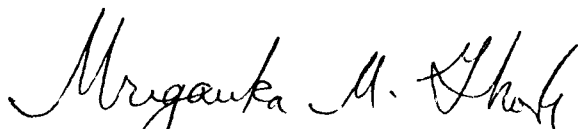


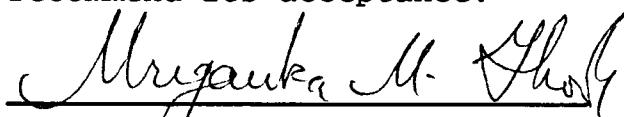
To the Graduate Council:

I am submitting herewith a thesis written by ICK TAE YEOM entitled "Mobilization of Soil-Bound Polycyclic Aromatic Hydrocarbons Using Surfactants". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.



Mriganka M. Ghosh, Major Professor

We have read this thesis and
recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a Master's degree at The University of Tennessee, Knoxville, I agree that the Library shall make it available to borrows under rules of the Library. Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgement of the source is made.

Permission for extensive quotation from or reproduction of this thesis may be granted by my major professor, or in his absence, by the Head of Interlibrary Services when, in the opinion of either, the proposed use of the material is for scholarly purposes. Any copying or use of the material in this thesis for financial gain shall not be allowed without my written permission.

Signature Yeom Guk Me

Date Oct. 5, 1992

MOBILIZATION OF SOIL-BOUND POLYCYCLIC AROMATIC
HYDROCARBONS USING SURFACTANTS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

ICK TAE YEOM

December, 1992

Copyright © Ick Tae Yeom, 1992

All rights reserved

ACKNOWLEDGEMENT

I would like to acknowledge with profound gratitude my debt to my major professor, Dr. Mriganka M. Ghosh, who has given me invaluable advice and encouragement with great patience for the past two years. I would like to extend my gratitude to the other committee members, Dr. Kevin Robinson and Dr. Chris Cox, for their comment and assistance during the research. I also would like to thank Dr. John Graveel, who provided soil samples and useful information on soil characteristics. I wish to thank Rebecca Pullen and Arup Bandyopadhyay who have helped me in the laboratory with warm friendship.

I am indebted to my fellow Koreans, including Pastor Ingil Cho and the members of Knoxville Korean Baptist Church who provided me with spiritual encouragement and friendship. Finally, I would like to thank my parents for their constant and dedicated loving support. Their self-sacrificing love should be rewarded.

Thank God and all of you.

ABSTRACT

Batch experiments were performed to estimate the effectiveness of surfactant in mobilizing soil-bound PAHs. The desorption of naphthalene and phenanthrene from soils of varying f_{oc} was determined using two nonionic alcohol ethoxylate surfactants. A dramatic enhancement of desorption (80 - 95%) was obtained after one day of washing with surfactants, but relatively high surfactant doses (2 or 3 orders magnitude greater than CMC) were required. Kinetics of surfactant-enhanced desorption was also investigated using soils contaminated for different periods of time. The efficiency of surfactant washing was found to be significantly affected by the kinetics of both PAH adsorption and desorption: long contamination periods and short surfactant-washing periods resulted in decreased desorption of PAH. Both an equilibrium partitioning model and a radial diffusion model were used to analyze the results of PAH adsorption/desorption obtained in this study. The desorption data for soils of relatively long contamination age (22 days) were well described by the radial diffusion model while those from soils of short contamination age (1 day) were described better by the equilibrium model. From a practical standpoint, the radial diffusion model appears to be appropriate for use in the field because of the long contamination history of most hazardous waste sites.

Keywords: polycyclic aromatic hydrocarbons, soil, remediation, surfactant, desorption, mass transfer, models

TABLE OF CONTENT

	PAGE
Chapter 1. INTRODUCTION	1
1.1 Remediation of PAH-Contaminated Soils	2
1.2 Role of Surfactants in PAH Mobilization	3
1.3 Objectives and Scope	5
Chapter 2. LITERATURE REVIEW	7
2.1 Sorption of PAH	9
2.2 Surfactant-Soil Interaction	18
2.3 Mobilization of Soil-Bound PAH	23
Chapter 3. METHOD AND MATERIALS	35
3.1 Materials	35
3.2 Experimental Methods	40
Chapter 4. RESULTS AND DISCUSSION	51
4.1 Adsorption Studies with Hematite	51
4.2 Adsorption of PAH on Natural Soils	63
4.3 Desorption of PAH from Soil Using Surfactant	71
4.4 Modeling of PAH Desorption	96
Chapter 5. CONCLUSIONS	110
REFERENCES	114
APPENDICES	121
Appendix I. Preparation of PAH Stock Solution	122
Appendix II. Volatilization Loss of PAH Compounds	125
Appendix III. Correction of Results from Desorption Studies	129

Appendix IV.	Graphical Determination of CMC in Soil -Water Systems	131
Appendix V.	Desorption of PAH from Soil Using Surfactant	136
Appendix VI.	Radial Diffusion Model (After Wu, 1986)	140
VITA		145

LIST OF TABLES

TABLE	PAGE
2.1 Partitioning characteristics of selected PAH-surfactant systems	29
3.1 Summary of natural soil characteristics	37
3.2 Characteristics of test nonionic surfactants	38
3.3 Chemical characteristics of test PAHs	39
4.1 Surface characteristics of hematite	51
4.2 Partition coefficients of phenanthrene in natural soils	65
4.3 CMC of nonionic surfactants with or without soil	74
4.4 Soil organic carbon content (f_{oc}) corrected for surfactant adsorption	79
A.1 Percent solution residue after solid separation from various soil suspensions	129

LIST OF FIGURES

FIGURE	PAGE
2.1 Systematic description of surfactant-soil-PAH system	8
2.2 Solubilization of phenanthrene by a nonionic surfactant	24
3.1 Calibration curve showing total organic carbon (TOC) as a function of surfactant concentration	43
4.1 Kinetics of Aldrich humic acid adsorption on hematite	52
4.2 Adsorption isotherm of Aldrich humic acid-hematite system (concentration: 0-20 mg/L)	54
4.3 Adsorption isotherm of Aldrich humic acid-hematite system (concentration: 0-500 mg/L)	55
4.4 Determination of CMC of Igepal CA-720 in the presence of hematite	57
4.5 Adsorption isotherm of Igepal CA-720 on hematite	58
4.6 Adsorption isotherm of naphthalene on hematite	59
4.7 Distribution of K_{oc} values for varying f_{oc} values	60
4.8 Freundlich isotherm for naphthalene adsorption on hematite	62
4.9 Effect of f_{oc} on the linearity of adsorption isotherm	62
4.10 Desorption of naphthalene at varying surfactant doses	64
4.11 Adsorption isotherm of phenanthrene on soils with different organic carbon content	66
4.12 Effect of organic matter released from soil on K_{oc}	68
4.13 Effect of sorption equilibration time on the distribution of phenanthrene	70

FIGURE	PAGE
4.14 Determination of CMC of Igepal CA-720 in aqueous solution	72
4.15 Determination of CMC of Brij 30 in aqueous solution	73
4.16 Determination of CMC of Igepal CA-720 in the presence of Lexington II soil	75
4.17 Sorption isotherm of Igepal CA-720 on soils	77
4.18 Sorption isotherm of Brij 30 on soils	78
4.19 Freundlich isotherms for the sorption of Igepal CA-720 on different soils	80
4.20 Freundlich isotherms for the sorption of Brij 30 on different soils	81
4.21 One-day desorption of naphthalene by from soils using Brij 30	83
4.22 Desorption of naphthalene by two different types of nonionic surfactants	84
4.23 Desorption of phenanthrene from Lexington soils using Brij 30	86
4.24 Isotherms for desorption of phenanthrene from various soils	88
4.25 Normalized distribution coefficient of PAH desorption at various surfactant doses	89
4.26 Recovery of naphthalene with repeated washings	92
4.27 One-day desorption of phenanthrene from Lexington II soil with different contamination ages	94
4.28 Effect of contact time on desorption of phenanthrene from Etowah soil with Brij 30	95
4.29 Comparison of theory and experiment using equilibrium model (phenanthrene desorption)	98
4.30 Comparison of theory and experiment using equilibrium model (naphthalene desorption)	99
4.31 Comparison of experiment and model prediction during desorption using radial diffusion model	103

FIGURE	PAGE
4.32 Comparison of experiment with model prediction during desorption using radian diffusion model	106
4.32 Comparison of theory and experiment using radial diffusion model	108
A.1 Percent loss of naphthalene by volatilization	127
A.2 Determination of CMC of Igepal CA-720 in the presence of Lexington I soil	131
A.3 Determination of CMC of Igepal CA-720 in the presence of Etowah soil	132
A.4 Determination of CMC of Brij 30 in the presence of Lexington I soil	133
A.5 Determination of CMC of Brij 30 in the presence of Etowah soil	134
A.6 Determination of CMC of Brij 30 in the presence of Lexington II soil	135
A.7 One-day desorption of phenanthrene from Lexington I soil using Brij 30	136
A.8 One-day desorption of naphthalene from Lexington I soil	137
A.9 One-day desorption of naphthalene from Etowah soil using Brij 30	138
A.10 One-day desorption of naphthalene from Lexington II soil using Brij 30	139

LIST OF NOTATIONS

A_{sp}	= specific activity of a radiolabeled compound, [mCi/mmol]
C_{aq}	= aqueous phase solute concentration, [M/L ³]
C_{dose}	= surfactant concentration added to soil, [M/L ³]
C_{surf}	= aqueous surfactant concentration, [M/L ³]
C_M	= surfactant micelle concentration, [M/L ³]
C_o	= octanol phase solute concentration, [M/L ³]
D_{eff}	= effective pore diffusivity of solute, [L ² /T]
D_m	= molar diffusivity of solute in water, [L ² /T]
E	= percent desorption, [%]
F	= fraction of sorbent exhibiting instantaneous sorption, [-]
f	= fugacity of a compound, [atm]
$f_{c, Hu}$	= fractional organic carbon content of humic acid, [-]
f_o	= reference state fugacity, [atm]
f_{oc}	= soil organic carbon content, [-]
f'_{oc}	= f_{oc} corrected for sorbed surfactant, [-]
$f_{oc, s}$	= fractional organic carbon content of surfactant, [-]
k	= first-order rate constant for mass-transfer nonequilibrium model, [1/T]
K_d	= apparent soil-water distribution coefficient, [M/M]
K_F	= Freundlich isotherm partitioning coefficient, [L ³ⁿ M ⁻ⁿ]
K_m	= micelle-water partitioning coefficient, [mole/mole]
K_{oc}	= K_p normalized to sorbent organic carbon, [M/M]
K_{ow}	= octanol-water partitioning coefficient, [mole/mole]

K_p = equilibrium soil-water partitioning coefficient, [M/M]
 $K_{p,cmc}$ = soil-monomeric surfactant solution partitioning coefficient, [M/M]
 $K_{p,cmc}'$ = $K_{p,cmc}$ corrected for surfactant adsorption, [M/M]
 M_w = molecular weight, [M/mole]
 n = Freundlich isotherm parameter, [-]
 n_a = intra-aggregate porosity of soil particles, [-]
 n_{aq} = number of moles of solute in aqueous pseudophase, [-]
 n_{mic} = number of moles of solute in micellar phase, [-]
 n_{sorb} = number of moles of solute in sorbed phase, [-]
 $n_{sorb,init}$ = n_{sorb} before addition of surfactant solution, [-]
 q = sorbed phase solute concentration, [M/M]
 q_{cmc} = q at equilibrium with CMC surfactant solution, [M/M]
 q_{max} = maximum sorbed phase solute concentration, [M/M]
 r = radial distance, [L]
 R = conversion factor for surfactant concentration, [M/mole]
 R' = activity-concentration ratio, [DPM/M]
 S = aqueous solubility, [M/L³]
 S_{mic} = solubility at a particular surfactant concentration greater than CMC, [M/L³]
 S_{cmc} = solubility at the CMC surfactant solution, [M/L³]
 $S(r)$ = local sorbed phase concentration of a solute as a function of r , [M/L³]
 S_1 = solute concentration in instantaneous sorption domain, [M/M]
 S_2 = solute concentration in rate-limited sorption domain, [M/M]

v_a = volume of surfactant solution added to soil, [L³]
 v_c = contaminant velocity in the subsurface, [L/T]
 v_w = water velocity in the subsurface, [L/T]
 V_w = molar volume of water, [L³]
 w_s = concentration of soil, [M/L³]
 x_a = mole fraction in aqueous pseudophase, [-]
 x_m = mole fraction in micellar pseudophase, [-]
 α, β = constants
 γ = activity coefficient, [-]
 ϵ = soil porosity, [-]
 ρ_b = soil bulk density, [M/L³]
 ρ_s = dry soil density, [M/L³]
 Φ = conversion factor (2.22×10^6), [DPM/ μ Ci]

ABBREVIATIONS

AHA = Aldrich humic acid
 CMC = critical micelle concentration in aqueous solution of surfactant
 CMC_{eff} = CMC in soil-surfactant aqueous suspension
 DOM = dissolved organic matter
 GMD = geometric mean diameter
 HOC = hydrophobic organic compound
 LEA = local equilibrium assumption
 PAH = polycyclic aromatic hydrocarbon
 PSD = particle size distribution
 SOM = soil organic matter

CHAPTER 1. INTRODUCTION

Widespread contamination of groundwater and soil by toxic or hazardous organic pollutants is of growing concern. Most often these compounds are hydrophobic in nature. As a rule, they bind tenaciously to soil in both vadose and saturated zones and persist in the environment for a long time. Of organic contaminants identified thus far in soils and groundwater, polycyclic aromatic hydrocarbons (PAH) constitute a major group. Because of their persistence and slow rates of transport, new cases of groundwater contamination are likely to be found for years to come. The fate and transport of these compounds in the environment are greatly influenced by their sorptive interactions with soils and sediments. Once adsorbed, their aqueous concentrations may be greatly attenuated resulting in a low-level source of ground water pollution over a long period of time. Generally, HOCs present a difficult remediation problem because of their extensive sorption to the soil matrix. Remediation involves expensive, often impractical, on-site treatment of pumped groundwater or removal of soil for off-site incineration. An understanding of how these pollutants persist or degrade in the environment is essential for evaluating the effectiveness of remediation technologies such as soil washing, bioremediation, soil venting, or others. Quite possibly, the key to successful remediation by any process may lie in the enhancement of

desorption of these compounds from soil.

1.1. REMEDIATION OF PAH-CONTAMINATED SOILS

Polycyclic aromatic hydrocarbons are nonpolar, neutral, hydrophobic organic molecules comprised of two or more fused benzene rings. Though natural fires in woods and grasslands may contribute to their presence in the environment, anthropogenic sources constitute by far the largest contributors. These compounds may be released to the environment through the disposal of coal tar and other coal processing wastes, petroleum sludges, asphalt, creosote and other wood preservative wastes and soot (Mueller et al., 1989). Hydrophobic in nature, PAH compounds are strongly adsorbed on soils. The management strategies employed to restore PAH-contaminated soil are difficult to implement. Pump-and-treat technology is frequently used to cleanup PAH-contaminated sites. Because of their low aqueous solubilities and high affinity for aquifer solids, pumping may remove only a small fraction of these contaminants; the remainder, while bound to solid, continues to serve as a reservoir for groundwater contamination over a long period of time. Biotechnology is being increasingly used to reclaim contaminated soils and groundwater. Studies have shown that 2- or 3-ringed PAHs are completely biodegradable and may be utilized as primary substrate by PAH-degrading microbes.

Recently, *in-situ* bioremediation of contaminants has been proposed for their ultimate removal from aquifers (Compeau and Mahaffey, 1990). However, the success of biological remediation is most often limited by the availability of substrate. The extensive adsorption of PAH compounds to soil matrix protect them from microbial attack and they are not readily available for biodegradation (Alexander, 1981; Ogram, et al., 1985; Robinson and Novak, 1990). Therefore, desorption and transfer of such contaminants to the aqueous phase is an essential prerequisite for any bioremediation scheme.

1.2 ROLE OF SURFACTANTS IN PAH MOBILIZATION

Most often remediation of soils and sediments contaminated with polycyclic aromatic hydrocarbons is limited by their slow rate of release from solids. Any remediation scheme, biological or physicochemical, must include mobilization of sorbed PAH as an essential step. Recently, surfactant chemicals have received considerable attention because of their potential for mobilizing soil-bound hydrophobic organic matter; they solubilize organic compounds that are otherwise sparingly soluble in water. Surfactant molecules are amphipathic: they have both polar and nonpolar regions on the same molecule; at high concentrations they aggregate to form micelles. Incorporation of HOCs, PAHs for example, into hydrophobic core of aqueous-phase surfactant

micelles - even when such contaminants are bound to soil - dramatically increases their solubility. By promoting desorption/mobilization of contaminants, surfactants may increase the efficiency of physical treatment technologies including pump-and-treat processes or other soil-washing operations. By the same token, these chemicals may serve as adjuvants in bioremediation by making contaminants available to degradative microorganisms. Their net effect on contaminated soil may be estimated by comparing the distribution of PAH compounds between immobile aquifer material and the mobile aqueous phase in systems with and without surfactants; specifically, the partitioning behavior of PAH between different phases: sorbent phase, aqueous pseudophase containing surfactant monomers, and micellar phase may be experimentally determined. While transfer of PAH molecules from soil to aqueous phase is obviously the key step in surfactant-aided mobilization of PAHs, its mechanism is not clear. However, evidence is mounting that sorption and desorption of PAH and other HOCs in soils are long-term nonequilibrium processes. In such systems, equilibrium, vis-à-vis partitioning, is merely the boundary condition of a kinetically controlled mass transfer process. Therefore, the desorption of these compounds from soil, even when surfactants are employed, may be influenced by its contamination age. Currently, no information is available on the effect of nonequilibrium behavior of PAH sorption/desorption on

surfactant-mediated mobilization. Such information is essential for a realistic assessment of benefits of using surfactants in remediating sites that might have been contaminated with PAH over a long time, months to years.

1.3 OBJECTIVES AND SCOPE

While solubilization of HOC in aqueous solutions of surfactant micelles has been studied for many years, that in soil-water systems has been studied only recently. Solubilization in such cases involves partitioning of both HOC and surfactant between soil and water, the formation of surfactant micelle, which, in turn, causes partitioning of HOC between micellar and aqueous pseudophases. Seemingly a nonequilibrium process, the mobilization of PAH from soil by surfactant may also depend on the 'contamination history' of soil as well as time allowed for desorption.

The purpose of this study was to evaluate the efficiency of commercial surfactants in solubilizing soil-bound PAH and to investigate possible mass-transfer limitations in such reactions. Two nonionic surfactants, an alkylphenolethoxylate and an alkylethoxylate, were used. Prior to surfactant application, the adsorption of two PAHs: naphthalene and phenanthrene, on natural and constructed soils were studied and the degree of retardation of PAHs estimated. The kinetics of surfactant-mediated desorption of PAH from contaminated

soils was investigated over relatively long periods of time. Soils equilibrated with target PAH for different time periods ('contamination age') were used in desorption studies. Overall, four soils were used: laboratory-synthesized hematite coated with a commercial humic acid and three natural soils of similar textures but containing different amounts of organic carbon (f_{oc}).

