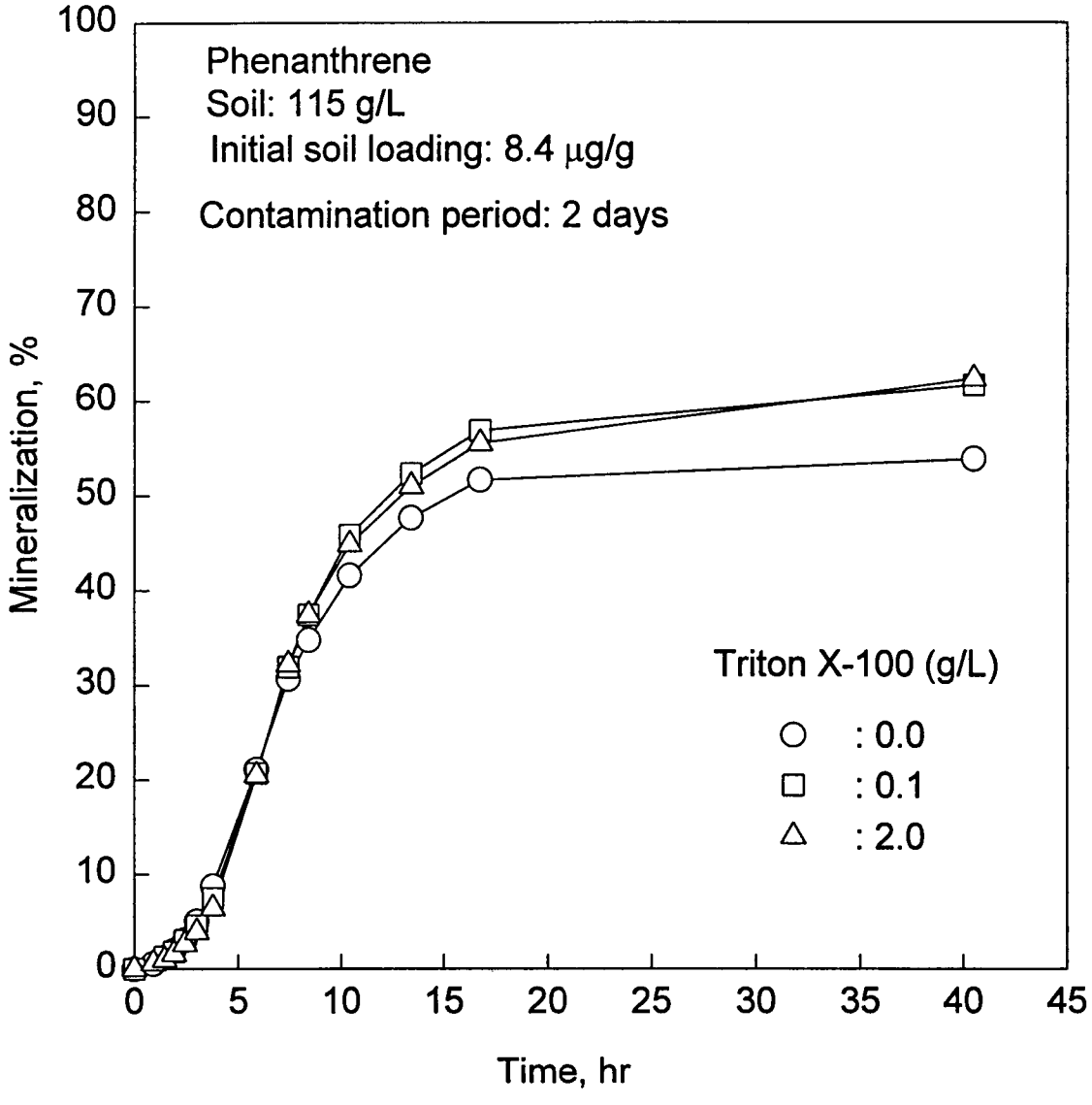


Figure 3. Mineralization of soil-bound phenanthrene in the presence of TritonX-100

limited by mass transfer, the aqueous PAH concentration during biodegradation would be controlled by the soil-water partitioning coefficient. The aqueous PAH concentration is given by (Eq. 15 of Part 2):

$$C_{aq} = \frac{q^{o}_{soil}}{1 + K_{soil-aq} W_{soil}} \tag{2}$$

The concentration of aqueous-phase PAH decreases upon surfactant addition. The decreased equilibrium aqueous-phase PAH is given by:

$$C_{aq} = \frac{q^{o}_{soil}}{1 + K_{soil-aq} W_{soil} + K_{m} S_{mic}} \tag{3}$$

Instantaneous equilibrium of PAH between the two phases is assumed *a priori*. Since the reported residence of a guest HOC in the micelle is of the order of microseconds (Almgren *et al.*, 1979; Hunter, 1987), the micelle-water partitioning can be regarded as an instantaneous process. However, desorption of soil-bound HOCs may not be fast even in soils with short contamination histories (Pavlostathis and Jaglal, 1991; Fu *et al.*, 1994). Following a relatively fast desorption period, the residual PAHs appear to desorb slowly. Surfactant may enhance the release of this desorption-resistant fraction (Yeom and Ghosh, 1993; Deitsch and Smith, 1995). Conceivably, the increased mass transfer of PAH, mediated by surfactants, could be negated by the decrease in the aqueous-phase

PAH. Thus, overall, surfactants may not directly contribute to mineralization of soil-bound PAHs. Mineralization experiments were conducted using a soil contaminated with phenanthrene for 10 months and the results were compared with those with the 2 day-contaminated soil. Significant mass transfer limitations would be expected in soils that had undergone long periods of weathering (Yeom and Ghosh, 1993; Hatzinger and Alexander, 1995). Mineralization of phenanthrene in the soils with no surfactant added are plotted as a function incubation time in Figure 4. The initial amount of radiolabeled phenanthrene in all soil slurries including the control (no soil) was about the same. Mineralization of phenanthrene in 10-month old soil was much slower than that in the 2-day old soil. As expected, the extent of retardation of mass transfer inversely correlates with the age of contamination. Enhancement of mineralization upon the addition of Triton X-100 is clearly demonstrated in Figure 5. The relative degree of mineralization in soils of longer contamination ages decreased with and without surfactant. However, the beneficial effect of surfactant on mineralization increases as the mass transfer limitation (or contamination age) increases. Bioremediation of field-contaminated soils, where release of contaminants is limited by poor mass transfer, may significantly benefit from surfactant washing of soils.

5.3 Biodegradation of PAHs in MGP Soil

Biodegradation of PAHs from the MGP soil with and without surfactant was investigated in batch systems using an enriched natural consortium of microorganisms

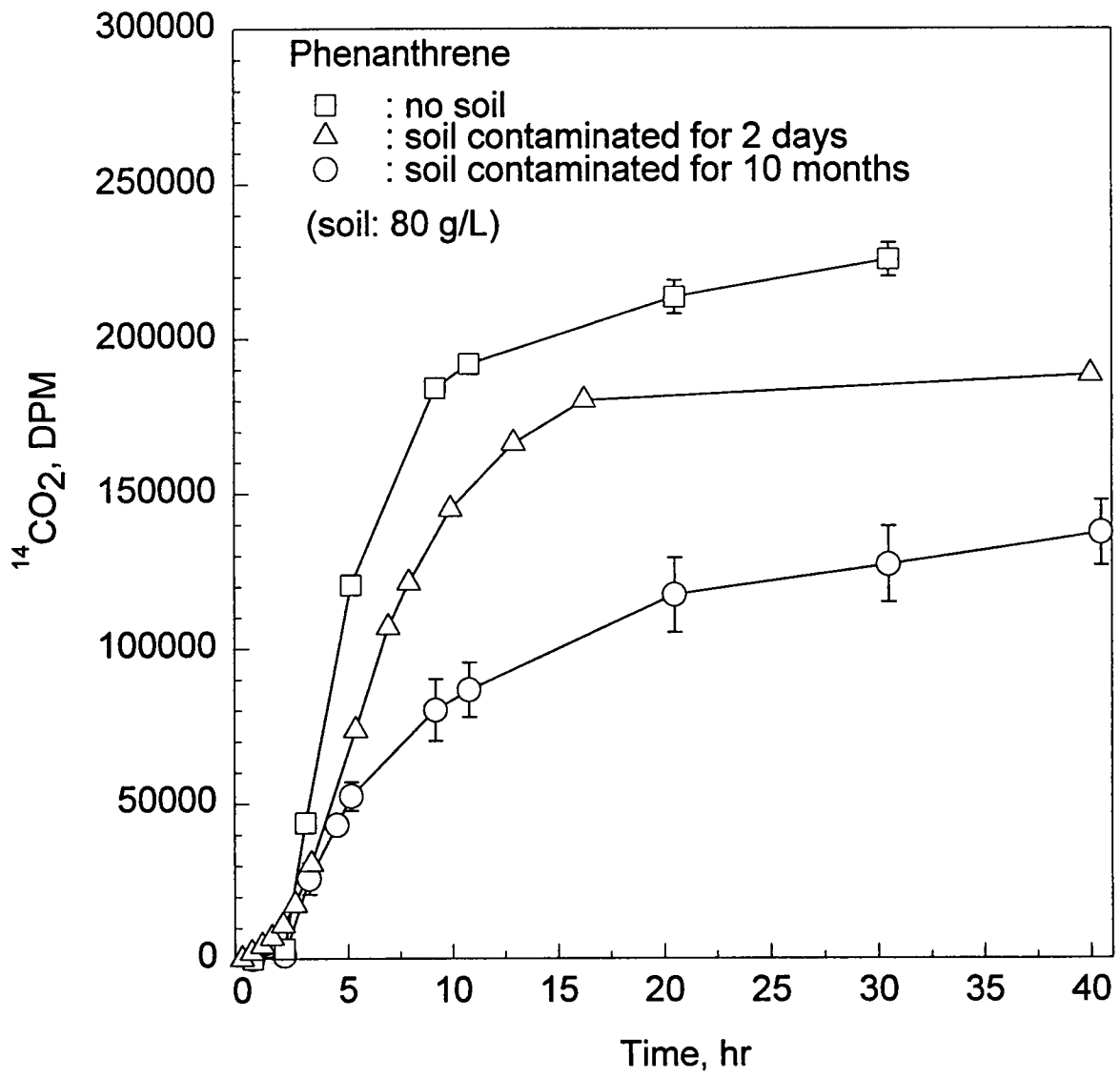


Figure 4. Effect of contamination age on mineralization of sorbed phenanthrene with no surfactant added

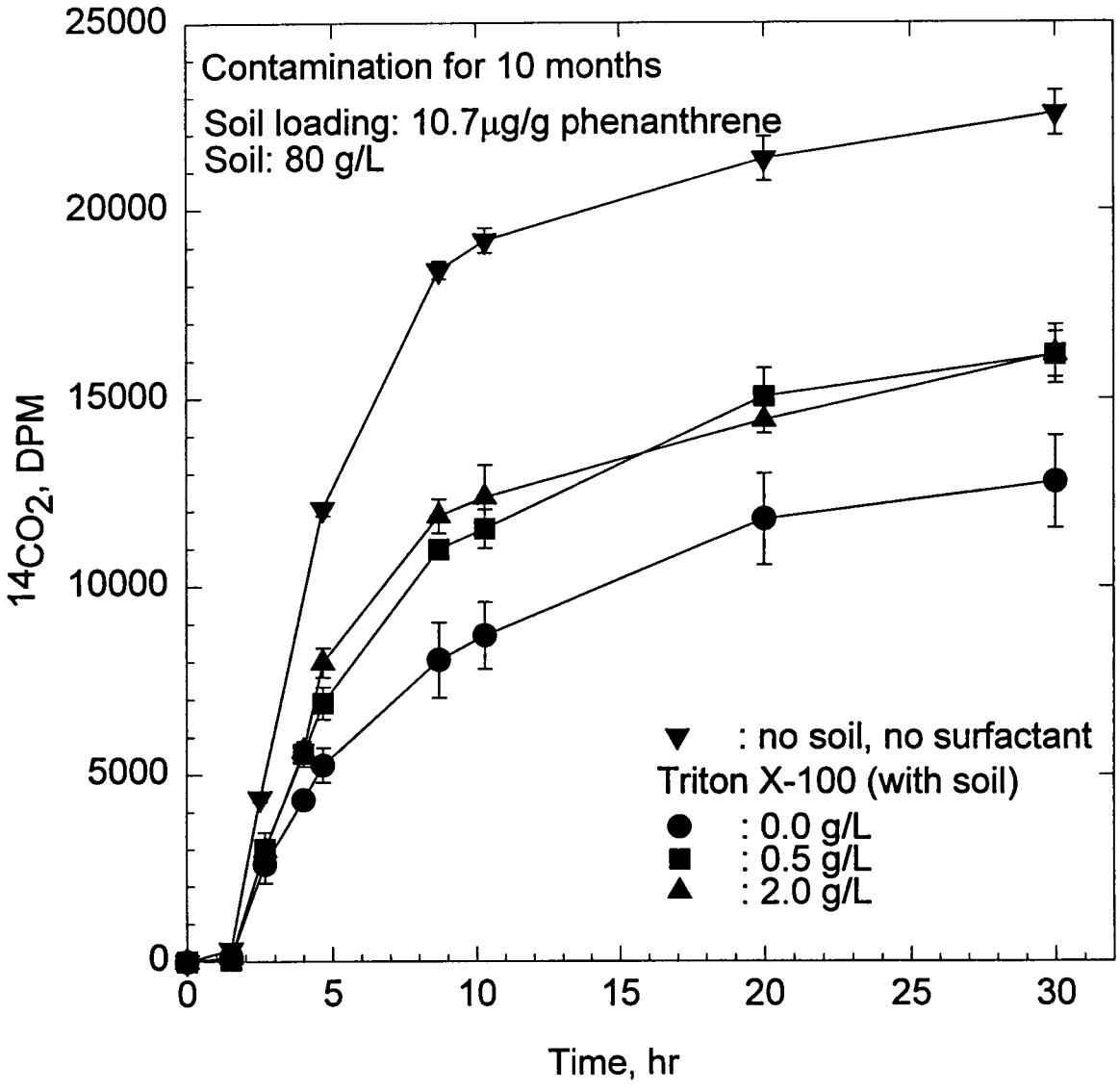


Figure 5. Mineralization of phenanthrene from soil contaminated for 10 months in the presence of Triton X-100

obtained from PAH contaminated soils. To determine the extent of surfactant biodegradation, PAHs in both aqueous and soil phases as well as the concentration of surfactant were monitored during biodegradation.

Surfactant Biodegradation:

Figure 6 shows the changes in aqueous surfactant concentrations during biodegradation. Except for Triton X-100, aqueous surfactant concentration rapidly decreased during the first 10 days. In a descending order of degradation, the surfactants can be arranged as follows: Tween 80 > Brij 30 > Brij 35 >> Triton X-100. Except for Triton X-100, all test surfactants were rapidly degraded regardless of initial surfactant concentrations. The changes in Triton X-100 concentration in aqueous phase for various initial dosages are shown in Figure 7. The slow decrease in surfactant concentration appears to be due to nonequilibrium sorption of surfactant to soil rather than biodegradation as shown earlier (Figure 5, Part 2). The observed decrease was nearly the same as the loss due to sorption in abiotic systems. To confirm this, biodegradation of 0.75 g/L and 2.5 g/L solutions of Triton X-100 by the mixed culture was separately determined in the absence of soil. No significant decrease in Triton X-100 concentrations was observed for the first 13 days. After 98 days, the concentrations decreased only slightly, 20% in the 0.75 g/L and 6 % in the 2.5 g/L.

The biodegradation of the test surfactants observed in the current study corroborates the literature well. Reportedly, the linear primary alcohol ethoxylates

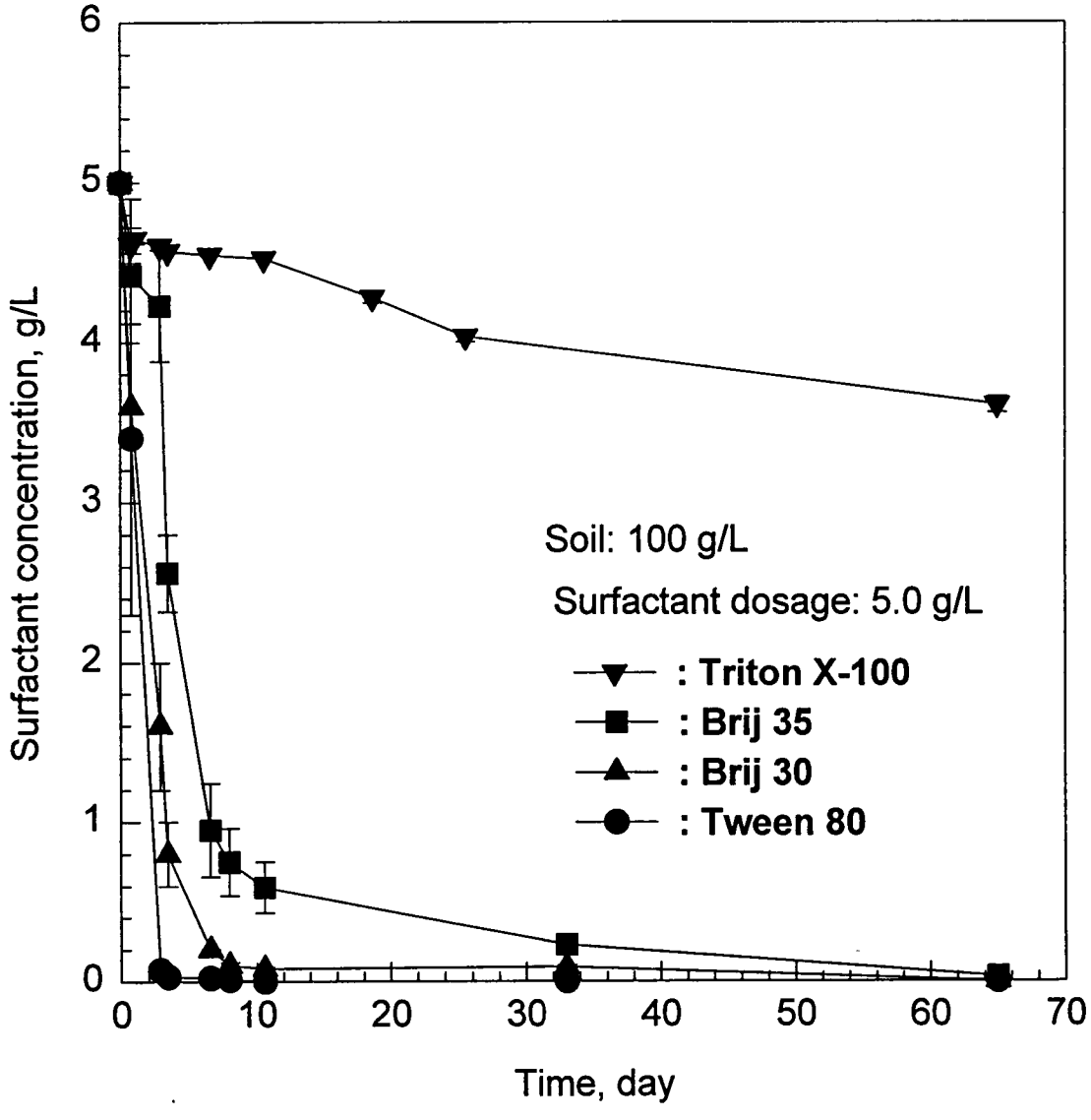


Figure 6. Biodegradation of surfactants

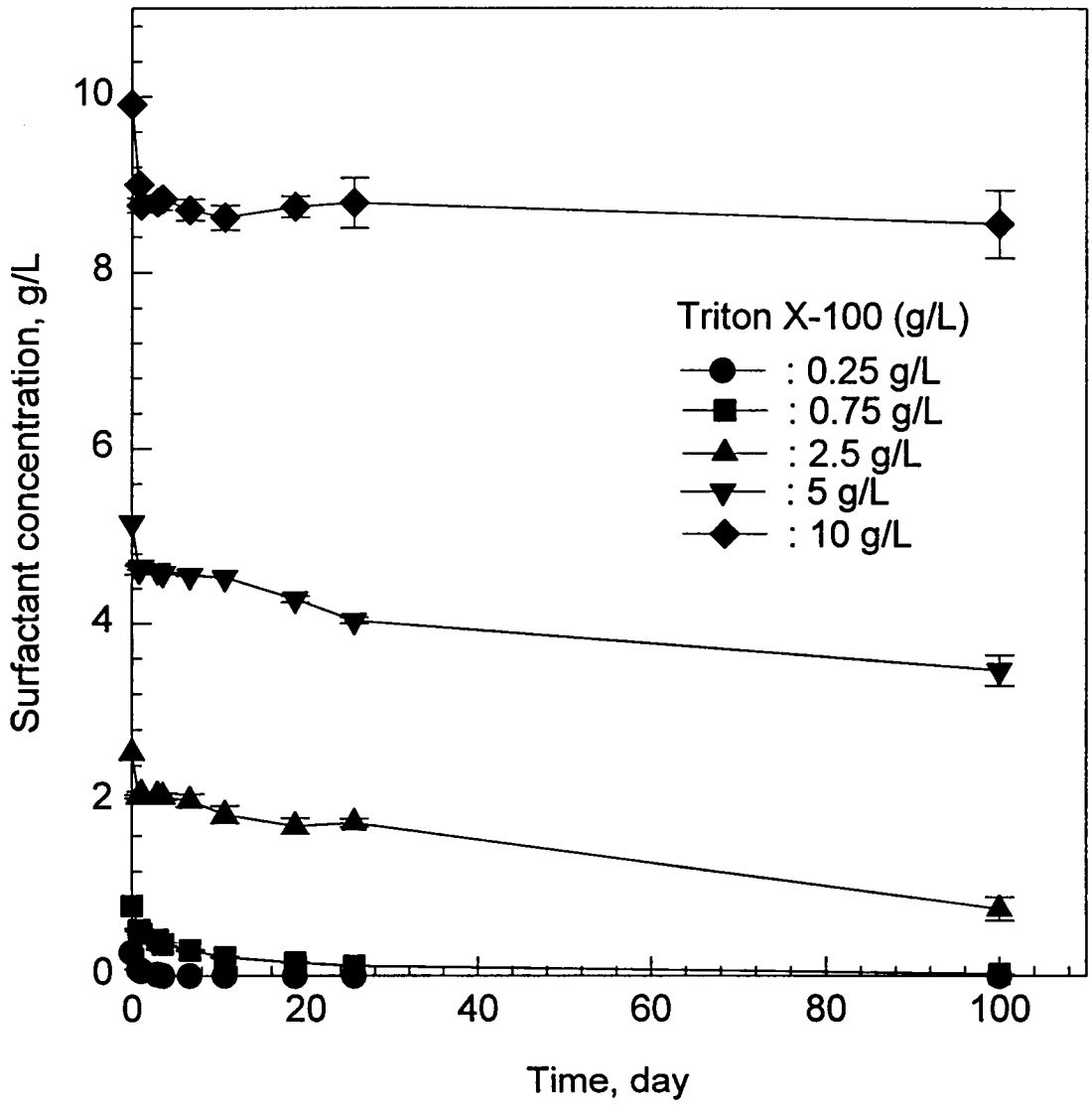


Figure 7. Changes in Triton X-100 concentration during biodegradation of PAHs

(LPAE), Brij 30 and 35, for example, are readily and completely biodegraded (Swisher, 1987); Manganelli (1956) and Minami (1958) observed degradation of Tween 80 in less than a day. However, biodegradation of branched alkylphenol ethoxylates (APE) surfactants such as Triton X-100 are controversial. Biodegradation of Triton X-100 reportedly ranges from 0 to 100 % (Huddleston, 1966; Lashen *et al.*, 1966; Conway and Waggy, 1966). Lack of acclimation of degradative bacteria has been suggested as one of the main causes underlying the observed variances (Lashen *et al.*, 1967; Mann *et al.*, 1971).