The specific objectives of this study were:

1. To determine the rate and extent of sorption of two PAHs: naphthalene and phenanthrene, on the following sorbents:
 - a) hematite coated with Aldrich humic acid
 - b) three natural soils: Lexington I, Lexington II, and Etowah, with f_{oc} of 0.9%, 3.4%, and 1.7%, respectively
2. To evaluate the solubility enhancement of soil-bound PAH by two nonionic commercial surfactants, an alkylphenolethoxylate and an alkylethoxylate, used at dosages above and below the CMC
3. To determine possible kinetic limitations in adsorption-desorption of PAH in natural soils
4. To evaluate applicability of existing equilibrium and kinetic models in predicting adsorption-desorption of PAH in natural soils

CHAPTER 2. LITERATURE REVIEW

The mobilization of soil-bound PAH using surfactant can be viewed as a multi-phase system (Fig. 2.1) consisting of a sorbent phase, an aqueous pseudophase containing surfactant monomers in it, a hydrophobic pseudophase of surfactant micelle, and possibly an air phase and pure solid PAH. The immobile sorbent phase may be hypothetically divided into two different domains: instantaneous sorption domain and rate-limited sorption domain. The effectiveness of a surfactant in mobilizing PAH depends on the relative transport and distribution of the PAH compound between these phases and domains. The interactions between phases also affect the PAH distribution by changing the availability of each phase. For a given soil-PAH-surfactant combination, the mobilization of PAH is dependent on various processes:

- (a) the sorption/desorption of PAH on soil
- (b) the interaction of PAH with surfactant monomer
- (c) the surfactant-soil interaction
- (d) the partitioning of aqueous phase PAH with the surfactant micelle
- (e) surfactant aggregate formation: micelle or lamellae.

The mechanistic or semi-empirical descriptions of these processes are reviewed in this chapter.

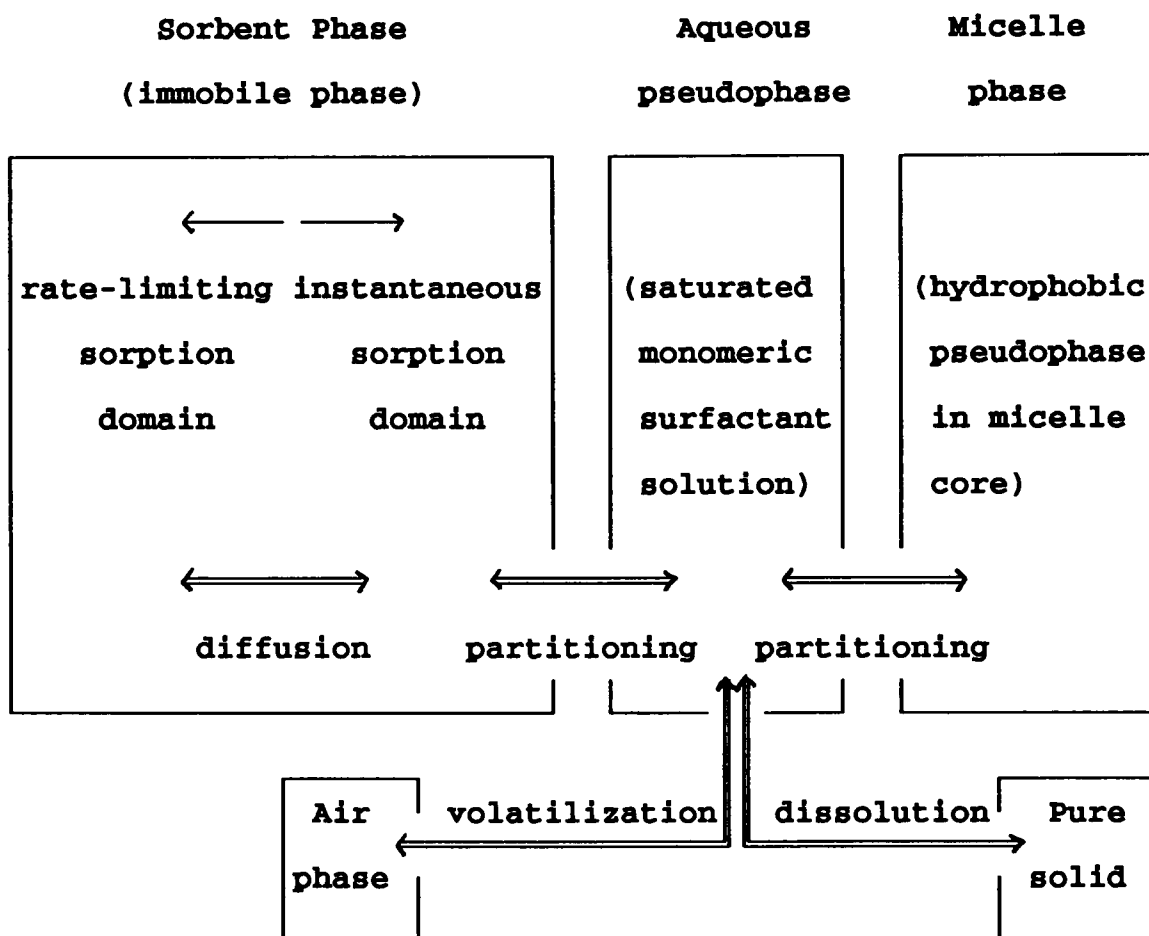


Figure 2.1 Systematic description of surfactant-soil system

2.1 SORPTION OF PAH

The fate and transport of contaminant in the subsurface are highly dependent upon their sorptive behavior. In addition to affecting physical movement of contaminants, sorption changes their availability for chemical or biological transformations. For hydrophobic organic compounds (HOCs), the effect of sorption is profound because it is the key process immobilizing contaminants in the subsurface. In such a case, knowledge of sorption is essential in developing any remediation technology. The mechanisms of sorption/desorption of organic compounds on soil are reviewed in this section.

2.1.1 Linear Partitioning of HOCs

Recently, Karickhoff et al. (1979) made a significant advance toward understanding the role of adsorption in the retardation of organics of widely different aqueous solubilities in soils of varying organic carbon contents (f_{oc}). The adsorption of PAHs and chlorinated hydrocarbons on natural sediments was found to be linear and the equilibrium between the aqueous and solid-phase concentrations, C_{aq} and q , respectively, could be described by a linear partitioning coefficient, K_p :

$$K_p = q/C_{aq} \quad (2-1)$$

K_p has been reported to be directly related to two important properties of reactants: the organic carbon content of sorbent (f_{oc}) and the hydrophobicity of sorbate. The correlation between K_{oc} , defined as the partitioning coefficient normalized for the organic carbon content of soil, and f_{oc} is linear (Karickhoff et al, 1979; Schwarzenbach and Westall, 1981):

$$K_{oc} = K_p / f_{oc} \quad (2-2)$$

The validity of K_{oc} has been verified for a wide variety of HOCs adsorbing on soils of widely varying organic carbon content (Hasset et al., 1980; Karickhoff, 1981). The effect of hydrophobicity of the adsorbate has been characterized by the relationship between K_p (or K_{oc}) and the octanol-water partitioning coefficient (K_{ow}) of the adsorbate. The hydrophobicity of organic compounds is usually measured by their K_{ow} values defined as:

$$K_{ow} = C_o / C_{aq} \quad (2-3)$$

where C_o is the concentration of an organic compound in the octanol phase. Typically, log-linear relationships between K_{oc} and K_{ow} have been reported for various HOCs (Karickhoff et al., 1979; Hasset et al., 1980; Schwarzenbach and Westall, 1981). In general, this relationship can be expressed by:

$$\log K_{oc} = \alpha \log K_{ow} + \beta \quad (2-4)$$

where α and β are fitting parameters for a given system. The values of α , β depend on the type of organic compound and the dimensional unit of the partitioning coefficient. With K_{oc} and K_{ow} expressed as a ratio of mole fractions, α and β values in the range of 0.99-1.00 and 0.32-0.35, respectively, were reported for PAHs by Hasset et al. (1980) and Karickhoff et al. (1979). Similarly, the water solubility of a solutes has also been correlated with K_{ow} (Karickhoff et al, 1979):

$$K_{ow} = 10^5 S^{-0.67} \quad (2-5)$$

where S is the solubility of a compound in $\mu\text{mol/L}$. From these relationships, K_{oc} can be estimated from more easily determined and widely cataloged molecular parameters. Further, from a knowledge of K_p , the velocity of a contaminant in the subsurface relative to water, can be estimated (Freeze and Cherry, 1979):

$$v_w/v_c = 1 + (\rho_b/\epsilon)K_p \quad (2-6)$$

where v_w and v_c are, respectively, velocities of water and contaminant, ρ_b is the bulk density of soil ($\sim 2 \text{ g/cm}^3$) and ϵ is the porosity, generally 0.3 - 0.5. From equations 2-2, 2-4, 2-5 and 2-6, one can obtain the following relationship for

the relative velocity of the contaminant:

$$\log(v_w/v_c) = \log(\rho_b/\epsilon) + \log(f_{oc}) - 0.67\log(S) + C \quad (2-7)$$

where C is a constant; C depends on α and β values in Eq. 2-4. For a given soil, the first term on the right hand side is constant. A series of $\log(v_w/v_c)$ vs. $\log S$ isopleths for various f_{oc} values can be plotted from which the degree retardation of a compound of known solubility in a given soil can be estimated. Theoretically, a linear sorption isotherm for HOCs can be justified from fugacity considerations (Karickhoff, 1984). Thermodynamically, at equilibrium, the fugacities (f) of a solute in the sorbed and solution phases are equal:

$$f^s = f^w \quad (2-8)$$

where the superscripts s and w refer to the sorbed and solution phases, respectively. The fugacity, in turn, is related to the concentration and activity coefficient of the solute in each phase.

$$\gamma^s f_o^s S = \gamma^w f_o^w C \quad (2-9)$$

where γ denotes an activity coefficient, f_o is the reference state fugacity and S and C represent concentration in the

sorbed and solution phases. Therefore, the ratio of concentrations at equilibrium is given by:

$$S/C = (f_o^w/f_o^s) (\gamma^w/\gamma^s) \quad (2-10)$$

Since f_o in each phase is constant, the partitioning of a solute depends on its activity coefficient in the two phases. In sufficiently dilute system, typical of most environmental situations involving HOCs, the activity coefficient ratio approaches a constant value and a linear isotherm results. Chiou et al. (1979) stated that most hydrophobic compounds in the environment can be treated as 'dilute' solutions, based upon their aqueous solubility. Therefore, they may exhibit linear adsorption isotherms. Karickhoff (1981) also suggested that a linear isotherm may be exhibited up to a solution concentration of 10^{-5} M. The solubility of PAHs is well within this limit except that for naphthalene; therefore, a linear sorption isotherm may be expected. Even for naphthalene (solubility = 2.5×10^{-4} M) a linear isotherm was obtained with constructed soils having varying f_{oc} values (section 4.1.4).

2.1.2 Sorption Nonequilibrium

In modeling contaminant transport in the subsurface, the adsorption process is often simplified by assuming relatively fast attainment of equilibrium. The rate of sorption is assumed to be fast relative to other processes affecting

solute transport so that local equilibrium is established between the sorbent and the sorbate in the pore fluid. Because of the slow movement of water in the subsurface, the local equilibrium assumption (LEA) is widely used to describe distribution of HOC. However, evidence supporting the view that the rates of sorption and desorption of chemicals are controlled by diffusion is steadily increasing. Typically, a two-stage approach to equilibrium has been observed from batch experiments: a short initial period of fast uptake lasting from a few minutes to hours and a long period of much slower uptake lasting for days or months (Karickhoff, 1980; Ball and Roberts, 1985; Curtis et al., 1986; Wu and Gschwend, 1986). Various possible mechanisms for the nonequilibrium sorption of organic compounds have been discussed in detail by Brusseau and Rao (1989). Two different diffusion processes have been proposed as probable mechanisms for the nonequilibrium sorption of HOCs: retarded intraparticle diffusion and intraorganic matter diffusion (Brusseau and Rao, 1989; Brusseau et al., 1991; Ball and Roberts, 1991b).

Retarded intraparticle diffusion involves aqueous-phase diffusion of solute within soil micropores retarded by instantaneous sorption of solute to pore walls. The major assumptions of this model are:

- a) sorption at the sorbent-solvent interface is instantaneous and, therefore, the rate at which the solute is transported to the interface determines the

- overall rate of sorption;
- b) most soil organic matter, which controls the sorption of HOCs, reside inside the particle; and,
 - c) solute transport in the immobile region (intra-soil aggregates) occurs only by diffusion.

An alternate explanation for nonequilibrium adsorption is the diffusion of sorbate into the porous structure of sorbent organic matter. In this model, the two-stage sorption phenomenon can be explained as instantaneous sorption on the external organic matter surface during initial rapid uptake and subsequent slow diffusion into organic matter over a much longer period. Important assumptions involved in this theory are:

- a) sorbent organic matter has a porous structures within which a sorbate can diffuse; and
- b) sorption is mostly restricted to external surface site of soil.

Depending on the appropriateness of assumptions in each theory, either or both diffusion mechanisms may be responsible for nonequilibrium adsorption. Various modeling approaches using intraparticle diffusion or intrasorbent diffusion have been discussed by Brusseau and Rao (1989). Wu and Gschwend (1986) developed a spherical-aggregate model to describe intra-aggregate diffusion of solute during sorption. The local volumetric concentration of sorbed compound ($S(r)$),

expressed as a function of radial distance r from the center of the aggregate, is given by:

$$\partial S(r)/\partial t = D_{eff}[\partial^2 S(r)/\partial r^2 + (2/r)(\partial S(r)/\partial r)] \quad (2-11)$$

where D_{eff} is the effective diffusivity of sorbate molecules in cm^2/sec . D_{eff} is defined by:

$$D_{eff} = \frac{D_m n^2}{(1-n)\rho_s K_p + n} \quad (2-12)$$

where D_m is the molecular diffusivity in cm^2/sec in aqueous solution, n is the intra-aggregate porosity, and ρ_s is the dry solid density in g/cm^3 . Brusseau et al (1991) also proposed a bicontinuum model based on intrasorbent diffusion. First order mass transfer between two domains of the sorbent SOM: (1) instantaneous sorption domain, and (2) rate-limited domain, is assumed. The sorbate concentration in each domain is given by:

$$S_1 = FK_p C \quad (2-13)$$

$$dS_2/dt = k_1 S_1 - k_2 S_2 \quad (2-14)$$

where S is the sorbed phase concentration in each domain, F is the fraction of sorbent for which sorption is instantaneous,

and k_1 and k_2 are forward and reverse first-order rate constants, respectively.

From a practical point of view, appropriate estimation of diffusive resistance in the immobile phase, intra-aggregate pore or soil organic matter, for a given organic sorbate may be as important as the elucidation of the rate-limiting process. On the other hand, desorption of HOCs has not been investigated as comprehensively as their adsorption in spite of its practical importance. Since sorption is assumed to be a reversible process, desorption is often extrapolated from sorption results. However, adsorption-desorption often exhibit a hysteresis behavior and usually desorptive partition coefficients are much higher than the adsorptive counterparts (Karickhoff and Morris, 1985; Pavlostathis and Jaglal, 1991).

This may be the result from either a slow desorption of certain adsorbed fractions or irreversible sorption of certain fractions of the sorbate. Also, the hysteresis may be caused by a nonequilibrium behavior of sorption/desorption. Thus, it is necessary to distinguish between true irreversibility and the effect of desorption kinetics. Since sorption/desorption of HOCs is believed to be physically related rather than chemically, related, hysteresis may likely result from diffusion-controlled desorption (Brusseau and Rao, 1989). Considering the relatively short equilibration time (hours to days) used in desorption experiments, the higher desorptive partition coefficient might have been caused by a failure to

reach equilibrium. In such cases, hysteresis is a function of the equilibration time allowed for desorption. The occurrence of diffusion-controlled desorption of HOC and its effect on hysteresis is supported by the persistence of a contaminant residual upon consecutive reequilibration (Pavlostathis and Jaglal, 1991; Oliver, 1985).

2.2 SURFACTANT-SOIL INTERACTION

2.2.1 Surfactant Aggregate Formation

A surfactant molecule is amphiphilic, having both polar and nonpolar moieties. The polar moiety of the molecule has an affinity for water and other polar substances while the nonpolar moiety is hydrophobic. As a result of its amphiphilic nature, surfactant monomer in solution tends to be incorporated into other surfactant molecules forming a micelle, an organized chemical structure- sphere, oblate, or prolate-spheroid (Tanford, 1980). In the process of micellization, the hydrophobic surfactant moieties associate with each other and are directed inwardly, toward the center of aggregate, forming a hydrocarbon-like core, while the hydrophilic moieties are oriented toward the aqueous solvent (Bendedouch et al., 1983; Halle and Carlstrom, 1981). Thus, the core of a micelle constitutes a hydrophobic pseudophase that is distinct in its properties from the polar solvent (Hunter, 1987). Some surfactants at high concentrations can

produce bilayer aggregates, lamellae, which are much larger than micelles (Mitchell et al., 1983). Typically, micellization or lamellization begins at a critical surfactant concentration (CMC: critical micelle concentration or CAC: critical aggregate concentration), usually at about the solubility of the surfactant monomer (Rosen, 1989). If surfactant concentration is greater than the CMC or CAC, the solution is saturated with surfactant monomer and additional surfactant is incorporated into the bulk solution through micelle or lamellae formation. Therefore, when surfactant is present in bulk solution in excess of the CMC or CAC, it creates a two-phase solution consisting of a surfactant micelle or bilayer lamellae phase and a saturated surfactant monomer phase.

Since the aggregation of surfactant, whether micellization or lamellization, brings about abrupt changes in size and number of particles in solution, many physical properties of solution, most notably surface tension, undergo a sharp break near the CMC or CAC of surfactant (Rosen, 1989). The break in surface tension occurs at CMC or CAC. Surface tension of aqueous surfactant solution linearly decreases with log scale increment of surfactant monomer. At concentrations near CMC or CAC, the solution is saturated with surfactant monomer and surface tension attains a minimum value that remains constant with increasing dosage.