Aqueous-Phase PAH:

In Figure 8, aqueous phenanthrene concentrations in Triton X-100 solution during biodegradation are compared with those in abiotic controls. Aqueous-phase PAHs were monitored during biodegradation till they were analytically undetectable. In abiotic controls, phenanthrene concentrations initially increased with time as a result of its kinetically-limited release from soil and decreased slowly, presumably because of the loss of aqueous surfactant due to sorption to soil. In biodegradative samples, the change in aqueous phenanthrene concentration exhibited an increase for the first 1-2 days followed by a rapid decrease during the next 6 to 10 days, finally reaching a constant minima.

Any inference as to the behavior of PAHs in such system would only be speculative. Suffice it to say that the rate of release of contaminants from soil relative to the rate of their biodegradation must play a significant role in controlling their fate in weathered

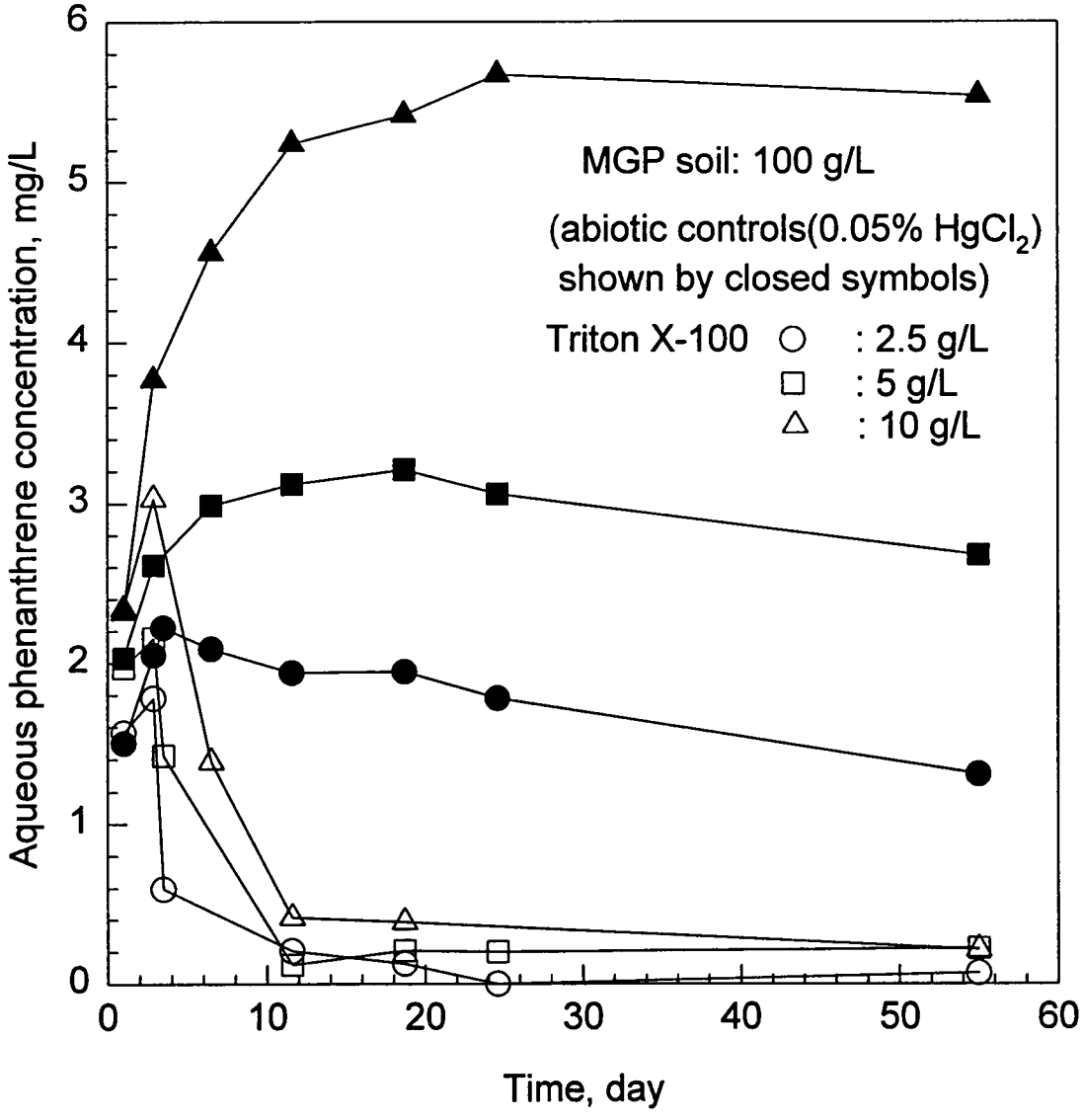


Figure 8. Aqueous phase phenanthrene concentration during biodegradation at various Triton X-100 dosages

soils. Seemingly, phenanthrene biodegradation required an acclimation period of 1-2 days. Once the cells are acclimated, biodegradation of phenanthrene proceeded at rate faster than the rate of mass transfer from soil. Consequently, there was a net decrease in the aqueous-phase concentration. After the concentration reached a minimum value, biodegradation was strictly limited by the mass transfer of substrate from soil.

With Brij 35 or Tween 80, the aqueous concentration of phenanthrene rapidly decreased regardless of surfactant dosage (Figure 9). Though the decrease in aqueous phenanthrene is assumed to be caused by biodegradation, conceivably phenanthrene from solution might have readsorbed to soil as the molecules were released from the surfactant micelles once the surfactants themselves were rapidly biodegraded (Figure 6).

The change in aqueous-phase PAH concentration resulting from biodegradation are shown by the chromatograms of aqueous samples (Figures 10 and 11) obtained at various times during biodegradation. Figure 10 shows chromatograms of aqueous PAHs released from the MGP soil washed with 2.5 g/L of Triton X-100 and Figure 11 shows those obtained for soils washed with 2.5 g/L of Brij 35. Both chromatograms show the disappearance of 2-3 ring compounds initially followed by a slow decrease of larger PAH molecules with greater number of benzene rings. After 26 days, Brij 35 was completely biodegraded and consequently no surfactant was available for micellar solubilization of PAHs. Absence of significant PAH peaks only confirmed this. Brij 35 does not show significant UV absorbance or fluorescence. Therefore, its concentration was measured by the surface tension method rather than HPLC.