2.2.2 Sorption of Nonionic Surfactant in Soil-Water Systems

In systems of surfactant solution and soil, a fraction of the surfactant sorbs onto soil (Urano et al., 1984; DiToro et al., 1990). The adsorption of surfactant can be estimated for the two different components of a soil: mineral and soil organic matter. Soil mineral generally consists of silica and clay particles, which are predominantly negatively charged. Sorption of nonionic surfactants on soil minerals reportedly follows a Langmuir type (monolayer coverage) isotherm which reaches a plateau near or above CMC (Partyka et al., 1984; Rosen, 1989; Aston et al., 1989). However, Urano et al. (1984) showed that the sorption of nonionic surfactants on mineral surface of soil containing moderate amount of organic matter (more than 1%) is minor in comparison to sorption on organic matter itself. They studied the sorption behavior of two nonionic surfactants at concentrations less than CMC on soils with different f_{oc} values. It was observed that the amount of nonionic surfactant sorbed to soil at a given aqueous concentration was proportional to the f_{oc} of soil. Recently, Liu et al. (1991a) also investigated the sorption of different types of nonionic surfactants, three micelle-forming and one lamellae-forming, onto soils with f_{oc} of 1 % and 1.5 %. For both micellar and lamellar surfactants, the sorption was well characterized by the Freundlich isotherm at aqueous concentrations less than the CMC or CAC. The Freundlich isotherm takes the form;

$$q = K_F C_{aq}^{1/n} \quad (2-15)$$

where K_F is a measure of sorption capacity and $1/n$ is an indicator of sorption intensity. At surfactant concentrations greater than the CMC, different sorption behavior was observed for the two surfactant types. Micelle-forming surfactants showed maximum sorption near CMC with no increase above CMC; seemingly, micelles do not sorb well to soil. The nonadsorbance of micelles directly from bulk solution onto surfaces was also reported by Clunie et al. (1983) and Rosen (1989). By contrast, lamellar surfactant (Brij 30) showed a maximum sorption at an aqueous surfactant concentration much higher than the CMC, followed by a decrease in sorption. Such a sorption behavior is indicative of interactions between the lamellae in solution and the sorbed surfactant bilayer. The relative dominance of interlamellar attractive force over interlamellar repulsive force may be responsible for the decrease in sorption of lamellar surfactant at very high concentrations (Mitchell et al., 1983). However, information on the sorption of lamellar surfactant above CMC is too sparse to make such generalizations.

In batch experiments, the aqueous concentration of micellar surfactant can be determined from:

$$C_{aq} < \text{CMC} : \quad q = K_F C_{aq}^{1/n} \quad (2-16)$$

$$C_{aq} = C_{\text{dose}} - q w_s \quad (2-17)$$

$$\begin{aligned}
 C_{aq} > \text{CMC} : \quad C_{aq} &= C_{\text{dose}} - q_{\text{max}} w_s \\
 &= C_{\text{dose}} - K_F (\text{CMC})^{1/n} w_s
 \end{aligned}
 \tag{2-18}$$

where C_{aq} is the aqueous surfactant concentration at equilibrium with q , the surfactant equilibrium concentration sorbed on soil, C_{dose} is the solution surfactant concentration initially added to soil, q_{max} is the maximum sorption density of surfactant, and w_s is the concentration of soil. Sorption of nonionic surfactants onto soil may produce two significant effects on the efficiency of surfactant-enhanced solubilization of PAHs. (1) Surfactant sorption may increase the f_{oc} of soil, resulting in the modification of sorptive characteristics of PAHs. In soil/water systems with surfactant present, the f_{oc} of soil should be corrected for sorbed surfactant:

$$f'_{oc} = f_{oc} + (f_{oc,s} q) \tag{2-19}$$

where $f_{oc,s}$ is the fractional organic carbon content of surfactant. (2) Surfactant sorption may also reduce the amount of available surfactant in bulk solution, thus much greater amount of surfactant may be required to attain CMC. The increased CMC dosage or 'effective CMC' of surfactant in soil/water systems can be calculated from:

$$CMC' = CMC + qW_s \quad (2-20)$$

For micellar surfactants, q is a constant and represents the solid-phase concentration (q_{CMC}) at equilibrium with CMC. The concentration of surfactant micelle, C_M , in the bulk solution can be determined from:

$$C_M = C_{dose} - CMC - q_{CMC}W_s \quad (2-21)$$

2.3 Mobilization of Soil-Bound PAH

2.3.1 Solubilization of PAHs

The solubility of hydrophobic organic compounds in nonionic surfactant solutions having concentrations greater than the CMC was found to be orders of magnitude greater than their corresponding aqueous solubilities (Edwards et al., 1991b; Kile and Chiou, 1989). A typical plot of solubility of phenanthrene against surfactant concentration is shown in Fig. 2.2; solubility is relatively constant until the CMC is reached beyond which it increases approximately linearly with surfactant concentration. The slope of the curve represents the number of moles of phenanthrene solubilized per mole of surfactant added to solution and is defined as the molar solubilization ratio (MSR) (Atwood and Florence, 1983). That the solubility increases only at surfactant concentration greater than CMC indicates that solubilization is directly

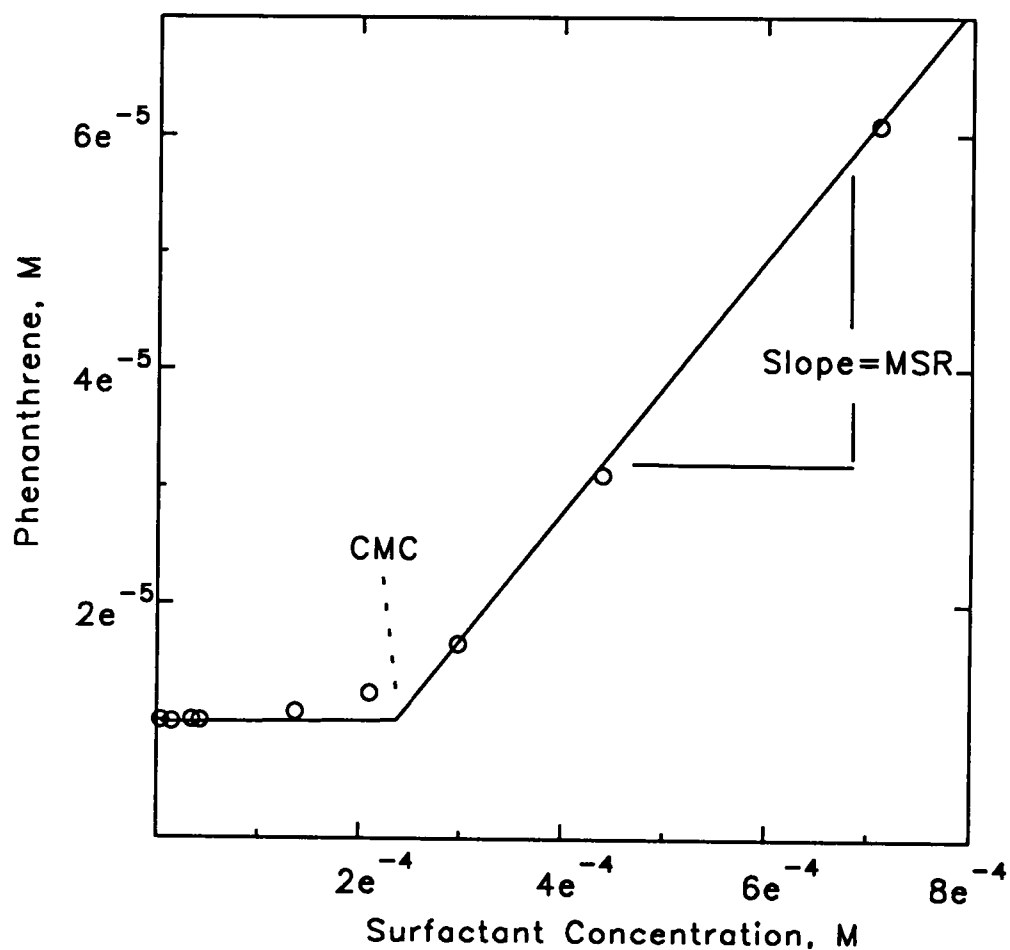


Figure 2.2 Solubilization of phenanthrene by a nonionic surfactant, $C_{12}PE_{12}$ (Igepal CA-720) The slope of the post-CMC relationship is equal to the molar solubilization ratio (Source: Edwards et al., 1991)

related to micelle formation. Although in some cases a small increase in PAH solubility was reported at sub-CMC surfactant dosage (Aronstein et al., 1991), enhancement of solubilization by monomeric surfactant seems to be negligible in comparison to that by surfactant micelles (Jafvert, 1991b; Edwards et al., 1991a, 1991b). The extent of solubilization has been reported to be dependent on a number of factors. If the mechanism of solubilization of HOCs by surfactant involves their partitioning into the hydrophobic core of micelles, the amount of material solubilized may depend on the relative size of micelle and solubilize. The solubilization efficiency may increase as the size of micelle or aggregation number increases and/or the size of solubilize decreases (Rosen, 1989). The polarity of the solubilize may affect the degree of solubilization; for PAHs, the more hydrophobic the compound, the greater the solubility enhancement (higher K_m) (Edwards et al., 1991a). The solubilizing power of surfactants was also reported to depend on surfactant structure, micelle geometry, ionic strength, and temperature (Rosen, 1989). In general, because of their lower CMC values, nonionic surfactants are known to be better solubilizing agents than ionic surfactants in dilute solutions (Saito, 1967; Tokiwa, 1968). Liu et al. (1991b) compared the effectiveness of several nonionic and anionic surfactants in solubilizing PAHs in soil-water suspensions. It was found that the most effective surfactants were nonionic octyl- and

nonyl- phenylethoxylates with 9 to 12 ethoxylate units. Reportedly, the rate of solubilization is directly proportional to the surfactant concentration above the CMC and increases with polarity and decreases with molecular weight of the solubilize (Carroll, 1981).

The solubilizing efficiency of surfactant can be quantified by employing either of two parameters, the molar solubilization ratio (MSR) and micelle/aqueous-pseudophase partitioning coefficient (K_m). Both parameters have been found to have constant values over a wide range of surfactant concentrations in the presence of a separate HOC-phase. The MSR represents the solubilizing efficiency of a surfactant (Atwood and Florence, 1983). In the presence of excess HOC (crystalline), the MSR can be calculated as follows:

$$MSR = (S_{mic} - S_{cmc}) / (C_{surf} - CMC) \quad (2-22)$$

where S_{mic} is the total apparent solubility of HOC in moles per liter at a particular surfactant concentration greater than CMC, S_{cmc} is the apparent solubility of the HOC at the CMC, and C_{surf} is the surfactant concentration at which $S_{HOC,mic}$ is evaluated. Since MSR, by definition, assumes the aqueous pseudophase to be saturated with HOC, it is constant only when a separate HOC-phase is present. Hence, in systems not in contact with a separate phase of HOC, the use of MSR may be inappropriate. An alternate way to quantify the solubility

enhancement of HOCs is to use a molar partitioning coefficient, K_m , to characterize the partitioning of an organic compound between micelles and aqueous pseudophase; it is defined as (Hayase and Hayano, 1977):

$$K_m = X_m/X_a \quad (2-23)$$

where X_m is the mole fraction of the compound in the micellar pseudophase and X_a is the mole fraction of the compound in the aqueous pseudophase. In the presence of a solid HOC phase, K_m can be calculated from experimental measurements using the following equations:

$$X_m = (S_{mic} - S_{cmc}) / (S_{mic} - S_{cmc} + C_{surf} - CMC) \quad (2-24)$$

$$X_a = S_{cmc} V_w \quad (2-25)$$

$$K_m = (S_{mic} - S_{cmc}) / \{ (S_{mic} - S_{cmc} + C_{surf} - CMC) (S_{cmc} V_w) \} \quad (2-26)$$

where V_w denotes the molar volume of water, 0.0185 L/mole at 25°C, and S denotes the solubility of HOC at various surfactant concentrations, as defined by the suffixes. From Eqs. 2-22 and 2-24, X_m can be expressed in terms of MSR:

$$X_m = MSR / (MSR + 1) \quad (2-27)$$

and, correspondingly, K_m is expressed as (Edwards et al., 1991a):

$$K_m = \text{MSR} / [(\text{MSR}+1) (S_{\text{cmc}} V_w)] \quad (2-28)$$

In contrast to MSR, the value of K_m is not affected by the presence of pure HOC-phase. Thermodynamically, it represents the equilibrium partitioning between two pseudophases, in which there is a fixed ratio between the concentrations of each phase. In this respect, K_m is analogous to K_{ow} , the octanol-water partitioning coefficient. In fact, Valsaraj and Thibodeaux (1989) demonstrated a linear relationship between $\log K_m$ and $\log K_{ow}$ for various HOCs in micellar sodium dodecylsulfate. The relationship takes the form:

$$\log K_m = \alpha \log K_{ow} + \beta \quad (2-29)$$

The correlation constants α and β depend on the type of surfactant (Valsaraj and Thibodeaux, 1990) and also on the unit of the partitioning coefficient. For PAHs, the value of α was reported to be close to unity for an anionic surfactant (sodium dodecylsulfate) and less than unity (0.8 to 0.9) for nonionic surfactants (alkylphenol polyoxy-ethylenes) (Jafvert, 1991b; Edwards et al., 1991a).

In Table 2.1, the MSR, K_m and K_{ow} values for naphthalene,

phenanthrene and pyrene in the presence of two nonionic surfactants, an alkyl polyoxyethylene (Brij 30) and an alkylphenol polyoxyethylene (Igepal CA-720), are listed.

Table 2.1. Partitioning characteristics of selected PAH-surfactant systems.

PAH compound	Surfactant	Notation	MSR ^a	LogK _m ^a	LogK _{ow} ^b
naphthalene	Brij 30	C ₁₂ E ₄	3.17×10 ⁻¹	4.59	3.36
naphthalene	Igepal CA-720	C ₈ PE ₁₂	3.23×10 ⁻¹	4.63	3.36
phenanthrene	Brij 30	C ₁₂ E ₄	1.52×10 ⁻¹	5.57	4.57
phenanthrene	Igepal CA-720	C ₈ PE ₁₂	1.04×10 ⁻¹	5.68	4.57
pyrene	Brij 30	C ₁₂ E ₄	7.15×10 ⁻²	6.53	5.18
pyrene	Igepal CA-720	C ₈ PE ₁₂	4.25×10 ⁻²	6.01	5.18

^a From Edwards et al. (1991b)

^b From Karickhoff et al. (1979)

2.3.2 Mobilization of PAHs in Soil-Water System

Recently, surfactants were used for removing hydrophobic organic contaminants such as anthracene (Vigon and Rubin, 1989), PCBs (McDermont et al., 1989), and DDT and trichlorobenzene (Kile and Chiou, 1989) from soil. In batch tests, up to 80 % of pyrene and anthracene could be recovered from a soil having $f_{oc}=0.96\%$ using nonionic surfactants of ethoxylated alcohols (Liu et al., 1991b). Anionic surfactant dodecylsulfate (DS) also showed a similar efficiency in mobilizing phenanthrene and pyrene from soils with f_{oc} ranging 0.95 to 1.7 % (Jafvert, 1991b). In both cases, no substantial

enhancement of desorption was observed until the aqueous surfactant concentration was close to CMC at which desorption abruptly increased, slowly approaching a maxima at very high surfactant concentrations. These observations are consistent with the proposed mechanism for surfactant solubilization of HOCs. In soil-water systems, HOC is distributed between the soil and aqueous phases. When surfactant is introduced at solution concentrations greater than the CMC, a micellar phase is created. The ability of micelle to incorporate HOC in aqueous pseudophase makes the system unstable and causes a concentration gradient between phases. Consequently, a transport of HOC from soil phase to the aqueous pseudophase, finally to micellar phase, occurs until a new equilibrium is reached. The efficiency of a surfactant in mobilizing HOC from soil depends on its CMC, the extent of its sorption to soil, and its solubilization efficiency. The first two factors determine the amount of micelles available for solubilization at a given dosage while the third represents the amount of HOC accommodated in a unit amount of micelle. For a given soil-HOC system, these factors are surfactant-specific. Recently, Abdul and Gibson (1990) compared the effectiveness of ten surfactants in washing oil from a sandy aquifer material. The commercial surfactants tested included four main groups: (1) ethoxylated alcohols (nonionic), (2) ethoxylated nonylphenols (nonionic), (3) sulfates (anionic), (4) sulfonated (anionic). Alcohol ethoxylates were found to

be most efficient in solubilization and dispersion of oils with low aqueous solubilities. Liu et al. (1991b) also found alcohol ethoxylates to be most effective in mobilizing soil-bound PAHs. Seemingly, the relatively low CMC values and non-reactivity with inorganic salts in aqueous or in mineral medium, partly contribute to the high performance of alcohol ethoxylates (Rosen, 1989). In addition, they are preferred to other surfactants for *in-situ* washing of contaminated soils since they cause minimum dispersion of soil colloids (Abdul and Gibson, 1991).

Quantitative models of surfactant-enhanced mobilization of HOCs from soil have been developed by combining two linear partitioning models: sorption/desorption of HOC between soil and aqueous phase, and HOC distribution in bulk solution between aqueous pseudophase and micellar phase. The primary assumptions in these models are: (1) complete reversibility of partitioning of contaminant between three different phases - soil, monomeric surfactant solution, and micelle, and (2) relatively fast attainment of equilibrium. Edwards et al. (1991b) developed a mathematical model to determine the equilibrium distribution of PAH between different phases: sorbed phase, aqueous pseudophase, and micellar phase. The amount of PAH in each phase at equilibrium was calculated using partitioning coefficients between phases and mass balance equations. Similarly, Jafvert (1991b) proposed more simplified equation for the distribution coefficient (K_d) of

PAH between soil and bulk solution. Using two experimental correlations: $K_{oc} = 0.48K_{ow}$ and $K_m = 0.15K_{ow}$, K_d was given by:

$$K_d = 0.48K_{ow}f_{oc}/[1.0 + 0.15K_{ow}(C_M)] \quad (2-30)$$

where K_d is directly proportional to f_{oc} of soil and inversely to aqueous concentration of surfactant micelle (C_M). As discussed earlier, characterization of partitioning between phases with simple partition coefficients is essential in modeling subsurface contaminant transport mediated by micellar surfactants. However, the assumption of relatively fast attainment of sorption equilibrium and its reversibility may be inappropriate. While the equilibrium partitioning of PAH between aqueous pseudophase and micellar phase is believed to be attained within a day (Jafvert, 1991a; Edwards et al., 1991a), the sorption and desorption of PAH appear to be long-term processes controlled by diffusion. Considering the fact that actual contaminated sites may have been exposed to contaminants for a few months to many years, the effect of sorption nonequilibrium on surfactant-enhanced desorption may be significant. Currently, no information, however, is available on such effects.

2.3.3 Equilibrium Model

When surfactant solution is applied to PAH-contaminated soil, a mass balance of PAH yields:

$$n_{aq} + n_{sorb} + n_{mic} = n_{sorb,init} \quad (2-31)$$

where n_{aq} is the number of moles of PAH in the aqueous pseudophase, n_{sorb} in the sorbed phase, n_{mic} in the micellar phase, and $n_{sorb,init}$ represents the number of moles of PAH initially sorbed onto the soil before the addition of surfactant solution. The term on the right hand side can be expressed as a function of surfactant dose and PAH concentration in aqueous pseudophase (Edwards et al., 1991b). For a soil pre-contaminated with PAH, $n_{sorb,init}$ can be determined using the following equation:

$$n_{sorb,init} = K_d C_{aq,init} W_{soil} V_a \quad (2-32)$$

By incorporating the expression for the amount of PAH in each phase into the mass balance equation (2-30), the PAH concentration in aqueous pseudophase, C_{aq} , for a given surfactant dose can be calculated by the following expression:

$$C_{aq} = [-b + (b^2 - 4ac)^{0.5}] / (2a) \quad (2-33)$$

where $a = (K_{p,cmc} W_s) (1 - K_m V_w)$

$$b = (K_m V_w) (C_{dose} + K_p C_{init} W_s - (CMC) - q_{cmc} W_s)$$

$$c = -K_p C_{init} W_s$$

$K_{d,cmc}$ denotes soil-water partitioning coefficient of PAH

between soil and monomeric surfactant solution (CMC) and C_{aq} is PAH concentration in aqueous phase at equilibrium in g/mL. From the C_{aq} value, the distribution of PAH between phases can be calculated and the percent desorption of soil-bound PAH obtained by:

$$E(\%) = 100 \times (n_{sorb,init} - n_{sorb}) / n_{sorb,init} \quad (2-34)$$

CHAPTER 3. METHODS AND MATERIALS

3. 1 MATERIALS

3.1.1 Soil

One constructed and three natural soils were used in this study. To understand the mechanism(s) of PAH desorption from contaminated soil, hematite coated with humic acid was chosen as the sorbent at the beginning of this study; the physical and chemical characteristics of this adsorbent were completely defined using standard analytical techniques. However, in the later part of this study, natural soils were used to obtain a more realistic estimate of the effectiveness of commercial surfactants in mobilizing PAHs.

3.1.1.1 Constructed soil - Hematite

Hematite was synthesized from 0.17 M reagent grade FeCl_3 solution adjusted to pH 12 with CO_2 -free water (Murphy et al., 1990). The precipitate was dialyzed in dialysis membrane (MWCO= 6,000) against deionized water until the external solution maintained a relatively constant conductivity. The resulting goethite was freeze-dried and converted to hematite by heating at 700°C. Synthesized hematite was pulverized and sieved through U.S.S. #100 (149 μm); it was then equilibrated for 24 hours with various amounts of humic acid (Aldrich Chemical Co.) containing 38% by weight of total carbon

($f_{c,Hu}=0.38$) to obtain a coating of organic carbon. Soil thus constructed was repeatedly washed with 0.1 M NaClO_4 solution until the TOC of the supernatant was below 1 mg/L. Humic acid-coated hematite with values of f_{oc} in the range of 0.0008% to 0.45% were prepared; the f_{oc} values were computed from:

$$f_{oc} = (f_{c,Hu}) \{ [\text{Hu}]_{\text{added}} - [\text{Hu}]_{\text{aq}} - \sum [\text{Hu}]_{\text{washed}} \} / w_s \quad (3.1)$$

where $f_{c,Hu}$ = fraction carbon of humic acid = 0.38

w_s = concentration of soil mineral (g/L)

$[\text{Hu}]$ = concentration of humic acid (g/L)

3.1.1.2 Natural Soil

Three natural soils, Etowah, Lexington I and Lexington II, with soil organic carbon contents (f_{oc}) of respectively, 1.7, 0.9, and 3.4%, were used. The chemical characteristics of the soils were obtained from the Soil & Plant Science Department at the University of Tennessee and are summarized in Table 3.1. After air-drying, the soils were pulverized and sieved through U.S.S. #100 (149 μm).

3.1.1.3 Characterization of Soils

Characterization of hematite: The OH-site density, intrinsic acidity constants, and pH_{zpc} of the mineral were obtained using well established pH-stat titration techniques (Ghosh and Yuan, 1987). Two grams per liter of hematite suspension at

different ionic strengths (0.001 - 0.1 M) were titrated with varying amounts of 0.1 M HCl and NaOH under nitrogen gas atmosphere using a Metrohm Titroprocessor (Metrohm Co., CH-9101 Herisau, Switzerland).

Table 3.1 Summary of natural soil characteristics

	Etowah	Lexington I	Lexington II
Sand*	26.5%	7.8%	8.2%
Silt*	40.5%	81.1%	82.1%
Clay*	33.0%	10.1%	9.7%
Organic carbon content (f_{oc})	1.682%	0.903%	3.40%
Surface area (m^2/g)	78	147	141
Geom Mean Dia (μm)	37.4	29.0	29.6

* Percent constituents were estimated from the particle size distribution of the soils : sand ($50\mu-2mm$); silt ($2\mu-5\mu$); clay ($<2\mu$).

Surface area analysis: Surface areas of hematite and natural soils were measured using a surface area analyzer (Micromeritics Model ASAP 2000). One gram of each soil was added into a tared glass tube and degassed at $350^\circ C$; the tube was reweighed and the exact weight of degassed soil determined. The surface area of soil was then measured using

5-point BET adsorption isotherm of N_2 . To avoid any uncertainty caused by the presence of soil organic matter (SOM) (Pennel and Rao, 1992), the organic matter of natural soils was completely removed by using standard methods (ASA, 1965) prior to surface area measurements.

3.1.2 Surfactants

One alkylphenol ethoxylate, Igepal CA-720, and one alkylethoxylate, Brij-30, were obtained from Aldrich Chemical Co. and used as received from the supplier without further purification. Both of these surfactants are nonionic but form different types of aggregates; at high concentrations the former produces micelle while the latter lamellae. Reportedly, these nonionic surfactants have a relatively strong ability for solubilizing PAHs (Liu et al., 1991b). The characteristics of test nonionic surfactants are given in Table 3.2.

Table 3.2 Characteristics of test nonionic surfactants

Surfactant	Average Molecular Formula	Symbol	Average Molecular Weight (g/mole)
Igepal CA-720	$C_8H_{17}-C_6H_4-O(CH_2CH_2O)_{12}H$	$C_8PE_{12}^a$	735
Brij-30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	$C_{12}E_4^a$	363

^a P denotes phenyl group ($-C_6H_4-$) and E denotes ethoxylate group ($-CH_2CH_2O$).

3.1.3 Polycyclic Aromatic Hydrocarbon (PAH)

Two PAHs, naphthalene and phenanthrene (Sigma Chemical Co.) were used as sorbates throughout this research. ^{14}C -labeled naphthalene and phenanthrene were obtained from Sigma Chemical Co. and used as received from the supplier without further purification. Each radiolabeled PAH was supplied as a solid and dissolved into 20 mL of methanol in a 25-mL vial wrapped with aluminum foil. These radiolabeled PAH stock solutions were stored in a refrigerator at 4°C. The properties of naphthalene and phenanthrene are given in Table 3.3.

Table 3.3 Chemical characteristics of test PAHs (25°C)

	Naphthalene	Phenanthrene
Molecular weight	128	178
Aqueous Solubility (mg/L)	34.4	1.3
Specific activity (mCi/mmol)	10.3	13.1
Vapor pressure (mm Hg, 0°C)	0.005	6.8×10^{-4}
$\log K_{ow}$	3.6	4.46
K_{oc}	1300	2.3×10^4

3.2 EXPERIMENTAL METHODS

3.2.1 Surfactant Sorption Studies

Two different measurements were made to determine the extent of surfactant sorption in a soil/water system : surface tension, and total organic carbon (TOC). The first measurement is suitable for aqueous phase surfactant concentrations less than the critical micelle or aggregate concentration (CMC or CAC), while the second is appropriate for surfactant concentration greater than the CMC or CAC.

3.2.1.1 Surface Tension Measurement

a) Aqueous solution of surfactant: All glassware used in surface tension measurements were cleaned with chromic acid and rinsed three times with hot tap water and two times with deionized (DI) water, then oven-dried at 103°C before use. Surfactant solutions of varying concentrations, 10^{-6} to 10^{-2} M, were prepared in DI water. Twenty five milliliters of each solution were placed in a prewashed 100-mL beaker, then the surface tension was measured at $25 \pm 1^\circ\text{C}$ by a Tensiomat (Model 21, Fisher Co.). Prior to the measurement, 3-point calibration of the tensiomet was performed by adjusting the arm length of the torsion balance. After calibration, the clean platinum-iridium ring of the tensiomet was suspended in the solution from a torsion balance and the force (dynes/cm), required to pull the ring free from the solution was measured. The

measurement was repeated several times till a constant value was obtained. The ring was cleaned between measurements with acetone followed by heating of the ring until it glowed red in a gas flame. The measured surface tension values were then plotted against the logarithm of surfactant concentration (mol/L); CMC or CAC was determined as the concentration beyond which surface tension remained constant.

b) Soil/water solutions of surfactants: Batch soil slurries were prepared in 25-mL Corning round bottom glass centrifuge tubes. Each tube had 2 g soil, and 25 mLs of surfactant solution varying in concentration from 10^{-6} to 10^{-2} M. Five milligrams of mercuric chloride were also added to the tubes to prevent any bacterial growth during the adsorption experiment. The tube was sealed with Teflon-lined septa and screw cap. Having been mixed for a few seconds in a vortex mixer, the suspensions were transferred to an end-over-end rotary mixer (Wheaton Co.) and shaken at 22 rpm for 24 hours to attain adsorption equilibrium (Liu et al., 1991b). Then, the suspensions were centrifuged for 40 minutes at $5000\times g$ and the supernatant carefully decanted into 100-mL beaker. The surface tension of each aqueous solution was measured and plotted against the logarithm of initial surfactant dosage (mol/L). All samples were analyzed in duplicate and average values reported.

3.2.1.2 Total Organic Carbon Analysis

The total organic carbon (TOC) content of surfactant solution was measured over a concentration range of 10^{-4} to 10^{-2} M using a TOC analyzer (Dohrman Model DC-80). The measured TOC values were plotted against corresponding surfactant concentrations to obtain the calibration curve shown in Fig. 3.1. Since the test surfactant solution is homogeneous, the TOC of a surfactant is linearly proportional to its concentration. The slope of this calibration curve represents the mass of organic carbon per mole of surfactant. This ratio was used to convert the measured TOC (mg/L) value of a surfactant solution to its molar concentration.

$$C_{\text{surf}} \text{ (mol/L)} = \text{TOC (mg/L)} \times \frac{1}{R \text{ (mg TOC/mol surfactant)}} \quad (3.2)$$

where C_{surf} is the aqueous concentration of a surfactant and R is the conversion factor obtained from the calibration curve. The soil suspensions, equilibrated with surfactant solutions, were centrifuged and the TOC of the supernatant measured; the surfactant concentration in the bulk supernatant was determined using Eq. 3.2. With high surfactant doses ($>10^{-2}$ M), the supernatants were appropriately diluted to obtain values within the detection limit of the TOC analyzer (4000 mg/L or less). Blank solutions comprising of soil/water suspensions only (no surfactants) were used to correct

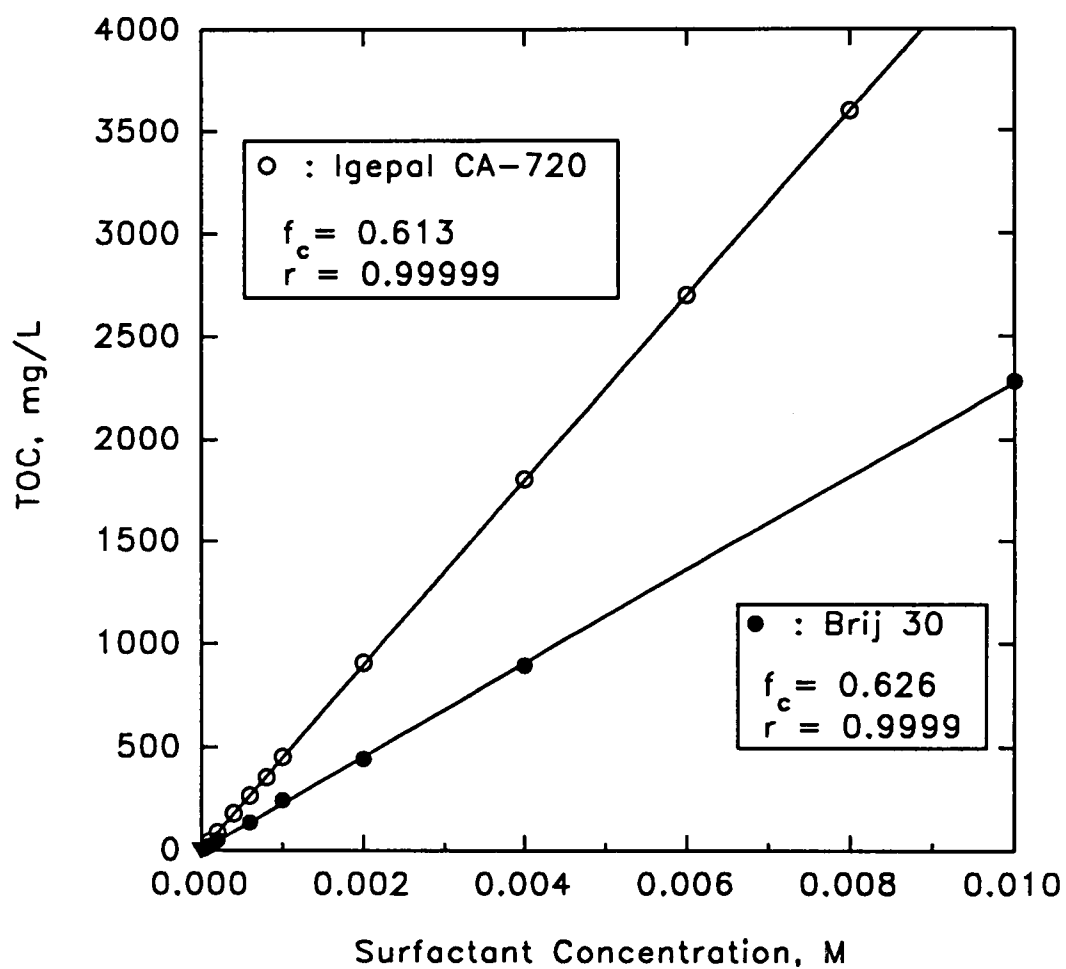


Figure 3.1 Calibration curve showing total organic carbon (TOC) as a function of the bulk solution nonionic surfactant concentration: Brij 30 and Igepal CA-720

measured TOC values for dissolved organic carbon released from soil.

3.2.2 PAH Adsorption on Soil

3.2.2.1 PAH Sorption Isotherm

A PAH stock solution consisting of a predetermined mass ratio of radiolabeled to non-labeled PAH was prepared and sterilized as described in Appendix I. The activity of the stock solution was determined before the experiments were conducted, by counting the decay rate in the solution using a Beckman LS 500 TD liquid scintillation counter (LSC). One milliliter of the stock solution was taken into a 20-mL scintillation vial containing 10 mL of Beckman Ready Safe scintillation cocktail and hand-mixed vigorously for a few seconds. For the first few hours after the sample was prepared in a scintillation vial, the measured activity showed a significant fluctuation. Therefore, samples were stored overnight prior to activity analysis to obtain reliable values. The decay per minute (DPM) was counted using H-number quench and compensation technique. Also, the background DPM rate was measured for the scintillation cocktail alone; the average background decay rate (≈ 40) was subtracted from the measured DPM. To eliminate any artifact caused by biodegradation of PAH during the long equilibration period, the soils and tubes were sterilized before sorption tests.

Twenty five-mL glass centrifuge tubes containing 2 g of soil were autoclaved for 40 minutes at 121°C. Sterilization of soil by autoclaving was preferred to adding an inhibitor to the solution. Reportedly, autoclaving does not affect the sorption behavior of hydrophobic organic compounds (Ball, 1989). Twenty five milliliters of stock PAH solution of varying concentrations were then added to the tubes containing autoclaved soil. The tubes were capped with screw caps lined with Teflon septa and aluminum foil. The contents were mixed in a vortex mixer for a few seconds, then the tubes were mounted on an end-over-end rotary mixer and equilibrated for 8 days at room temperature. Mixing of the tubes was performed at 22 rpm continuously for the first day, then for 30 minutes every 4 hours for the rest of the experiment. Previous studies showed that more than 95% of equilibrium sorption capacity of soil was attained in 8 days under similar mixing conditions. The equilibrated suspensions were centrifuged at 5000×g for 40 minutes. One milliliter aliquots of supernatant were taken and analyzed for activity with at least 95% confidence level and the result corrected for background decay. The corrected DPM values were converted to PAH concentration using the specific activity of radiolabeled PAH compound and the mass ratio of radiolabeled to non-labeled PAH. The amount of PAH sorbed per unit weight of soil, q ($\mu\text{g/g}$), was determined from the difference in DPM values of the aqueous phase before and after sorption:

$$q = [DPM_o - DPM_e] [1 / (A_{sp} \Phi)] [M_w] / [w_s] \quad (3.3)$$

where DPM_o is the activity per mL added initially, DPM_e is the activity remaining per mL of supernatant after equilibration, A_{sp} is the specific activity of a radiolabeled PAH (mCi/mmol), Φ is the conversion factor (2.22×10^6 DPM/ μ Ci), M_w is the gram molecular weight of PAH and w_s is the concentration of soil (g/mL). Background activity (≈ 40 DPM) was subtracted from each measured activity. To minimize vaporization loss of PAH, the head space of sample tube was maintained at 2 to 3 cm³, less than 12% of the volume of the tube. The adsorption of PAH on the cap lining was tested using a Teflon-lined cap, and an aluminum-lined cap. Significant sorption of PAH compounds on Teflon material was observed, specially for phenanthrene. Aluminum foil did not show a significant sorption of either naphthalene or phenanthrene and was, therefore, employed in this study. The integrity of sealing was checked by immersing empty tubes sealed the same way, into a water bath at 50°C for 10 minutes. The theoretically calculated gas pressure was 10.4 KPa and, under this pressure difference, no air bubble was observed. To further ensure that there is no significant sample loss during mixing, tubes containing PAH stock solution and no soil were mixed in a rotary shaker for one month; no significant decrease in solution activity ($< 0.1\%$) was observed. The loss of PAH due to head space

partitioning, leaking, or other source was carefully investigated: it was found to be insignificant under the experimental conditions used (Appendix II).