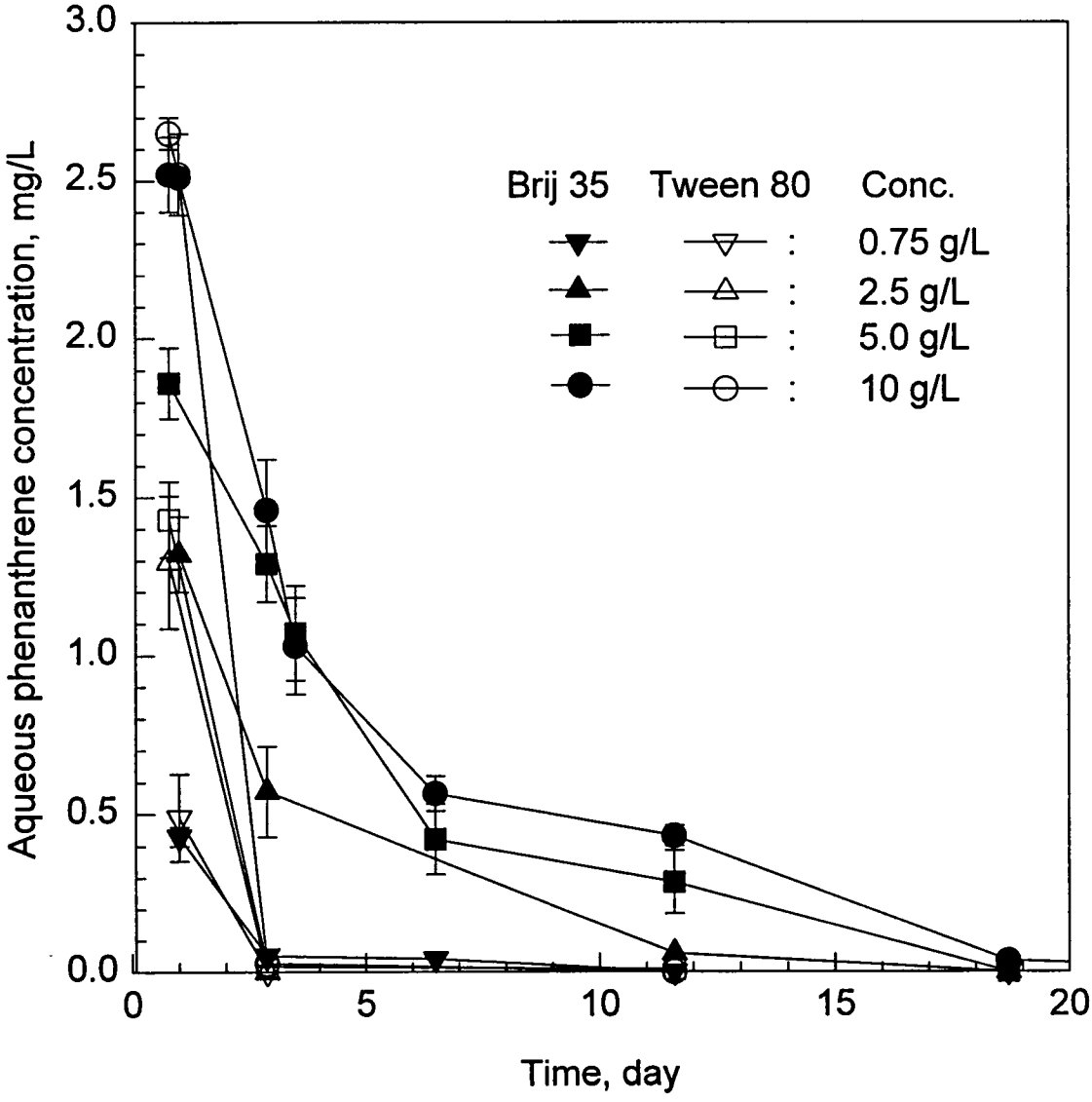


Figure 9. Changes in aqueous phenanthrene concentrations during biodegradation

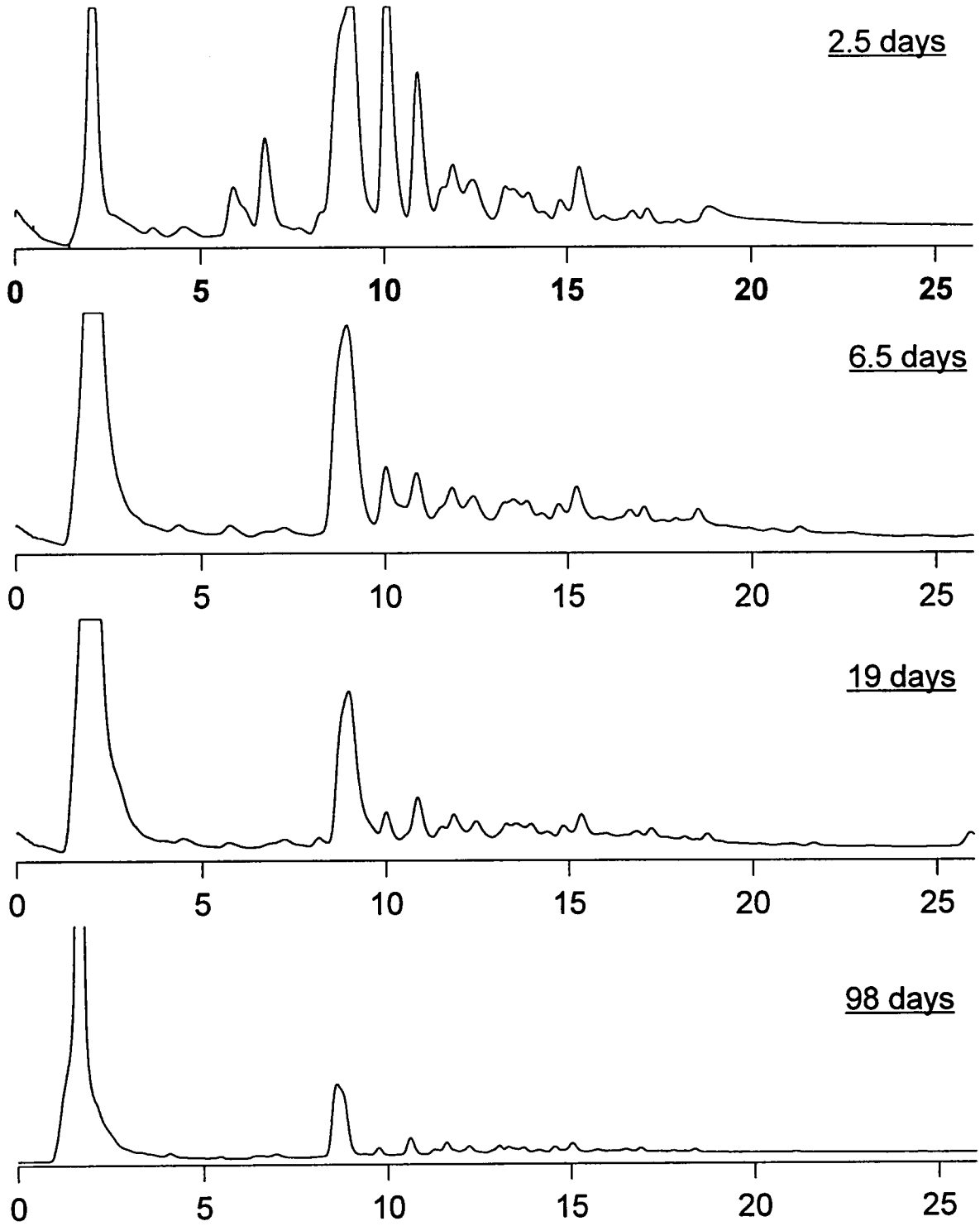


Figure 10. Dissapearance of PAHs from aqueous phase during biodegradation (2.5 g/L of Triton X-100)

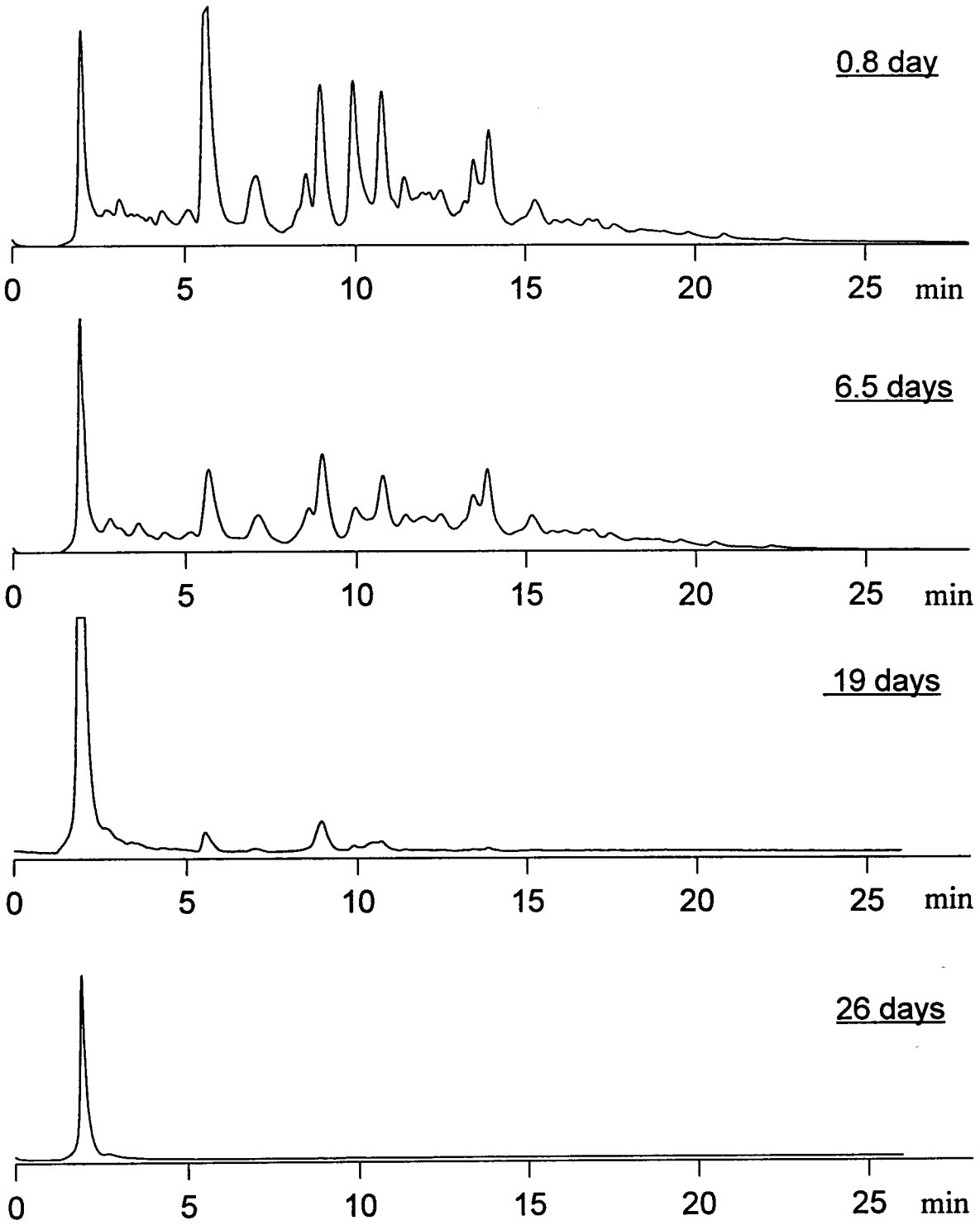


Figure 11. Disappearance of PAHs from aqueous phase during biodegradation (2.5 g/L of Brij 35)

Interestingly, the peak at an elution time of about 2-3 minutes slowly grew and then dissipated as biodegradation progressed. This peak most likely represents a byproduct of PAH biodegradation which initially accumulated as a result of rapid PAH biodegradation. By comparison, the corresponding peak for the abiotic control was much smaller. Also, the peaks appearing at the elution time of 2-5 minutes in biodegrading samples (first two chromatograms in Figure 11) were absent in abiotic controls.

PAHs in Soil Phase:

To determine the clean up levels attained, soil samples were collected from the reactors at given time intervals during the biodegradation test and residual PAHs in soil were measured. Figure 12 shows the changes in phenanthrene concentration in soil for different concentrations of Triton X-100 used in washing. Even without the surfactant, 40-45 % of soil-bound phenanthrene was degraded in 98 days. Triton X-100 significantly enhanced biodegradation during the first 4-5 days. Thereafter, a dosage-dependent removal was observed. At 0.25-0.75 g/L, removal by biodegradation gradually approached that obtained in samples with no surfactant (~ 45% in 98 days). At dosages of 2.5 g/L and above, 70-80 % of phenanthrene was biodegraded in 98 days. Biodegradation of phenanthrene in the presence of Tween 80 and Brij 35 are shown in Figures 13 and 14, respectively. Both surfactants initially enhanced biodegradation, but the rate slowed considerably thereafter. Tween 80 was biodegraded relatively fast (Figure 6) and was not available for enhancement of phenanthrene biodegradation (Figure

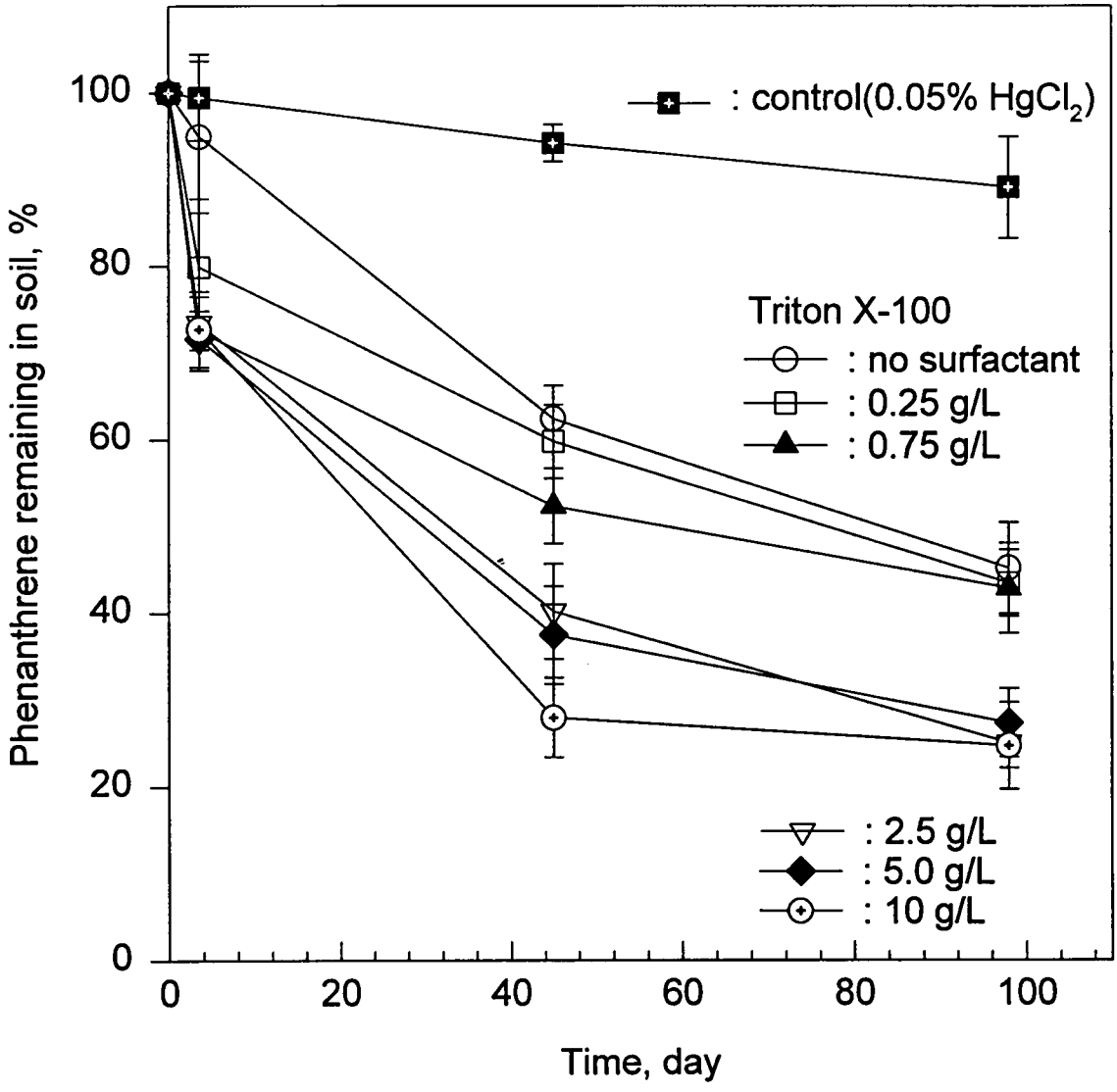


Figure 12. Biodegradation of phenanthrene in MGP soil in the presence of Triton X-100

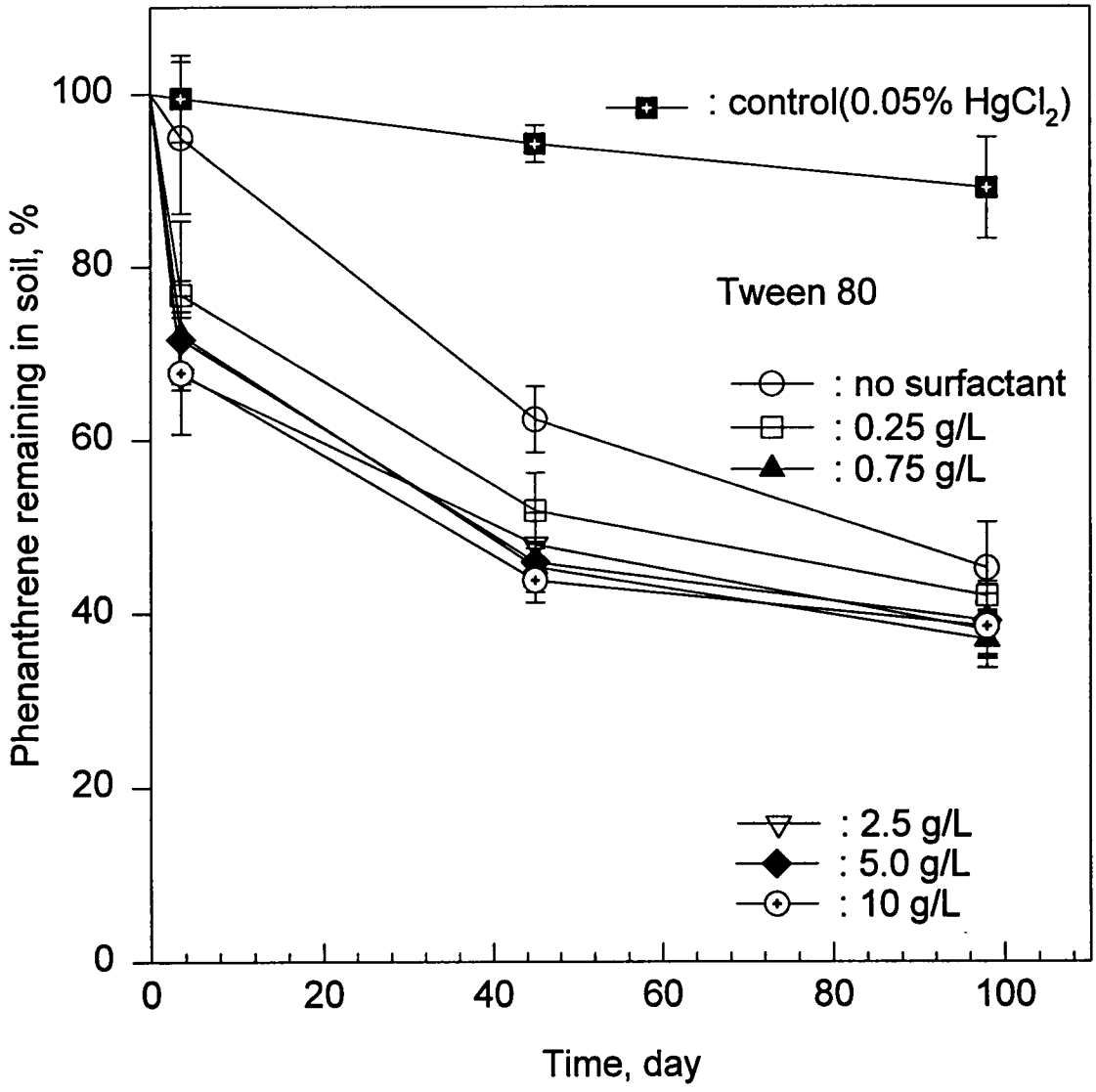


Figure 13. Biodegradation of phenanthrene in MGP soil in the presence of Tween 80

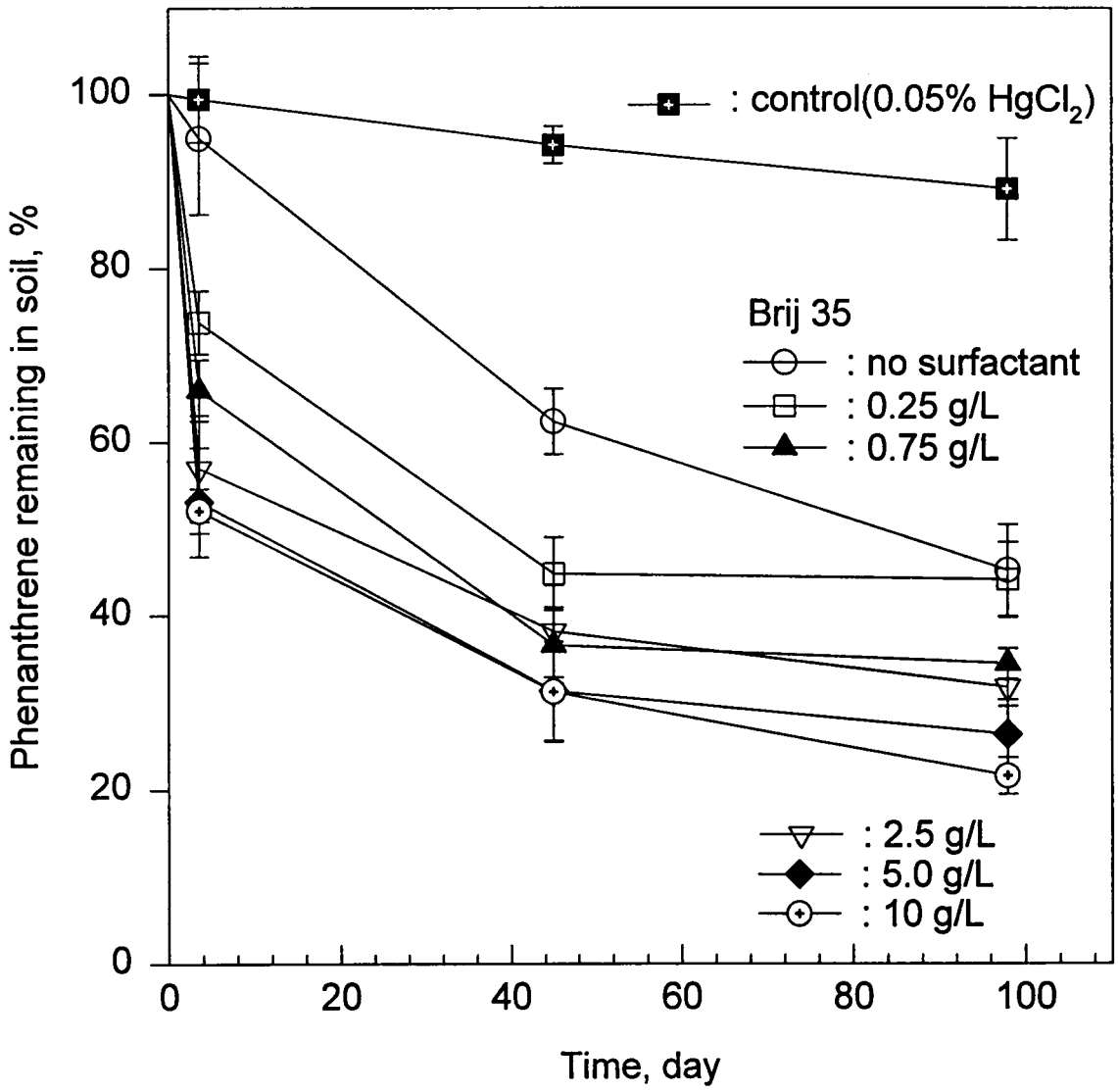


Figure 14. Biodegradation of phenanthrene in MGP soil in the presence of Brij 35

13). Brij 35 persisted somewhat longer and showed a greater enhancement of biodegradation. Seventy five to eighty percent of phenanthrene was biodegraded in 98 days in soils washed with Brij 35 compared to 60 percent biodegradation obtained with soils washed with Tween 80. Brij 35 continued to facilitate biodegradation up to 45 days by solubilizing soil-bound phenanthrene. Thereafter, the surfactant itself was biodegraded (Figure 6).

Concurrent biodegradation of five PAHs in surfactant-washed soils are compared in Figure 15 for four surfactants. Abiotic losses due to sorption were less than 10 % during the 45-day period of study. In the absence of any surfactant, 30-50 % biodegradation of the three 3- ring PAHs, fluorene, phenanthrene, and anthracene, occurred. Biodegradation of higher molecular-weight PAHs, pyrene and benzo(a)pyrene, was much smaller. Biodegradation of the three-ring PAHs was enhanced by surfactants. Of the surfactants tested, only Brij 35 and Triton X-100 exhibited any measurable improvement of biodegradation of pyrene and benzo(a)pyrene. Figure 16 shows bioremediation of the same five PAHs in the MGP soil washed with 0.25-10.0 g/L of Triton X-100. Enhancement of biodegradation occurred only at a Triton X-100 dosage of 2.5 g/L. No discernible improvement was observed by increasing the dosage.

5.4 Model Analysis

A major premise of the current work is that surfactants enhance biodegradation of PAHs in weathered soils by speeding up their release from soils which