3.2.2.2 The Kinetics of PAH sorption

The kinetics of adsorption of phenanthrene on three different soils (Etowah, Lexington I, II) was monitored over a time period of minutes to 22 days. Sample tubes, each containing 2 g soil were autoclaved and 25 mL of phenanthrene stock solution was added to each. Following vortex mixing for a few seconds, the tubes were mounted on a rotator and equilibrated for varying periods of time. Solid-liquid separation was obtained by both centrifugation and filtration and the supernatant or filtrate analyzed for activity. It should be noted that solid-liquid separation by centrifugation may not be appropriate for kinetic experiments. Since the initial sorption rate was fast while it took a relatively long time (40 min) to separate solids by centrifugation, estimates of such rates during the first 8 hr of sorption might well have been in error if samples were centrifuged without quenching the reaction. Therefore, an attempt was made to use filtration, instead of centrifugation, to obtain a faster separation of solids in the initial samples. However, the use of filtration is often limited by the sorption of PAHs on filter paper. Reportedly, silver filter (0.45 μ m Millipore Co.) and binder-free glass fiber filter (0.45 μ m Gelman Co.,

Type A/E) do not significantly bind hydrophobic organic compounds such as tetrachlorobenzene (TeCB) and tetrachloroethene (PCE) (Ball, 1989). To estimate the degree of PAH-binding, naphthalene and phenanthrene stock solutions were filtered through both filter media supported in a stainless steel holder with 2.5-mL glass syringe. Glass fiber filter exhibited 5% and 15% loss for naphthalene and phenanthrene, respectively. With repeated filtration (5-6 times) with saturated PAH solution, the loss was reduced below 1% for naphthalene; but, it was still significant for phenanthrene (> 5%). The silver filter, however, showed no significant sorption (< 1%) of either PAH compound even without any pretreatment of the filter medium. Thus, samples obtained during the first 24 hours of a kinetic experiments, solid separation was accomplished by filtration using silver filters; centrifugation was used for all samples collected beyond one day.

3.2.3 Desorption of PAHs

3.2.3.1 Surfactant-Enhanced Desorption

Batch desorption experiments were conducted to evaluate the efficiency of surfactants in mobilizing soil-bound PAH. Soils were precontaminated with saturated PAH solutions for different periods of time. Two grams of soil were placed in centrifuge tubes containing 25 mL PAH stock solution and the

suspensions equilibrated for 1 day, 8 days, and 22 days, using the procedure described in section 3.2.2.2. Following equilibration, the suspension was centrifuged for 40 minutes at 5000xg and the activity in the supernatant measured. The amount of PAH sorbed on soil, q ($\mu\text{g/g}$), was determined by Eq. 3.3. The suspension was centrifuged again and the supernatant decanted carefully. The last traces of the solution, 0.75 to 1.5 mL (3 to 6% of the original 25 mL aliquot of PAH solution) remained associated with soil and could not be recovered. Lest PAH is lost due to volatilization, "contaminated" soil samples were not air-dried. In desorption studies, each "contaminated" soil sample was spiked with 25 mL of the test surfactant solution (10^{-3} to 10^{-1} M) and mixed for 24 hours on a rotary shaker. The suspension was then centrifuged and the concentration of PAH in solution determined by LSC. This was used to calculate the amount of PAH desorbed by the surfactant. Conceivably, these estimates were somewhat higher than actual due to the traces of PAH solution that remained associated with soil and could not be recovered at the end of the sorption phase. However, the results were corrected for this component as shown in Appendix III. Percent desorption of PAH was calculated from:

$$\% \text{ Desorption} = \frac{100 \times \{ [\text{DPM}]_{\text{added}} - [\text{DPM}]_{\text{aq, ads}} - [\text{DPM}]'_{\text{surf}} \}}{\{ [\text{DPM}]_{\text{added}} - [\text{DPM}]_{\text{aq, ads}} \}} \quad (3.4)$$

where $[DPM]_{\text{added}}$ = activity of the PAH solution added to soil

$[DPM]_{\text{aq,ads}}$ = activity of the solution after a specific sorption time

$[DPM]'_{\text{surf}}$ = corrected activity of the surfactant solution after desorption

In determining the kinetics of desorption for soils contaminated for 22 days, each 2 g sample of "contaminated" soil was spiked with 25 mL of a stronger surfactant solution (3×10^{-3} M) and equilibrated for different time periods up to a month.

CHAPTER 4. RESULTS AND DISCUSSION

4.1 ADSORPTION STUDIES WITH HEMATITE

4.1.1 Characteristics of Hematite

The surface charge distribution of hematite in solutions of varying ionic strengths were obtained from pH-stat titrations while surface area was determined from nitrogen sorption per BET isotherm as discussed in chapter 3; the results are summarized in Table 4.1.

Table 4.1 Surface characteristics of hematite

pH _{zpc}	pK ₁ ^{int}	pK ₂ ^{int}	OH-site	Surface
			(mmol/g)	area (m ² /g)
8.3	6.8	9.7	9.84×10 ⁻⁵	10.4

4.1.2 Adsorption of Humic Acid on Hematite

The sorption of Aldrich humic acid (AHA) on hematite at varying initial pHs is shown in Fig. 4.1. Reportedly, the kinetics of sorption of humic material on minerals depends strongly on pH (Kummert and Stumm, 1980; Tipping, 1981, 1982). Although no attempt was made to keep pH constant in the

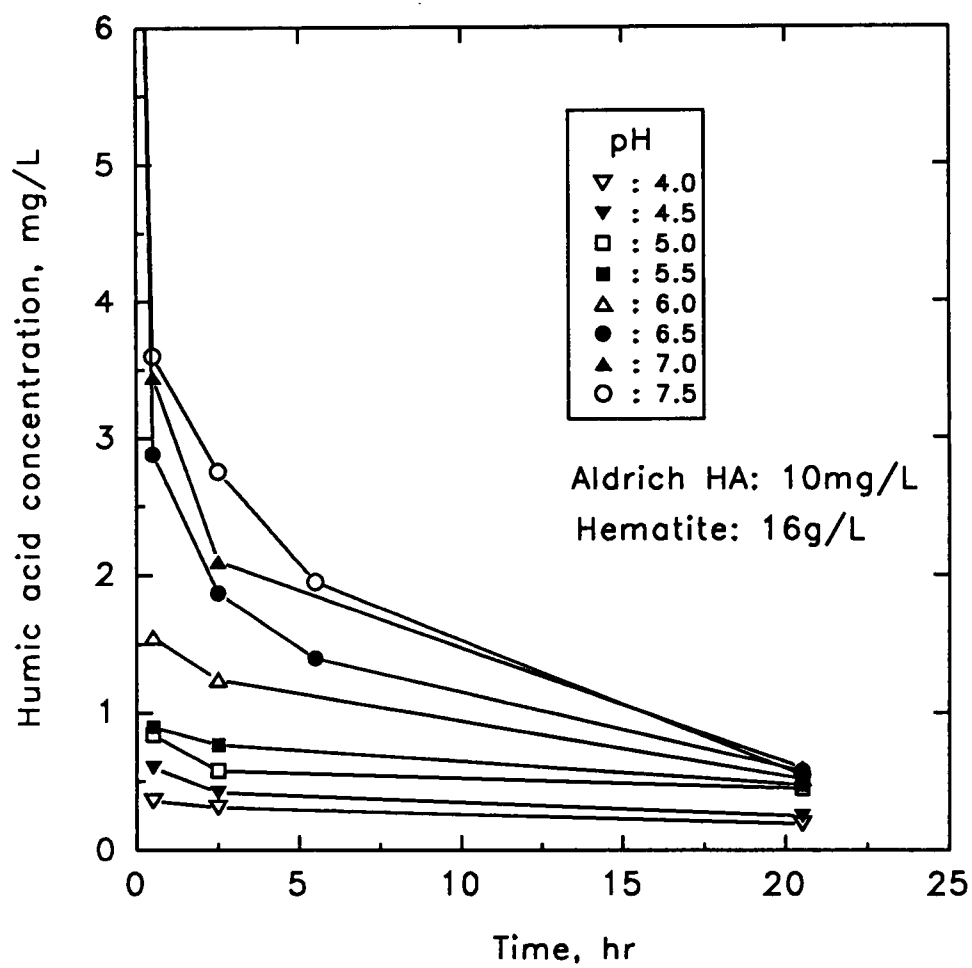


Figure 4.1 Kinetics of Aldrich humic acid adsorption on hematite

present study - only initial suspension pHs are shown in Fig. 4.1 - adsorption exhibited a weak minima at a pH of about 6.5 during the early period of adsorption (less than 5 hours). As adsorption occurs, the pH approached a uniform value, about 4.5, independent of the initial pH. Within 30 minutes, 65 to 90 percent of AHA adsorbed, the rate being inversely related to pH; at pH of 4.5, more than 98 percent adsorbed within 20 hours with no substantial increase thereafter (2-3 days). Therefore, in all subsequent experiments, the initial pH of AHA solution was adjusted to 4.5 before contacting the hematite and the suspension equilibrated for 20 hours. The adsorption isotherm of AHA on hematite in a 0.1 M ionic strength suspension is shown in Figs. 4.2. and 4.3. The isotherm displays two different sorption behaviors depending on the equilibrium concentration of humic acid in solution. At low concentrations, AHA had a high affinity for the iron-hydroxyl groups on hematite, well characterized by the Langmuir isotherm (inset of Fig. 4.2). After the rapid attainment of maxima ($57 \mu\text{g}/\text{m}^2$), sorption increased linearly with concentration. Similar results for the adsorption of humic substances on mineral surfaces were reported by others (Tipping, 1981; Murphy et al., 1990). This may be due to the hydrophobic humic-humic interaction resulting in multilayer sorption (Murphy et al., 1990).

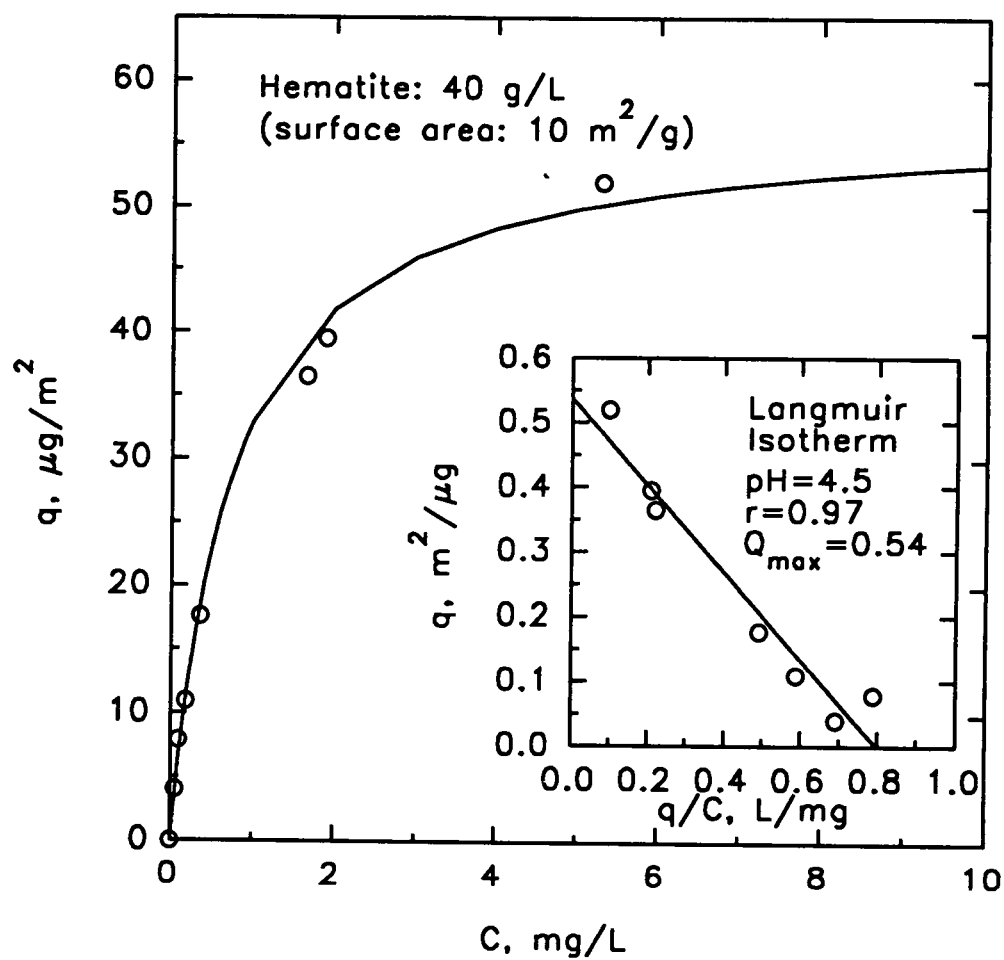


Figure 4.2 Adsorption isotherm of Aldrich humic acid-hematite system (concentration range: 0-20 mg/L)

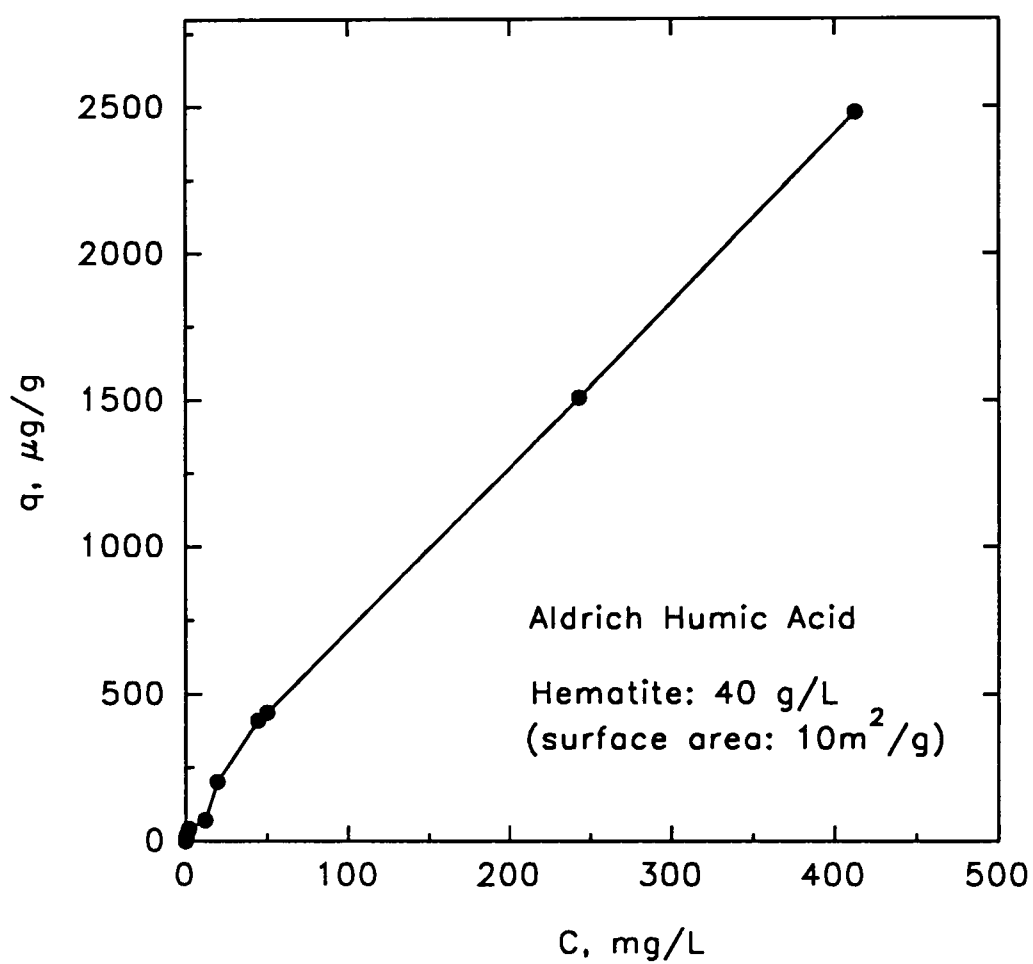


Figure 4.3 Adsorption isotherm of Aldrich humic acid-hematite system (concentration range: 0-500 mg/L)

4.1.3 Adsorption of Surfactant on Hematite

The CMC values of Igepal CA-720 in aqueous solution and in a soil-water suspension were obtained from surface tension measurements (Fig. 4.4); it increased nearly twofold in the presence of 40 g/L of soil. The sorption isotherm of Igepal CA-720 on AHA-coated hematite ($f_{oc}=0.45\%$) is shown in Fig. 4.5. The maximum adsorption was obtained very near the CMC of the surfactant ($CMC = 3.2 \times 10^{-4} M$). Surfactant micelles do not seem to adsorb well on hematite as indicated by no increase in sorption density beyond the CMC dosage. The CMC increase due to the presence of hematite corresponded to the increased sorption density of the surfactant on hematite ($12.2 \mu\text{mol/g}$ in Fig. 4.5). The f_{oc} of AHA-coated hematite increased to 1.07% due to surfactant sorption.

4.1.4 Adsorption of Naphthalene on AHA-Coated Hematite

The isotherms for the sorption of naphthalene on hematite with varying values of f_{oc} are shown in Fig. 4.6. Consistent with the sorption behavior of hydrophobic organic compounds on soil, the partitioning coefficient, K_p , given by the slope of these linear isotherms, increased with f_{oc} . Values of K_{oc} (K_p values normalized for f_{oc}) are plotted as a function of f_{oc} in Fig. 4.7. For low values of f_{oc} , K_{oc} values computed from K_p and f_{oc} (Eq. 2-2) were much larger than that predicted from the K_{ow} of naphthalene (Eqs. 2-4 and 2-5); at high f_{oc} values, the values computed by the two methods were comparable.