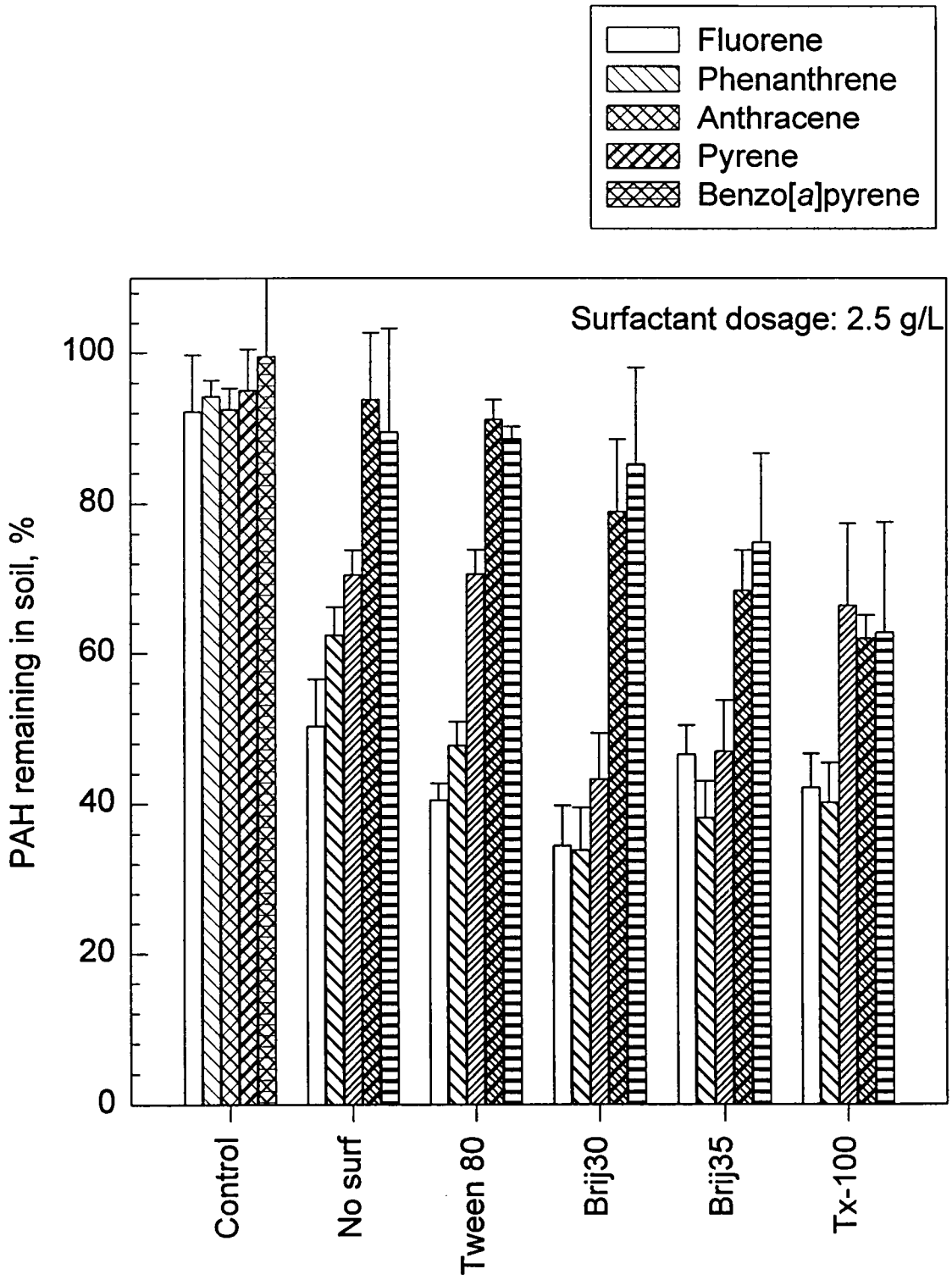


Figure 15. PAHs remaining in MGP soil after 45 days of biodegradation in the presence of various surfactants

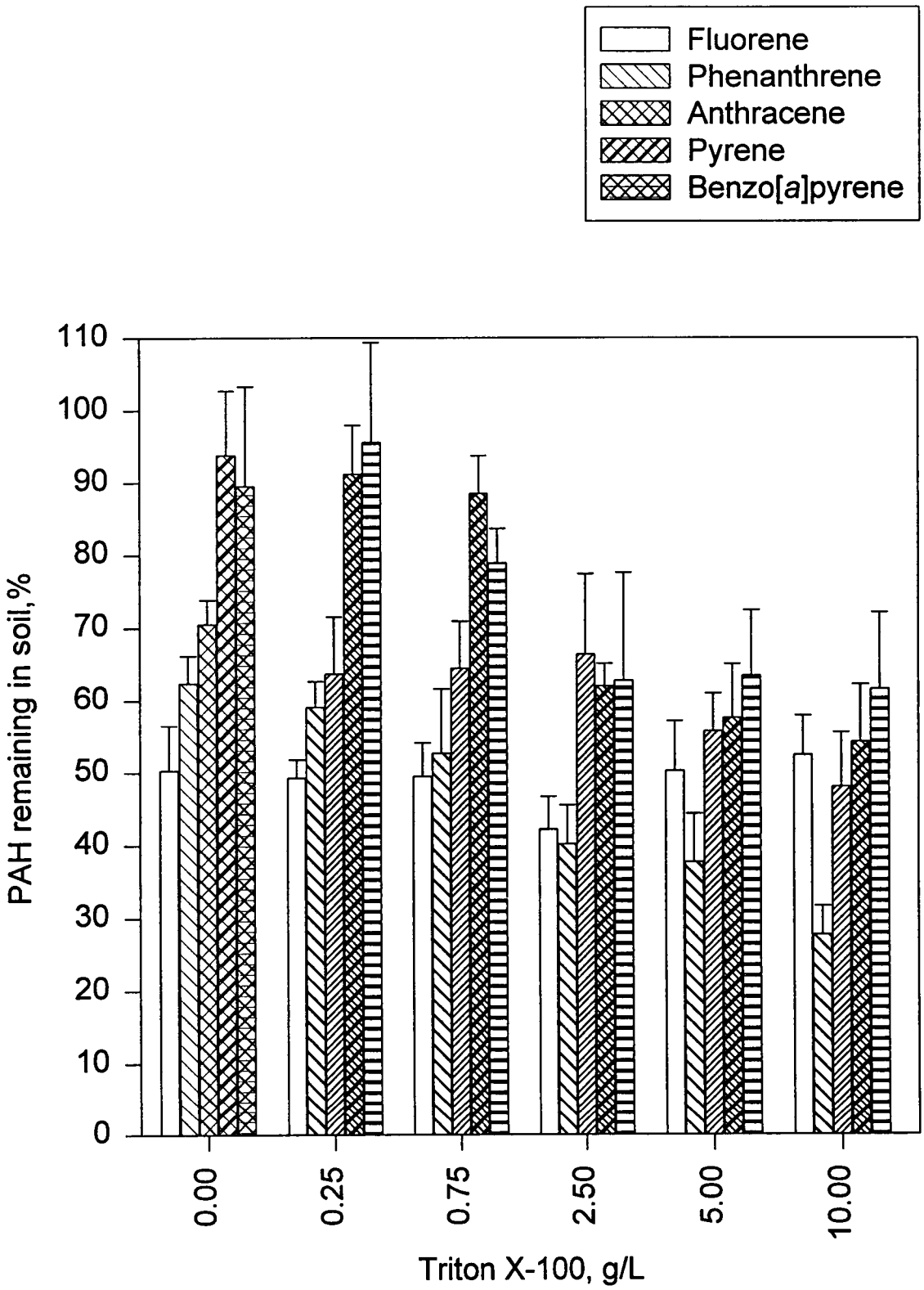


Figure 16. PAHs remaining in MGP soil after 45 days of biodegradation in the presence of Triton X-100

is otherwise severely limited by slow mass transfer. While the mass transfer enhancement by surfactants could be demonstrated by the increased soil/tar matrix diffusivity (D_S) and increased solubilization of PAHs at the soil-water interface as presented in Part 3, the effect of surfactant on biodegradation kinetics is not clear. Some researchers have suggested that addition of surfactant decreased the biodegradation rate for given substrate concentrations (Volkering *et al.*, 1995; Grimberg and Aitken, 1995). The decrease in biodegradation rate was attributed to the decrease in the concentration of substrate in the aqueous phase due to its partitioning into micelles. Seemingly, microorganisms can only degrade aqueous-phase PAHs. In this study, biodegradation rates were separately measured using leachate from the MGP soil obtained by washing with 5.0 g/L of Triton X-100 solution. A first order kinetic model was used to describe biodegradation of PAHs and the rate coefficient, k_{bio}, was estimated. The radial diffusion model used earlier (Part 3) to describe the release of PAH in abiotic systems was modified to include biodegradation. The mass balance including biodegradation is given by;

$$V_{aq}\left(\frac{\partial C_{aq}}{\partial t}\right)\left(1+K_m S_{mic}\right)+m_s\left(\frac{\partial \bar{S}}{\partial t}\right)-k_{bio}C_{aq}V_{aq}=0 \qquad (4)$$

One of the main difficulties in modeling PAH biodegradation in such systems is to include the effect of concurrent surfactant biodegradation. As a result of surfactant biodegradation, the solubility of PAH in aqueous phase changes with time and so does

the matrix diffusivity in the soil/tar phase. That the exact mechanism by which surfactants affect matrix diffusivity is not clearly understood makes it impossible to estimate the effect of surfactant biodegradation on matrix diffusivity. Therefore, the model presented here is applicable only to non-degrading surfactants such as Triton X-100.

Figure 17 shows the model prediction for phenanthrene biodegradation in the presence of no surfactant and 5.0 g/L Triton X-100. The values for mass transfer parameters, K_m and D_s/R^2 were obtained from Table 6 in Part 2 and Table 2 in Part 3, respectively, and the biokinetic rate constant, k_{bio}, was estimated to be 1.1 d^{-1} and 0.62 d^{-1} in surfactant-free and 5.0 g/L Triton X-100 solutions, respectively. The model prediction was corrected for abiotic losses, approximated by a linear function of time. The experimental results agreed reasonably well with model predictions indicating that enhanced bioremediation could conceivably be a direct result of enhanced mass transfer from soil.

Though the proposed model cannot be used to predict the effects of biodegradable surfactants, it may be used to estimate the relative significance of surfactant biodegradation in bioremediation. In Figure 18, the predicted biodegradation of phenanthrene in soils washed with Brij 30 and $C_{12}E_{10}$ were obtained assuming no biodegradation of the surfactants themselves. A value 0.62 d^{-1} for k_{bio}, same as that used for 5.0 g/L of Triton X-100, was used The large differences between the predicted values and the experimental results clearly demonstrate the importance of surfactant

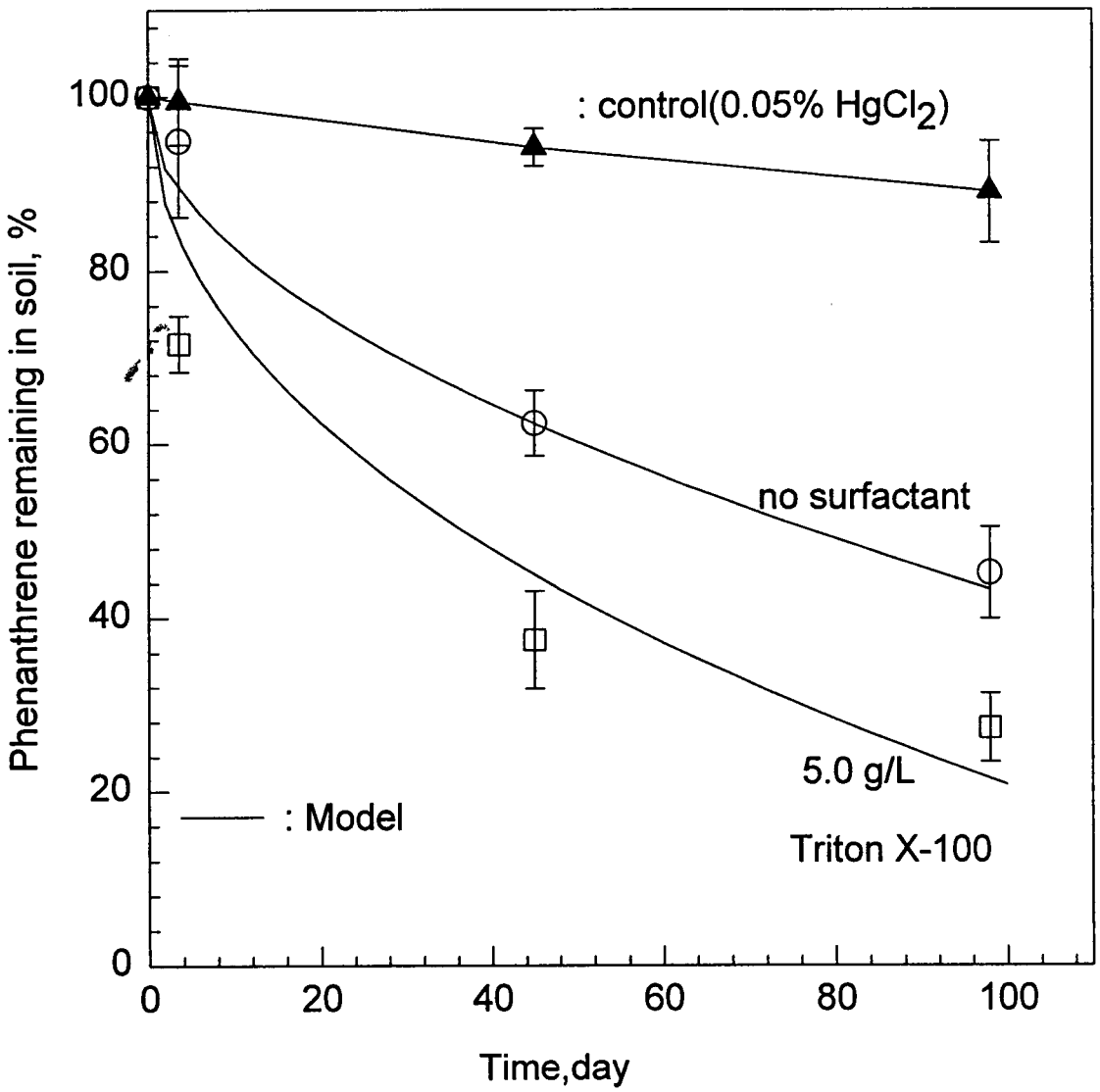


Figure 17. Comparison of predicted biodegradation of phenanthrene with measured values

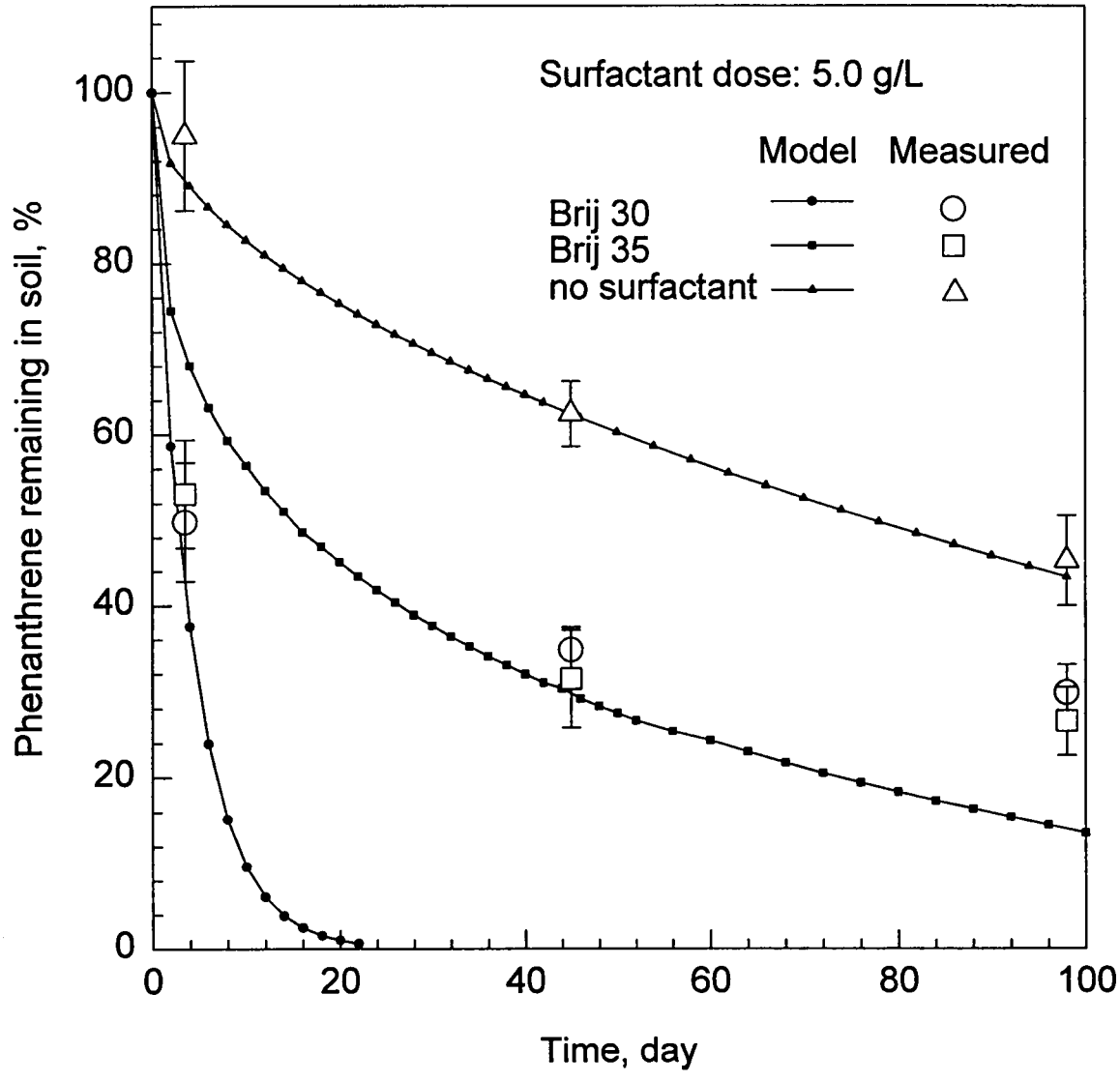


Figure 18. Model prediction of phenanthrene biodegradation assuming no surfactant biodegradation

biodegradation. For example, 95 % of phenanthrene would be biodegraded within 15 days in the presence of 5.0 g/L of Brij 30 if the surfactant were not biodegraded. With rapid biodegradation of the surfactants (Figure 6), only 54 % of phenanthrene was degraded in 45 days.

The dependence of surfactant-mediated bioremediation of MGP soils on the mass transfer and biodegradation rates of PAH is demonstrated in Figure 19 by performing a sensitivity analysis of the model for the two key parameters controlling each process: D_s/R^2 and k_{bio}. Based on the model analysis for various combinations of D_s/R^2 and k_{bio} values, contours describing the predicted percent biodegradation of phenanthrene in 10 days were obtained. In Part 3, a sensitivity analysis performed on the radial diffusion model clearly showed that surfactant-enhanced mass transfer is primarily governed by the diffusion parameter D/R^2 with micellar solubilization playing only a minor role. In the current sensitivity analysis, the value of K_m was made invariant. A value 24.3 L/g (K_m for phenanthrene with Triton X-100) was used. As seen in Figure 19, when the diffusivity is relatively low, the magnitude of k_{bio} does not affect biodegradation significantly. As D_s/R^2 increases, biodegradation becomes more sensitive to k_{bio} and it increases with increasing k_{bio}. Clearly, diffusivity enhancement is essential for successful remediation regardless of the biodegradation kinetics. On the other hand, when the value of k_{bio} is very low, the diffusivity enhancement by surfactant has a limited effect on overall biodegradation.. This implies that the mass transfer enhancement by surfactant is less beneficial to high MW PAHs which are generally quite

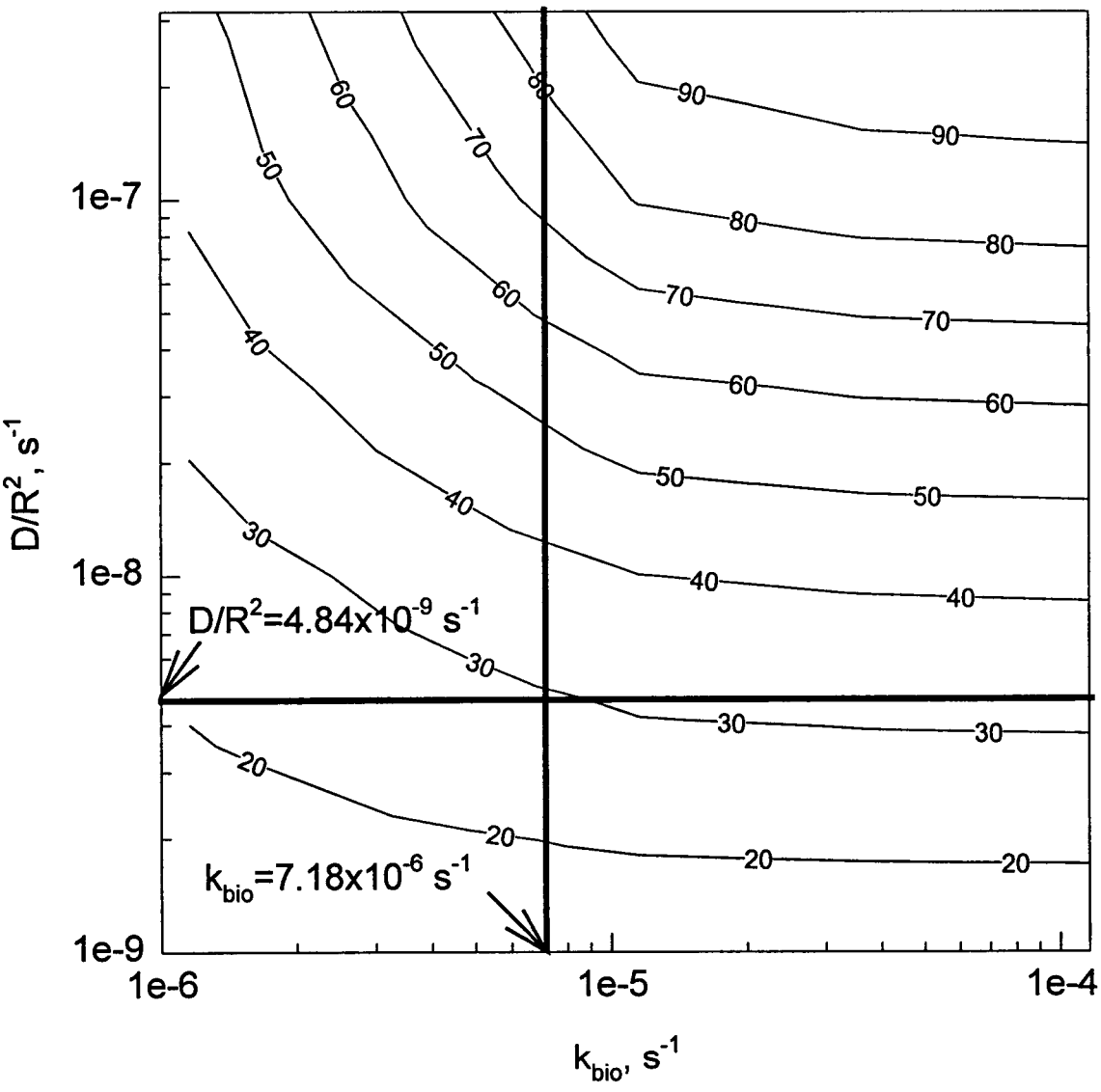


Figure 19. Effect of diffusivity parameter (D_s/R^2) and biokinetic rate coefficient (k_{bio}) on percent phenanthrene biodegraded in 10 days in the presence of 5 g/L Triton X-100 in simulated system

recalcitrant and thus have very small k_{bio} values.

5.5 Role of Surfactant in Bioremediation of MGP Soil

Surfactants affect the release of PAHs from soil and also the biodegradation of aqueous PAHs. It has been suggested that solubilized HOCs are bioavailable unless the surfactant is toxic to degradative microorganisms (Liu *et al.*, 1995; Volkering *et al.*, 1995). Mineralization experiments conducted in the present study also bore this out. The proposed mechanisms for the biodegradation of micelle-bound HOC involves partitioning of the solute from the micellar phase to the aqueous phase where it is biodegraded. Therefore, biodegradation rate is directly controlled by the aqueous-phase solute concentration only. Surfactants also help the mass transfer of HOC from soil or NAPL into the aqueous phase. The combined effects of a surfactant can be described using two extreme cases of mass transfer:

1) No mass transfer limitation: In this case equilibrium partitioning of PAH between water and soil/NAPL occurs instantaneously. Biodegradation rate is determined only by the aqueous phase substrate concentration. The equilibrium concentration of the solute in the aqueous phase and the corresponding biodegradation rate varies inversely with the amount surfactant added (Eqs. 2 and 3).

2) Mass transfer is very slow : Biodegradation is completely controlled by solute mass transfer from soil or NAPL into the aqueous phase. Usually, C_{aq} is near zero because biodegradation prevails over mass transfer, if sufficient oxygen and nutrient are

available. If surfactant enhances mass transfer of PAH from soil or NAPL to the micellar phase, it would indirectly facilitate biodegradation.