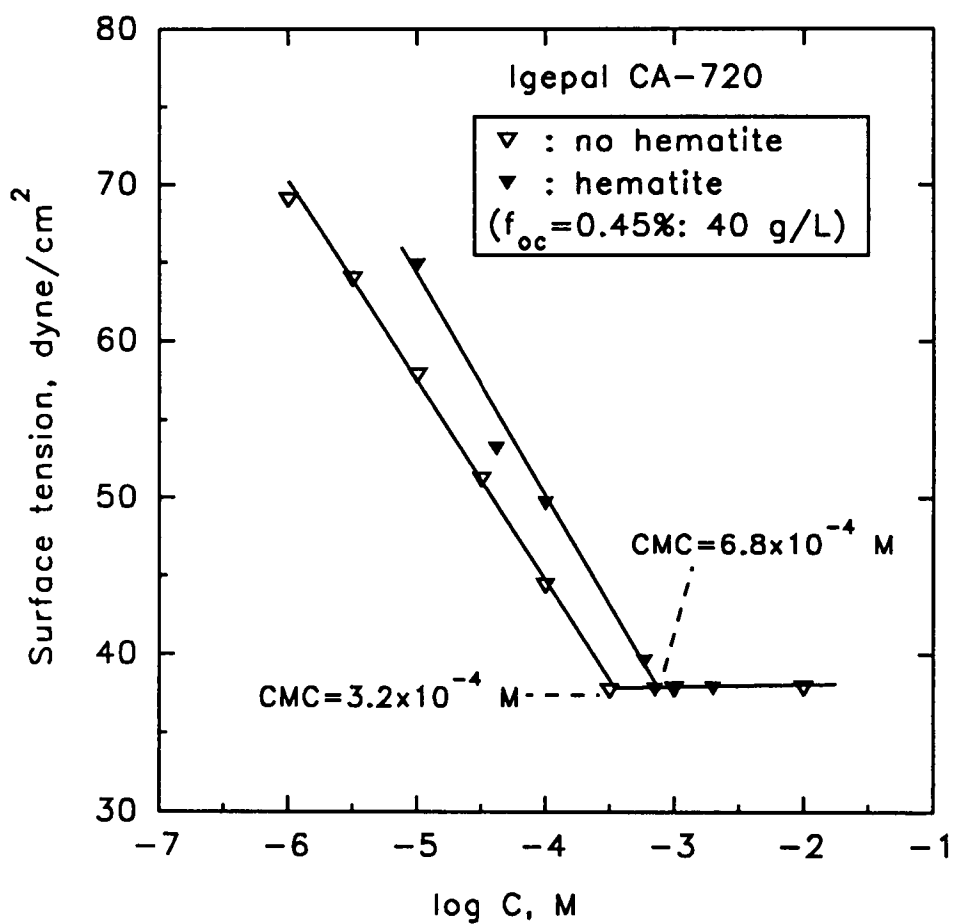


Figure 4.4 Determination of CMC of Igepal CA-720 in the presence of hematite coated with Aldrich humic acid

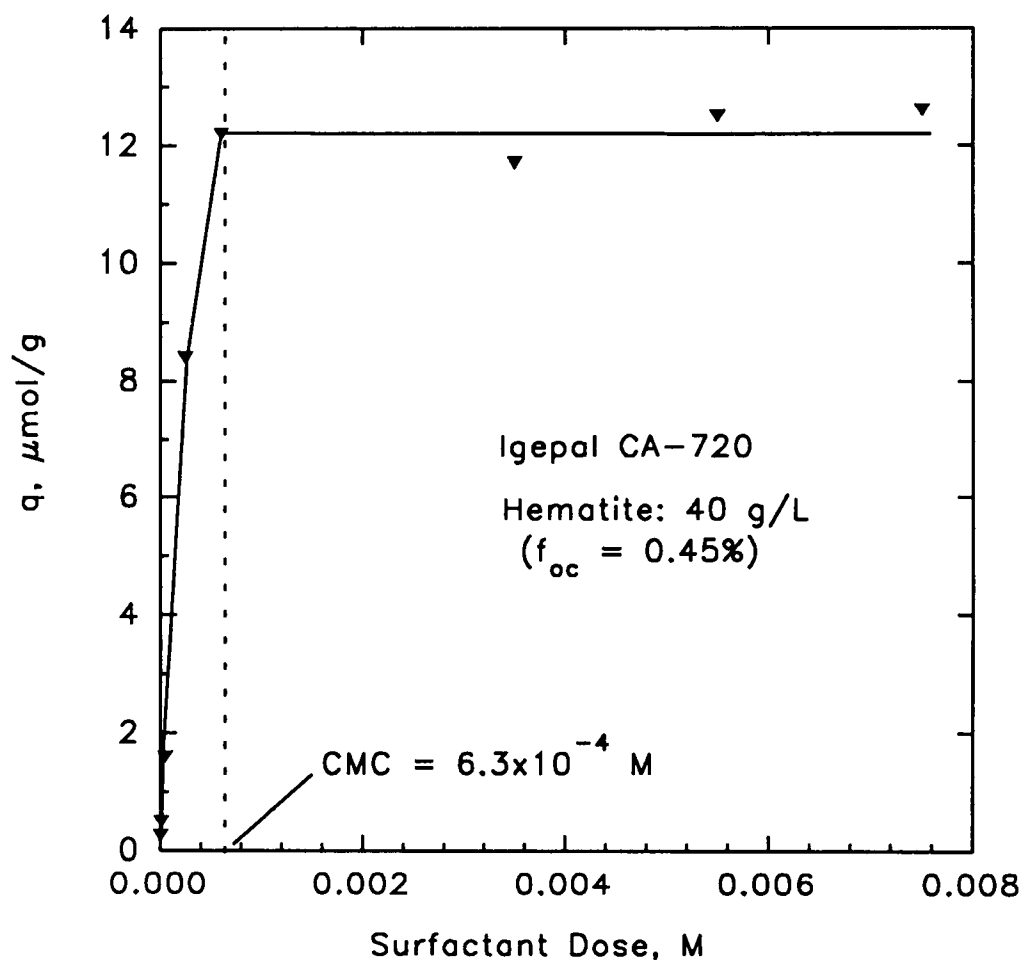


Figure 4.5 Adsorption isotherm of micellar Igepal CA-720 on hematite coated with Aldrich humic acid

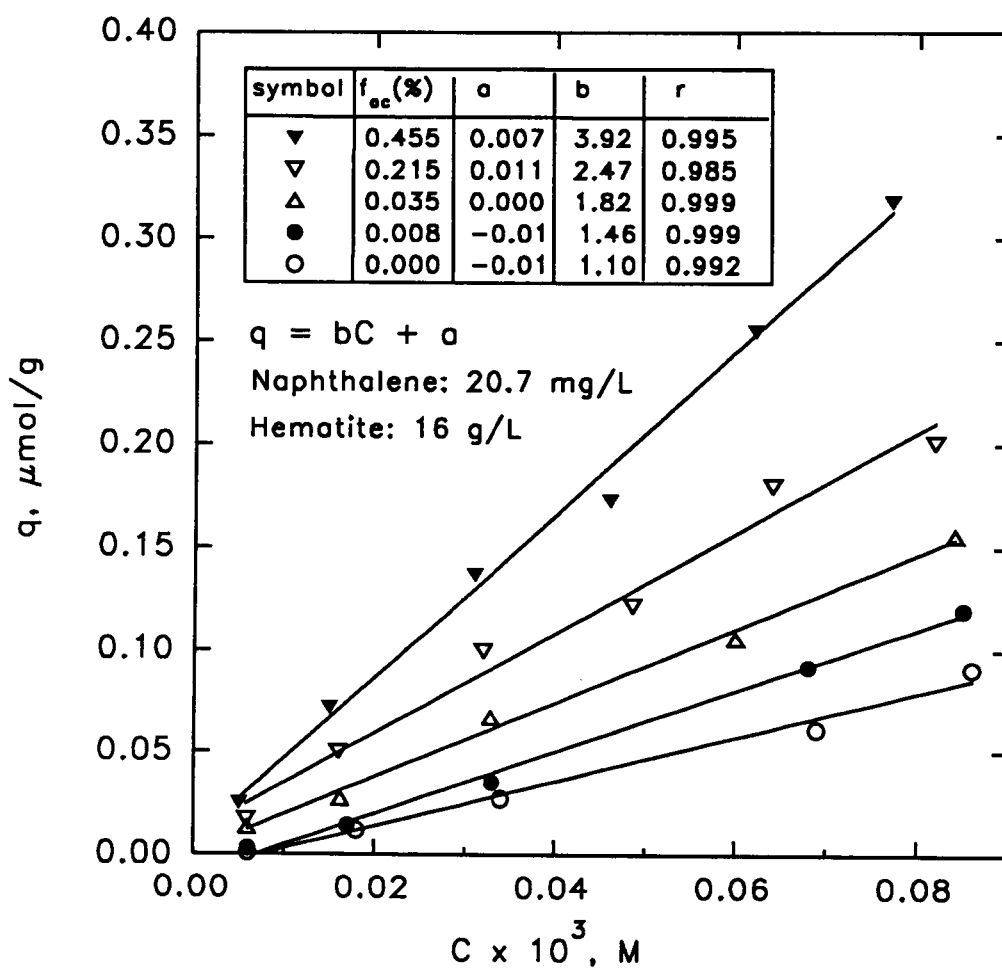


Figure 4.6 Adsorption isotherm of naphthalene on humic acid-coated hematite (equilibration time = 20 hours)

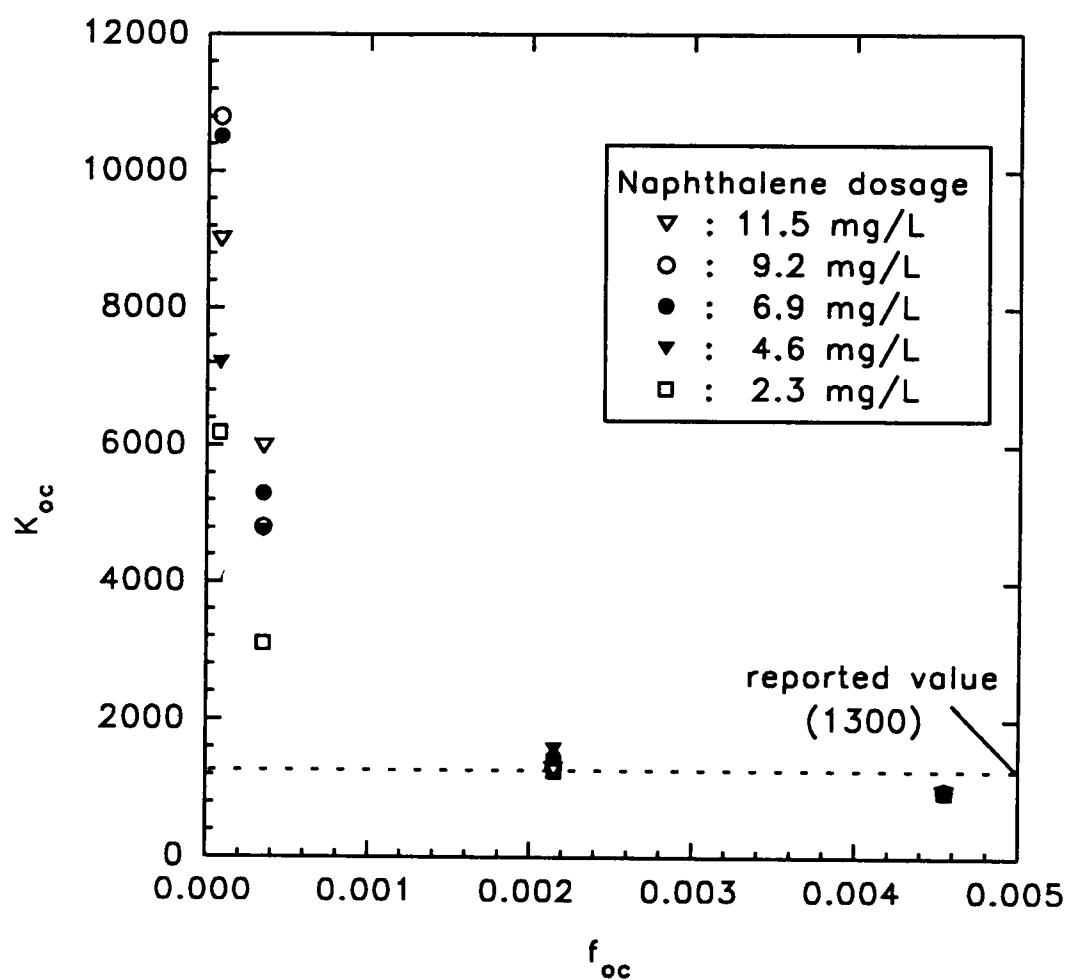


Figure 4.7 Distribution of K_{oc} values for varying f_{oc} values

Conceivably, a small but finite amount of sorption of naphthalene on bare hematite ($f_{oc}=0$) could occur in contrast to constant partitioning of the adsorbate only between soil organic matter and aqueous solution. The dependence of sorption on f_{oc} was further investigated using Freundlich isotherms. As shown in Fig. 4.8, the slope (n) of the isotherm for hematite with f_{oc} of 0 and 0.008% were much less than unity while those for soils with high f_{oc} were near unity. The deviation of n from unity was largest for bare hematite; it approached unity with increasing f_{oc} values indicating that the interaction of naphthalene with hematite mineral was nonlinear (Fig. 4.9). The nonspecific sorption of naphthalene on the bare mineral surface decreased with an increase in f_{oc} of hematite; above a certain value of f_{oc} , it was insignificant. At low values of f_{oc} , the mineral surface was only partially covered; the sorption sites consisted of both organic-coated and organic-free mineral surface and competitive sorption could occur under such conditions. From Fig. 4.2, the sorption density of AHA for monolayer coverage was 570 $\mu\text{g/g}$ with a resulting f_{oc} of 0.021 % (AHA had 37.3% organic carbon). As illustrated in Fig. 4.9, beyond a f_{oc} value of 0.021% n was constant and nearly unity. Seemingly, for soils with low f_{oc} values, competitive sorption on bare mineral and soil organic matter may be the mechanism responsible for nonlinear adsorption of HOCs.

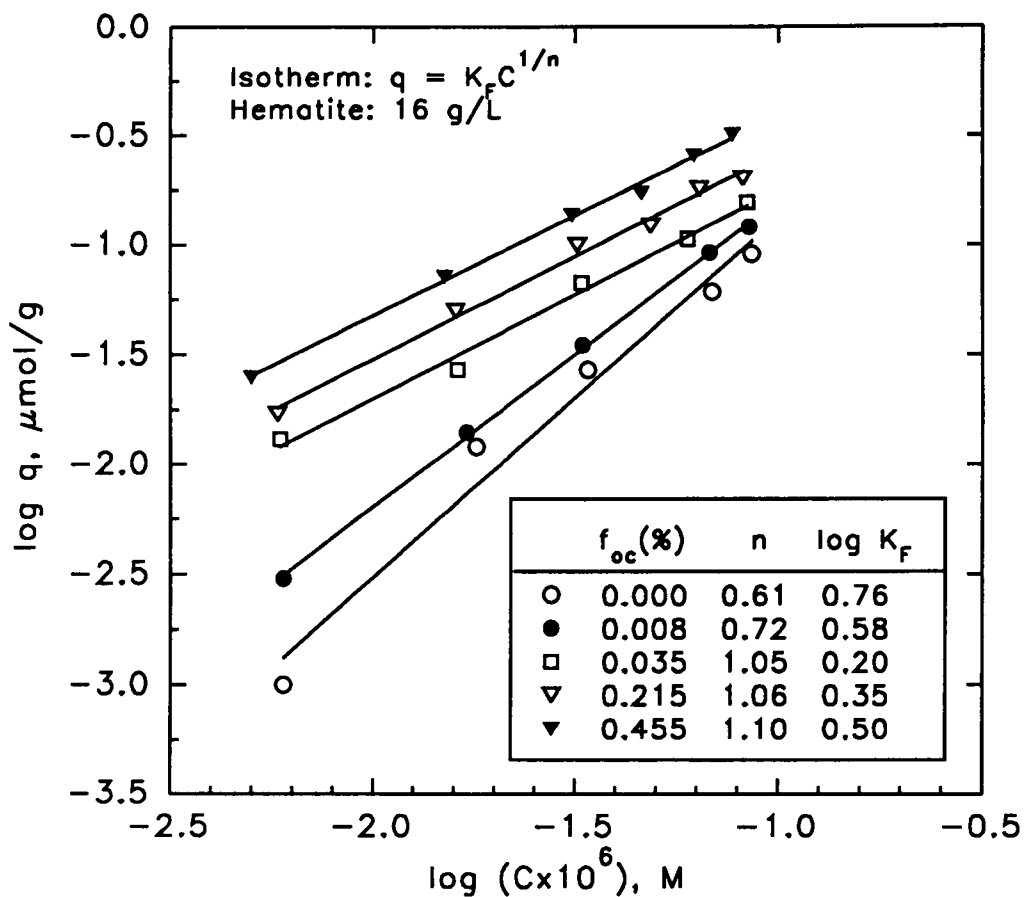


Figure 4.8 Freundlich isotherm for naphthalene adsorption on hematite coated with varying amounts of Aldrich humic acid

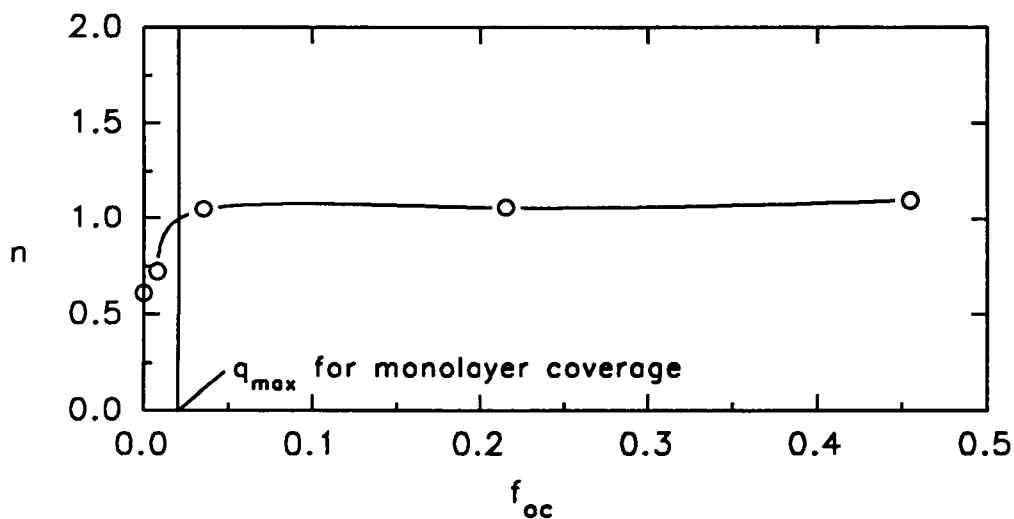


Figure 4.9 Effect of f_{oc} on the linearity of adsorption isotherm

4.1.5 Desorption of Naphthalene from Hematite with Surfactant

Limited studies were conducted to determine PAH desorption from organically coated minerals. Hematite coated with AHA ($f_{oc}=0.45$) was washed with DI water followed by washing with a surfactant solution (Igepal CA-720). With two washings of DI water, each for a period of one day, 75% of the sorbed naphthalene could be recovered. Up to 45% of the remainder (11% of the original) was recovered by a single wash of Igepal CA-720 for a total recovery of 86% (Fig. 4.10). Desorption of naphthalene at surfactant dosages below the CMC was minimal; however, desorption rapidly increased at dosages above CMC reaching a plateau at about 13 times the CMC dosage.

Considering that only 3% more of the naphthalene was desorbed by a third washing with DI water (results not shown), the surfactant solution significantly increased the mobility of sorbed naphthalene. Although results are not shown, it is worthwhile to mention that, with no prewashing with DI water, a single wash of surfactant was able to mobilize up to 84 % of the naphthalene bound to hematite.