How a surfactant might affect bioremediation of a given contaminated soil may very well depend on the extent of mass transfer limitation of contaminants in that soil. The age of contamination or weathering largely determines the benefits that may be expected from surfactant washing. Desorption of PAHs from a soil artificially contaminated for only 2 days will likely fall under Case 1 above. The improvement in mass transfer achieved with surfactants is negated by the nonavailability of micellar solute for biodegradation (Figures 2 and 3). In the 10-month old soil mass transfer limitations were significant and the benefits of surfactant-washing were clear (Figure 4). In most field contaminated soils such as MGP soils, mass transfer of contaminants occurs much more slowly and surfactants would help biodegradation by speeding up the release of contaminants.

Often a dimensionless ratio of two rate coefficients, k_{bio} and $k_{aq}a$, is used to describe the relative importance of mass transfer rate on biodegradation (Luthy *et al.*, 1994):

$$D_a = \frac{k_{bio}}{k_{aq}a} \tag{5}$$

where D_a is a Damköhler number, and k_{bio} and $k_{aq}a$ are the overall rate coefficients.

In cases where $D_a >> 1$, mass transfer controls biodegradation (Case 2) while biokinetics controls biodegradation when $D_a << 1$. Typically, the value of $k_{aq}a$ decreases with time if a contaminant is released from soil by matrix diffusion (Deitsch and Smith, 1995). In such cases, D_a decreases with time. Eventually mass transfer controls the overall biodegradation. The rapid decrease of total soluble phenanthrene in MGP soil slurries (Figure 8) indicated that biodegradation was faster than the release of contaminants. In the absence of surfactants, aqueous phenanthrene decreased below the detection limit (3 μg/L) in only 2 days. In such cases, biodegradation would be entirely controlled by the diffusion of contaminants through the soil-tar matrix.

One of the important factors limiting the benefits of surfactant washing in bioremediation is the biodegradation of the surfactant itself. While toxicity of surfactants has been a major concern so far in most studies with pure cultures (Aronstein and Alexander, 1992; Yeom *et al.*, 1993; Jahan and Maier, 1994; Tiehm, 1994), loss of surfactants due to biodegradation has received little or no attention. This is particularly important in field applications where consortia of microorganisms are at play. Nonionic surfactants have been reported to be rapidly and completely degraded by natural consortia of microorganisms with proper acclimation (Swisher, 1987). All surfactants except Triton X-100 were degraded relatively fast in the present study. Upon proper acclimation, even Triton X-100 may be degraded. Metabolism of surfactants is an issue that merits further study in relation to surfactant washing of weathered soils. Given that the rate of release of contaminants is extremely slow even with surfactant washing,

natural organisms may very well adapt themselves to the surfactants, and in the absence of sufficient primary substrates (target contaminants), may metabolize them. Conceivably, this may lead to desorption of soil-sorbed surfactants and adversely affect the release of soil-bound contaminants via surfactant-penetration and concomitant swelling of the soil-tar matrix. As discussed in Part 3, small number of ethoxylate groups and linearity of the carbon skeleton are the two structural characteristics of surfactants that mostly favor mass transfer of soil-bound PAHs. However, surfactants with such characteristics (i.e. Brij 30) are more easily degraded (Swisher, 1987) and their effects on biodegradation are limited.

Biodegradation was responsible for the poor performance of surfactants observed in this study. One advantage of biodegradable surfactants is that they reduce the risk of creating secondary contamination when applied *in situ*. The negative effects of surfactant biodegradation may be minimized by separating soil washing and biodegradation processes in the treatment scheme. In this treatment scheme, enhancement of contaminant diffusivity in soil should be the preferred characteristics for the selection of surfactant.

6 SUMMARY

The effects of nonionic polyethoxylated surfactants on biodegradation of PAHs in contaminated soils were investigated in batch experiments. Two different types of soils, artificially contaminated soils and a tar-contaminated soil from an MGP site were used. Mineralization of PAHs in the artificially contaminated soils was determined using pure cultures. Biodegradation of PAHs in the MGP soil was determined using a mixed culture enriched from contaminated field soils. PAH concentrations in both aqueous and soil phases were measured during biodegradation. Concurrent biodegradation of the surfactants was also measured. In addition, bioavailability of micellar PAHs was studied using naphthalene and Triton X-100.

High concentrations of Triton X-100 appeared to impede naphthalene mineralization when no naphthalene crystals were present. Mineralization of PAHs from soils contaminated for 2 days was not affected by surfactants while that of PAHs from soils contaminated for longer time periods was enhanced by surfactants. Biodegradation of PAHs from the MGP soil was enhanced at supra-CMC surfactant dosages. The enhancement by Tween 80, which was degraded the fastest, was less than that by other surfactants. All surfactants except Triton X-100 were biodegraded relatively fast (<20 days). Aqueous-phase PAHs depleted fast during biodegradation indicating that the rate of release of PAHs from soil controlled the overall biodegradation process. PAH concentrations in the soil decreased rapidly in the initial phase (< 3 d) and slowly

thereafter. A model combining mass transfer and biodegradation was used to predict the biodegradation enhancement. Although surfactants enhanced biodegradation of PAHs, the enhancement was limited due to the biodegradation of surfactant itself. When surfactant was not degraded, biodegradation enhancement of phenanthrene by surfactant could be explained by its increased rate of release from soil. The relative importance of mass transfer rate and biokinetics in bioremediation of MGP soil was demonstrated using ranges of values for the diffusivity parameter (D_s/R^2) and the biokinetic parameter (k_{bio}). Diffusivity parameter was shown to be more important than the biokinetic parameter in biodegradation of PAHs in weathered soils.

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PART 5

SUMMARY AND CONCLUSIONS

The effects of ethoxylated nonionic surfactants on the solubilization and biodegradation of individual PAHs from a weathered, coal-tar contaminated soil were studied in this research. Under abiotic conditions, surfactants significantly increased solubilization of soil-bound PAHs. A predictive model was developed to describe the solubilization of individual PAHs in multi-component coal tars commonly found in MGP soils. In this model, solubilization is described as a partitioning of PAHs between the two nonpolar organic phases: residual tar in soil and surfactant micelles. Surfactant-mediated enhancement of solubility can be described by two key parameters, namely the soil/tar-micelle partitioning coefficient ($K_{soil/tar\text{-}mic}$), which represents the affinity of a PAH for the surfactant phase relative to the soil/tar phase, and surfactant loading (SL), defined as the weight of surfactant added per unit weight of soil. The model satisfactorily described experimental data at relatively low surfactant loadings (<0.06 g/g soil). At higher surfactant loadings, equilibrium was not reached during the experimental period and therefore enhancement of solubility could not be determined. The performance of commercial surfactants were compared from their soil/tar-micelle partitioning coefficients. In decreasing order of the degree of solubilization achieved, the test surfactants are ranked as follows:

Brij 30 > $C_{12}E_{10}$ > Tween 80 > Triton X-100 > Brij 35.

Performance was inversely related to the HLB number of the surfactant.

Although surfactants enhanced the equilibrium partitioning at the soil/tar-micelle interface (micellar solubilization), the release of individual PAHs into solution was a slow rate-limited process, especially at high surfactant dosages. Release progressively

decreased as more PAHs were solubilized. Slow diffusion of PAH molecules through the soil/tar matrix, which consists of 75 % organic matter, is proposed as the mechanism responsible for the observed slow release of PAHs. To determine the maximum release of PAH achievable under such kinetic limitations, PAHs were extracted using Tenax resin. Tenax extracted only 18 % of soil-bound phenanthrene in 12 days. Significantly more phenanthrene could be extracted by repetitive washing with fresh surfactant solution. For example, 12 washings with 5.5 g/L Brij 30 extracted 90 % of phenanthrene from the soil. This is attributed to the increased diffusivity of PAH molecules within the soil/tar matrix. A radial diffusion model was used to quantify the increase in matrix diffusivity of PAHs. Surfactant enhanced the diffusivity of phenanthrene by up to two orders of magnitude. Sensitivity analysis of the two key model parameters, the diffusive transport and soil/tar-micelle equilibrium, defined by, respectively, D_s/R^2 and K_m, revealed that increasing matrix diffusivity was of much greater significance in enhancing the release of PAH from soil than increasing solubilizing capacity of a surfactant. The observed mass transfer enhancement by surfactants was attributed mainly to increased diffusivity. Penetration of surfactant molecules into the soil/tar matrix and subsequent swelling of the polymeric medium are suggested as a possible mechanism for the diffusivity enhancement.

Use of surfactants in bioremediation of contaminated soils stem from their ability to enhance solubilization of contaminants into the aqueous phase and thus making them more bioavailable. In using surfactants, their toxicity to degradative

microorganisms or biodegradation of the surfactants themselves must also be considered. Studies of surfactant-mediated biodegradation were conducted on MGP soils to evaluate these concerns. A mixed culture of PAH degrading microorganisms obtained from MGP sites was used. Active biodegradation of solubilized PAHs at surfactant concentrations of up to 10 g/L demonstrated that the surfactants were not toxic to the consortium of PAH-degrading microorganisms. Soil analysis during the biodegradation experiment showed that biodegradation of PAHs from the soil was enhanced by surfactant. Using 5 g/L Triton X-100 solution, 70-75 % of phenanthrene was biodegraded from the soil while 55 % was removed without surfactant. A radial diffusion model modified for first order biodegradation was tested for phenanthrene removal using separately estimated diffusivity parameter (D_S/R^2) and a first order biokinetic constant. Reasonable agreements between the model predictions and the measured values were observed. Biodegradation of Triton X-100 was not significant during the experiment. However, other surfactants were degraded at the initial stage of the experiment. Tween 80 and Brij 30 were completely degraded in 10 days while Brij 35 was degraded in 55 days. The observed enhancement of biodegradation was much smaller than what would be expected due to enhanced mass transfer caused by the surfactants were they not biodegraded themselves.

Based on the results of this study, the following conclusions were drawn:

1. Nonionic surfactants enhance the solubilization of PAHs in MGP soil. The solubility

enhancement depends on surfactant loading (SL) and soil/tar-micelle partitioning coefficient ($K_{soil/tar\text{-}mic}$).

2. Release of PAH from MGP soil is a slow, rate-limited process even in the presence of surfactants.

3. Surfactant increased both the extent and the rate of PAH solubilization from MGP soil. Up to 90 % of phenanthrene could be solubilized after 12 consecutive washes with fresh surfactant solution.

4. Surfactants increase the rate of PAH release mainly by increasing the diffusivity of PAH in the soil/tar matrix. Diffusivity increased by two orders of magnitude.

5. Surfactants are not toxic to the natural consortium of microorganisms commonly found in MGP soils.

6. Micelle-solubilized PAHs were completely biodegraded.

7. Biodegradation of PAHs is controlled by mass transfer even in the presence of surfactant.

8. Surfactants enhance biodegradation of soil-bound PAHs by enhancing their mass

transfer. However, such enhancement may be limited by the biodegradation of the surfactants themselves.

VITA

Ick Tae Yeom was born in Incheon, Korea on November 20, 1962. He attended elementary schools in Incheon and graduated from Bupyoung High school in February, 1981. The following March he entered Seoul National University and in February, 1985 received the degree of Bachelor of Science in Civil Engineering. He reentered Seoul National University in March, 1985 to pursue a Master of Science degree in Urban Engineering. However, his graduate study was interrupted by military service. In August, 1990 he came to the United States and began graduate studies at The University of Tennessee, Knoxville. In December, 1992, he received a Master of Science degree in Civil and Environmental Engineering. He continued his study at The University of Tennessee, Knoxville and received a Doctor of Philosophy in Civil Engineering in December, 1995.