4.2 ADSORPTION OF PAHS ON NATURAL SOILS

To obtain realistic information on the adsorption/desorption of PAH compounds in soil systems, all subsequent experiments in this research were conducted in batch systems using three soils of similar textures but having varying

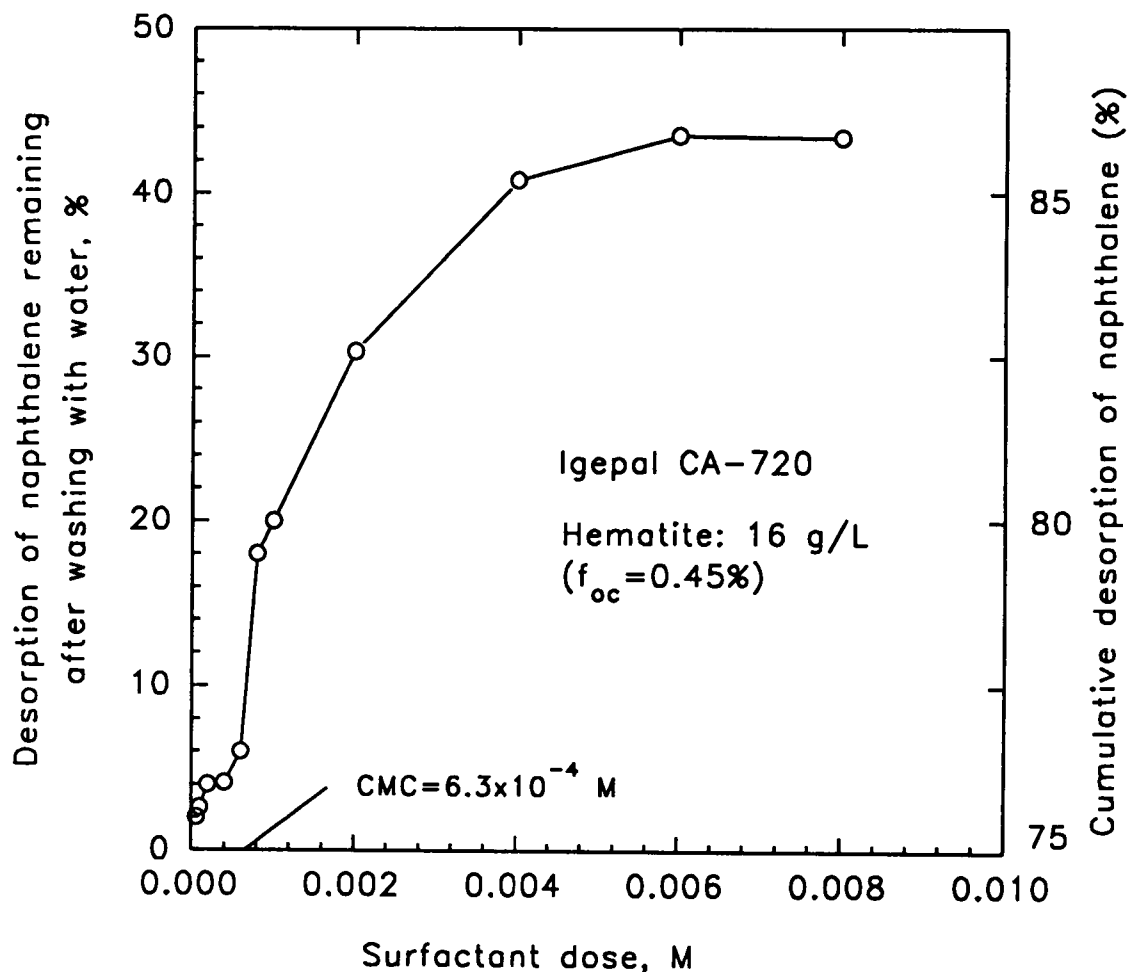


Figure 4.10 Desorption of naphthalene at varying surfactant doses (The soil was precontaminated with 22 mg/L naphthalene solution and washed twice with DI water, each for 1 day. Seventy five percent of naphthalene was desorbed by water washings and for the remainder, surfactant solution was applied.)

amounts of organic matter; two PAH compounds namely, naphthalene (solubility $\approx$ 22 mg/L) and phenanthrene (solubility $\approx$ 1 mg/L) were used. The effect of adsorption equilibration period on the subsequent desorption of PAH from these soils were investigated.

4.2.1 Adsorption of Phenanthrene

Isotherms for phenanthrene sorption on three natural soils with different values of f_{oc} are shown in Fig. 4.11. The K_p and K_{oc} values for each soil are listed in Table 4.2; also listed is the value of the coefficient computed using an empirical relationship between K_{oc} and K_{ow} (Karickhoff, 1981). The measured K_{oc} values were less than the value calculated from the K_{ow} of phenanthrene. Although the differences are

Table 4.2 Partition coefficients for phenanthrene in natural soils

	Lex I	Etowah	Lex II	K_{oc}^b
$f_{oc}(\%)$	0.9	1.7	3.4	
K_p^a	122	199	373	
K_{oc}^a	13556	11705	10971	17421 ^b

^aPartition coefficients are expressed in mass/mass units

^b $\log K_{oc} = 0.989 \log K_{ow} - 0.346$ (Karickhoff, 1981)

(K_{oc} and K_{ow} are expressed as a ratio of mole fractions)

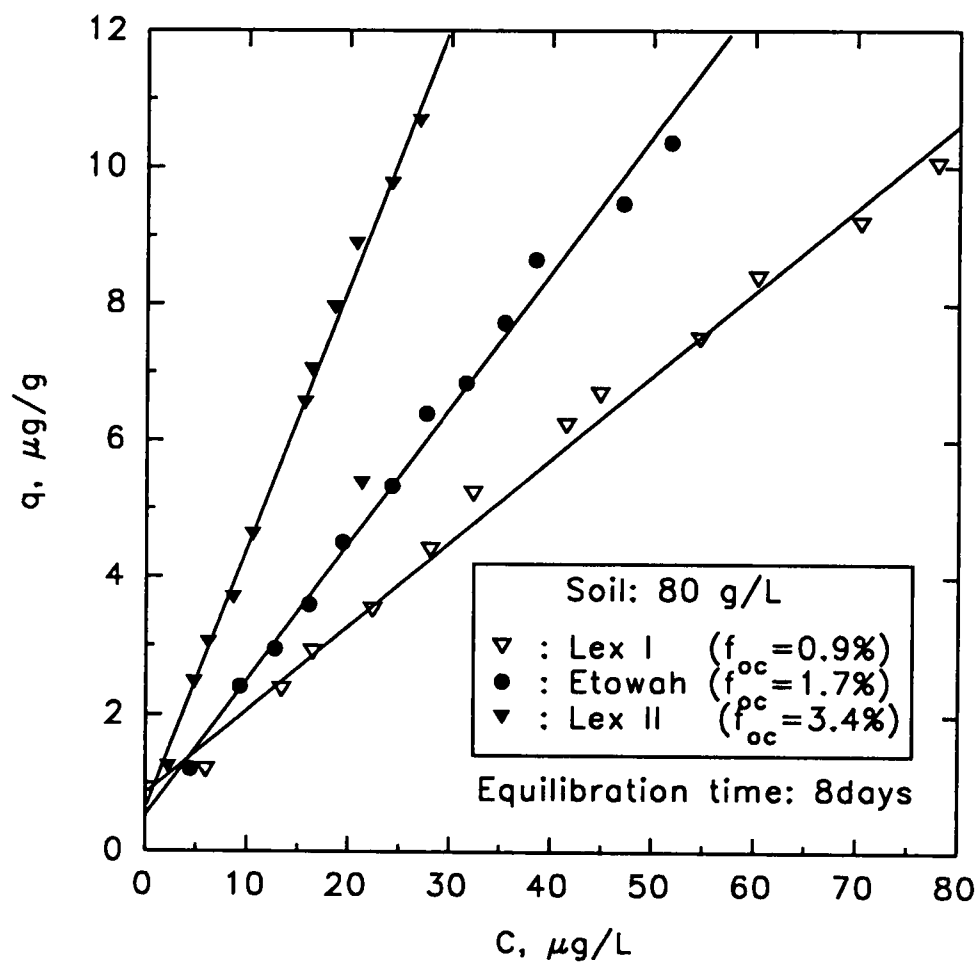


Figure 4.11 Adsorption isotherm of phenanthrene on soils with different organic carbon content (f_{oc})

well within standard errors of empirical relationship, they could also be due to artifacts caused by the release of soil organic matter (SOM) into solution during sorption. The dissolved organic matter (DOM) released from soil during sorption equilibration was estimated from an analysis of TOC of the supernatant. For Lex I, Etowah and Lex II soils these values were 11.08, 24.3 and 39.5 mg/L, respectively, in 80 g/L test soil suspensions. The corresponding decrease in f_{oc} was 0.014%, 0.03%, and 0.05%, respectively. Though the amount of organic matter released was insignificant, it may have significantly enhanced the solubility of HOC and, consequently, made its partition coefficient smaller (Chiou et al., 1987; Chin and Weber, 1989). In Fig. 4.12 the K_{oc} values from Table 2.2 are plotted against the DOM released from soil. Although precise evaluation of the effect of DOM on partitioning of HOC is beyond the scope of this study, suffice it to say that it may be necessary to prewash soil to minimize release of soil organic matter during sorption experiments. Slow kinetics of PAH adsorption on soils may also result in relatively small K_{oc} values in experiments of long duration.

4.2.2 Kinetics of Phenanthrene Adsorption

The influence of nonequilibrium kinetics of mass transfer on the sorption of PAH on soils was studied carefully using selected natural soils and phenanthrene. The apparent

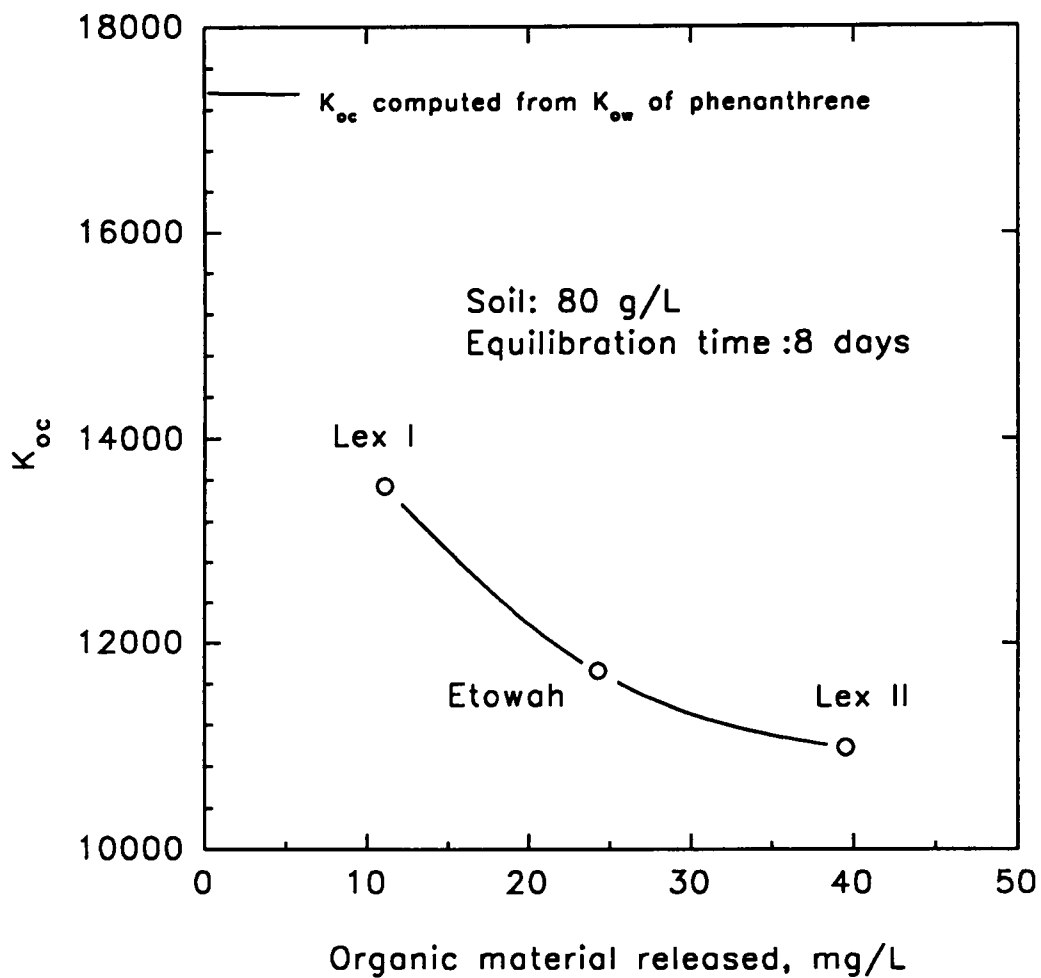


Figure 4.12 Effect of organic matter released from soil on K_{oc}

distribution coefficient (K_d) of phenanthrene for three soils are plotted against equilibration time in Fig. 4.13a. The K_d for all soils linearly increased with logarithm of equilibration time for the first 24-hr period. However, over extended periods, the increase in K_d was much slower for Lexington soils than for Etowah soil. Whereas K_d continued to increase for the Etowah soil, those for the Lexington soils became asymptotic after one day. The corresponding K_{oc} values for these systems are plotted in Fig. 4.13b. Despite the difference in the f_{oc} of these soils, K_{oc} values were similar; they became divergent only after one day. It is noteworthy that the two Lexington soils exhibited similar partitioning behavior despite their very different organic matter content. Seemingly, some factor other than f_{oc} is at play in controlling the slow, long-term sorption process - perhaps some geophysical characteristics of the soil particles such as intra-aggregate porosity and particle size distribution (PSD). If retarded intraparticle diffusion is the mechanism for the observed nonequilibrium sorption of PAH, the higher geometric mean particle size (GMD) of Etowah soil along with its high content of sand (Table 3.1) could be responsible for the observed temporal increase of the partitioning coefficients well beyond 24 hours. Additional sorption studies of longer duration, months to years, with soils of various physical and chemical properties are needed to fully understand the nonequilibrium behavior of sorption.

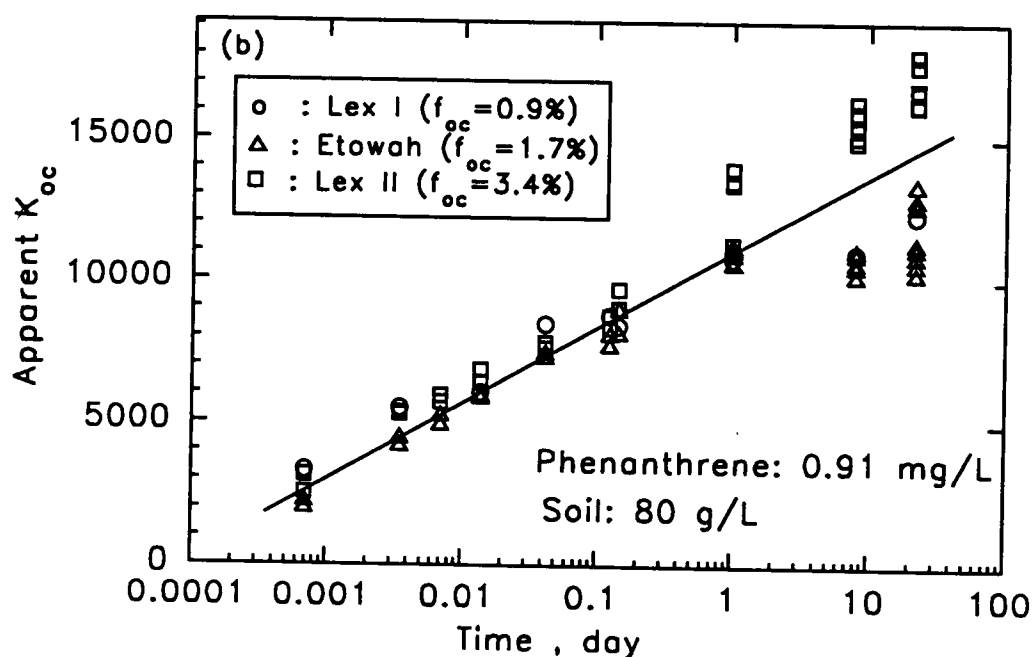
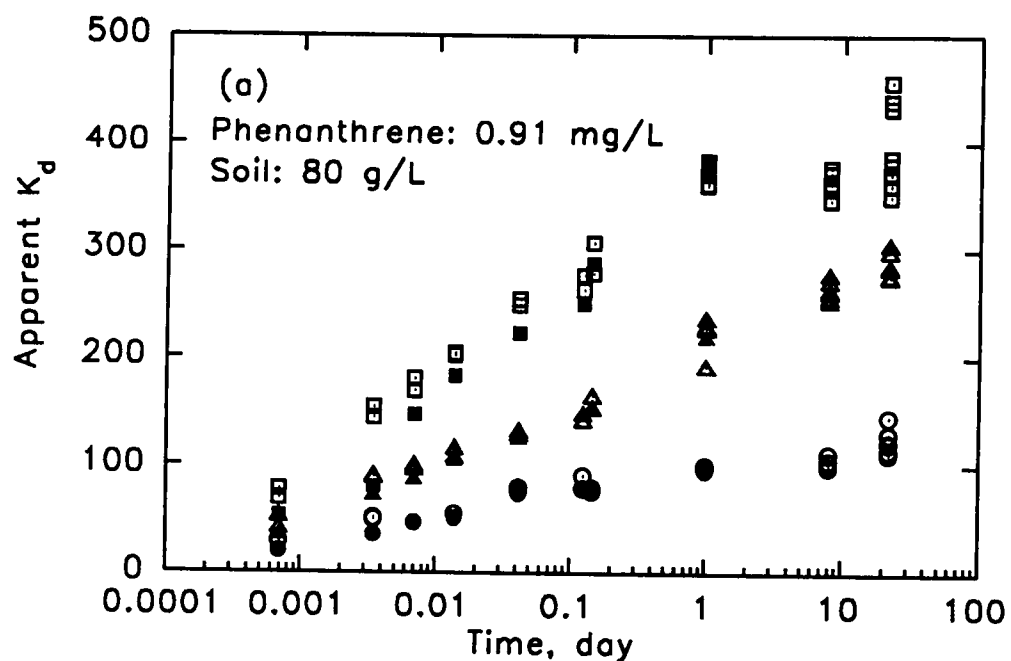


Figure 4.13 Effect of sorption equilibration time on the distribution of phenanthrene between the aqueous and solid phases in soils of varying organic carbon content (f_{oc}) (a) Apparent distribution coefficient, (b) Apparent organic carbon-normalized partitioning coefficient (K_{oc})

■ ▲ ● : result obtained by filtration,
□ △ ○ : result obtained by centrifugation)

4.3 DESORPTION OF PAH FROM SOIL USING SURFACTANT

4.3.1 Determination of CMC of Surfactants

The surface tension of aqueous solutions of the two nonionic surfactants used in this study, namely, Igepal CA-720, a lamellar surfactant, and Brij 30, a micellar surfactant, are plotted against surfactant concentration in Figs. 4.14 and 4.15, respectively. Since surface tension is essentially governed by the surface excess of surfactant monomers at the air-water interface, a constant surface tension indicates that surfactant monomer concentration at the interface has attained a maximum (Rosen, 1989). The point of inflection represents saturation concentration of the surfactant monomer at which micelles or aggregates begin to form. The inflection point is denoted by the critical micelle concentration (CMC). For lamellar surfactants, sometimes the inflection point is defined as the critical aggregate concentration (CAC). The observed CMC values for the two surfactants are compared in Table 4.3. The measured values compare well with those reported in the literature. In the presence of soil, much greater doses (2 to 20 times) were required to attain critical surfactant concentration at which micelles or aggregates formed. Soils have a significant adsorptive demand for surfactants. In such systems the surfactant dose at CMC consists of the CMC of the aqueous surfactant solution and the amount of surfactant adsorbed on

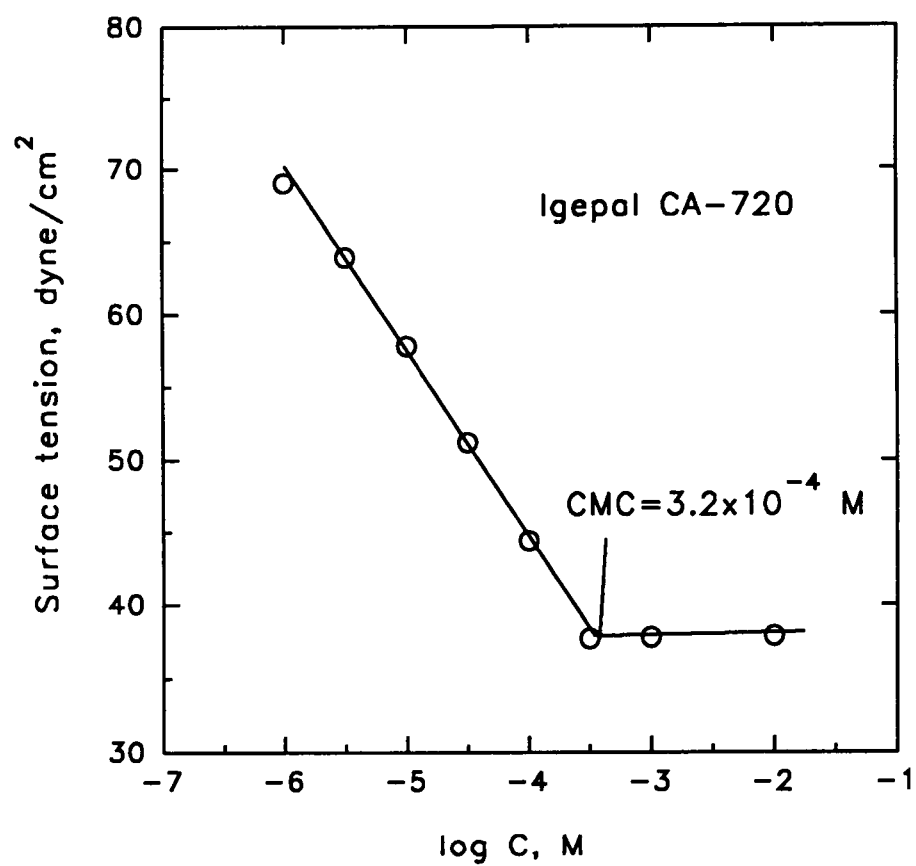


Figure 4.14 Determination of CMC of Igepal CA-720 in aqueous solution

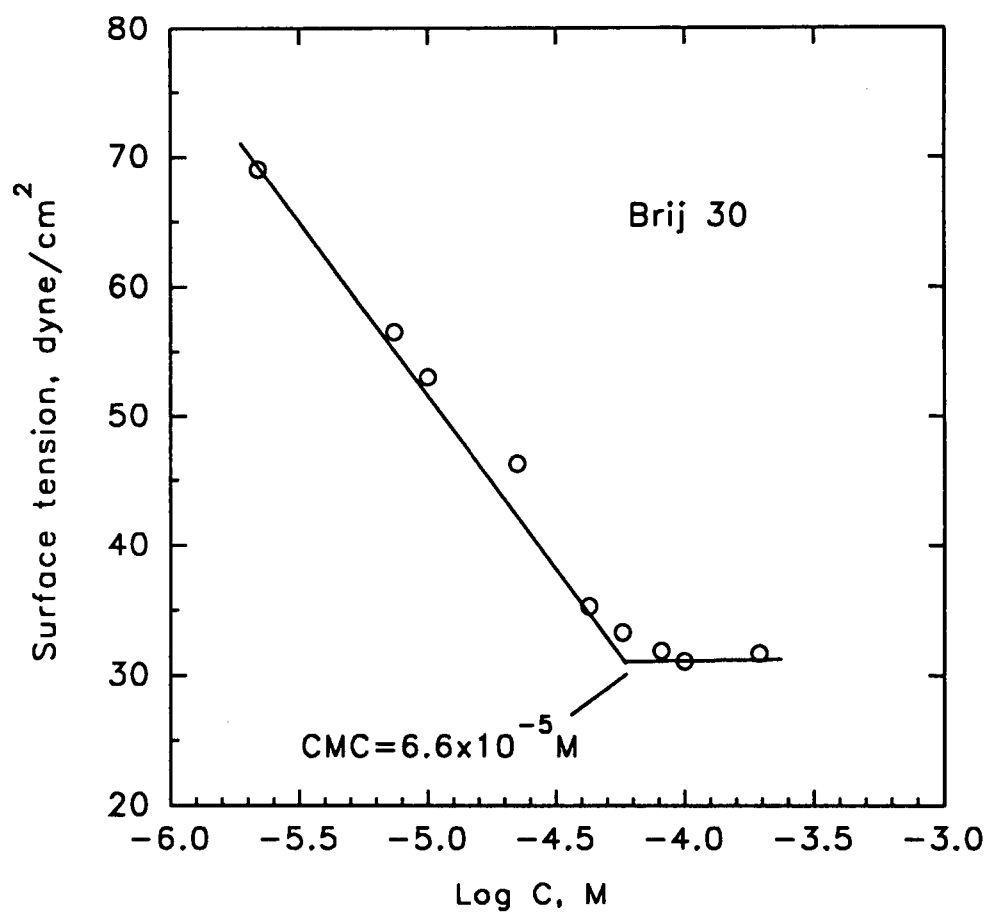


Figure 4.15 Determination of CMC of Brij 30 in aqueous solution

soil. A typical plot of surface tension of the surfactant Igepal CA-720 in the presence of Lexington II soil is shown in Fig. 4.16. Similar results for other surfactant-soil combinations are shown in Figs. A.2 through A.6 in Appendix IV. The CMC doses of the two surfactants in suspensions of the test soils are summarized in Table 4.3. The increase in the CMC dose of lamellar Brij 30 was much greater than that of micellar Igepal CA-720 due to its strong sorptivity.

Table 4.3 CMC of nonionic surfactants with or without soil

Aqueous Solution		Soil Suspension (80 mg/L)			
	This study	Literature	Lex I	Etowah	Lex II
	(M)	(M)	$f_{oc}=0.9\%$	$f_{oc}=1.7\%$	$f_{oc}=3.4\%$
Igepal CA-720	3.2×10^{-4}	^a 2.3×10^{-4} ^b 6.0×10^{-4}	4.3×10^{-4}	4.6×10^{-4}	5.1×10^{-4}
Brij30	6.6×10^{-5}	^a 2.3×10^{-5} ^c 6.5×10^{-5}	6.5×10^{-4}	1.6×10^{-3}	8.1×10^{-4}

^a Mukerjee and Mysels (1971)

^b Liu et al. (1991a)

^c Rosen (1989)

4.3.2 Adsorption of Surfactant on Soil

The concentration of surfactant in solution was measured using two methods: surface tension and TOC analysis. At concentrations less than the CMC, the aqueous surfactant

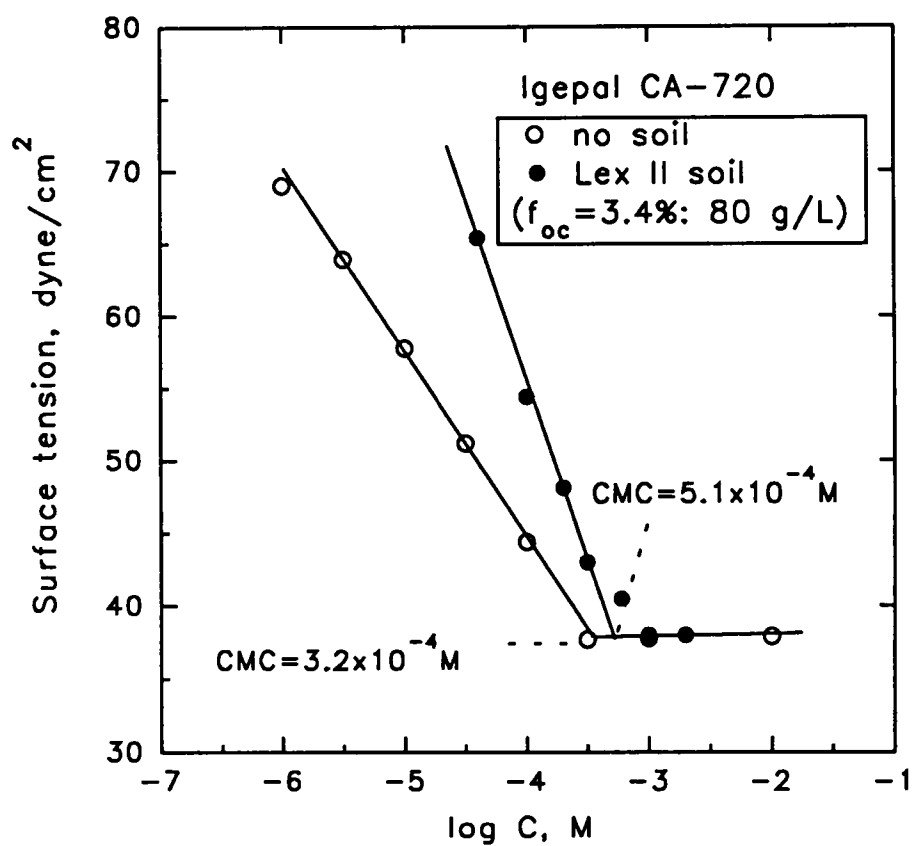


Figure 4.16 Determination of CMC of Igepal CA-720 in the presence of Lexington II soil

concentration in soil-water system was determined from surface tension measurements. At concentrations above the CMC, the aqueous surfactant concentration was determined from TOC measurements. The isotherms for the adsorption of Igepal CA-720 and Brij 30 are shown in Figs. 4.17 and 4.18, respectively. The micelle-forming surfactant Igepal CA-720 attained maximum sorption density at an aqueous concentration near its CMC (Fig. 4.17) consistent with observations made by Liu et al. (1991). Seemingly, surfactant monomers adsorbed well on soil. However, above the CMC, where most surfactant is present in the micelle form, the adsorption was relatively poor. Also, the maximum sorption density appears to correlate directly with f_{oc} . For the lamellae-forming surfactant, Brij 30, the maximum sorption density occurred at concentrations orders of magnitude higher than the CAC; also, in the lamellae form, the surfactant adsorbed at least as well as the monomer. At low concentrations, more intense and greater sorption occurred on Etowah soil than on the Lexington soils (Fig. 4.18). However, as surfactant dose increased, the sorption capacity of Etowah soil decreased while those of Lexington soils remained relatively constant.

The effect of soil f_{oc} on the observed sorption behavior of Brij 30 lamellar surfactant does not lend itself to meaningful interpretation. Interlamellar interaction as well as the lamellae-soil organic matter interaction may be responsible for this unusual sorption behavior (Mitchell et

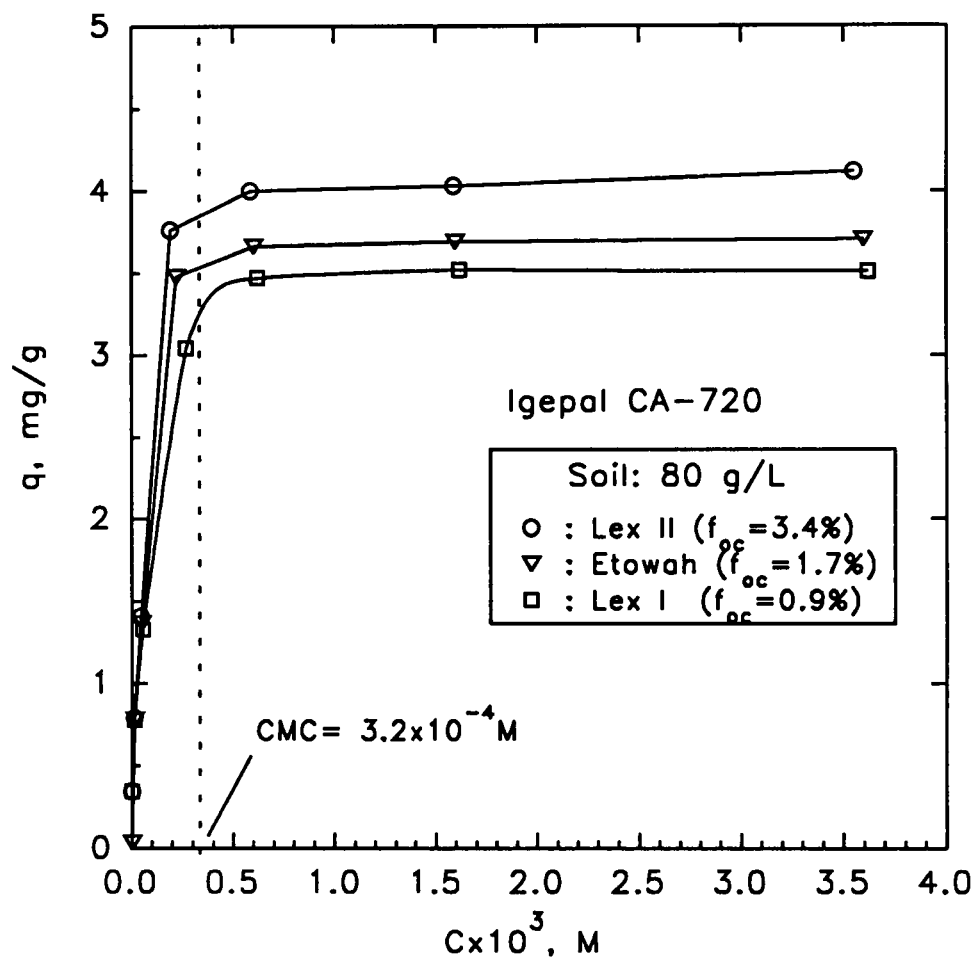


Figure 4.17 Sorption isotherm of Igepal CA-720 for Lex I, II, and Etowah soil (soil: 80 g/L; equilibration time: 1 day)

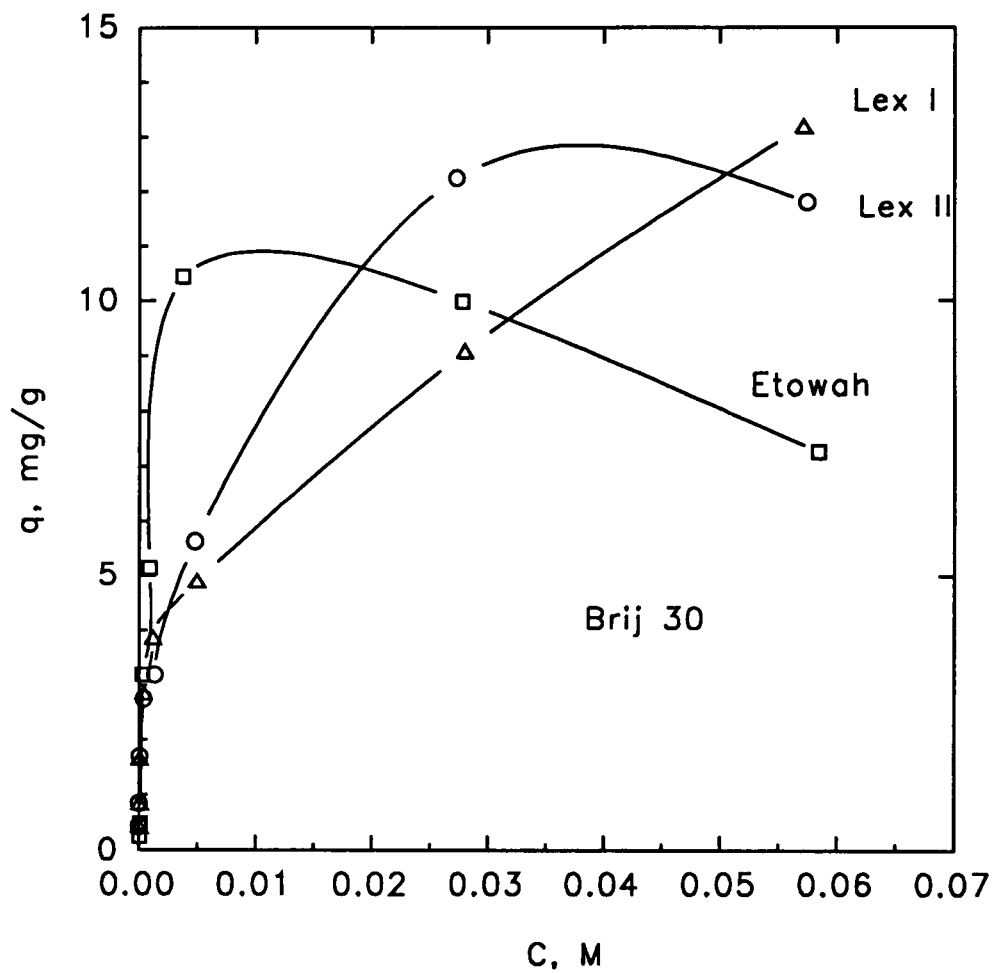


Figure 4.18 Sorption isotherm of Brij 30 for LexI, II and Etowah soil (soil: 80 g/L; equilibration time: 1 day)

al., 1983). The adsorption of both test surfactants in the sub-CMC concentration range is well characterized by the Freundlich isotherm (Figs. 4.19 and 4.20). In Fig. 4.19, as f_{oc} of soil increases, both sorption capacity (K_F) and sorption intensity ($1/n$) increase, indicating that sorption of Igepal CA-720 is mainly related to soil organic matter. For Brij 30, however, the sorption was characterized by the Freundlich isotherm only until maximum sorption density was attained.

As a result of surfactant sorption, the f_{oc} of soil significantly increased. The f_{oc} of soil at varying surfactant doses was calculated using Eq. 2-19 and are summarized in Table 4.4.

Table 4.4 Soil organic carbon content (f_{oc}') corrected for surfactant adsorption

soil	f_{oc}	f_{oc}' at C_{surf} (M)					
		Igepal (CMC=3.2E-04M)	Brij 30 (CMC=6.6E-05M)				
			0.001	0.002	0.006	0.010	0.030 0.060
Lex I	0.9	1.11	1.01	1.09	1.15	1.22	1.46 1.76
Etowah	1.7	1.91	1.71	1.89	2.02	2.37	2.36 2.16
Lex II	3.4	3.65	3.50	3.58	3.61	3.77	4.21 4.18

f_{oc}' = fraction organic carbon in soil (f_{oc}) corrected for adsorbed surfactant
No change in Igepal sorption occurred at $C_{surf} > CMC$

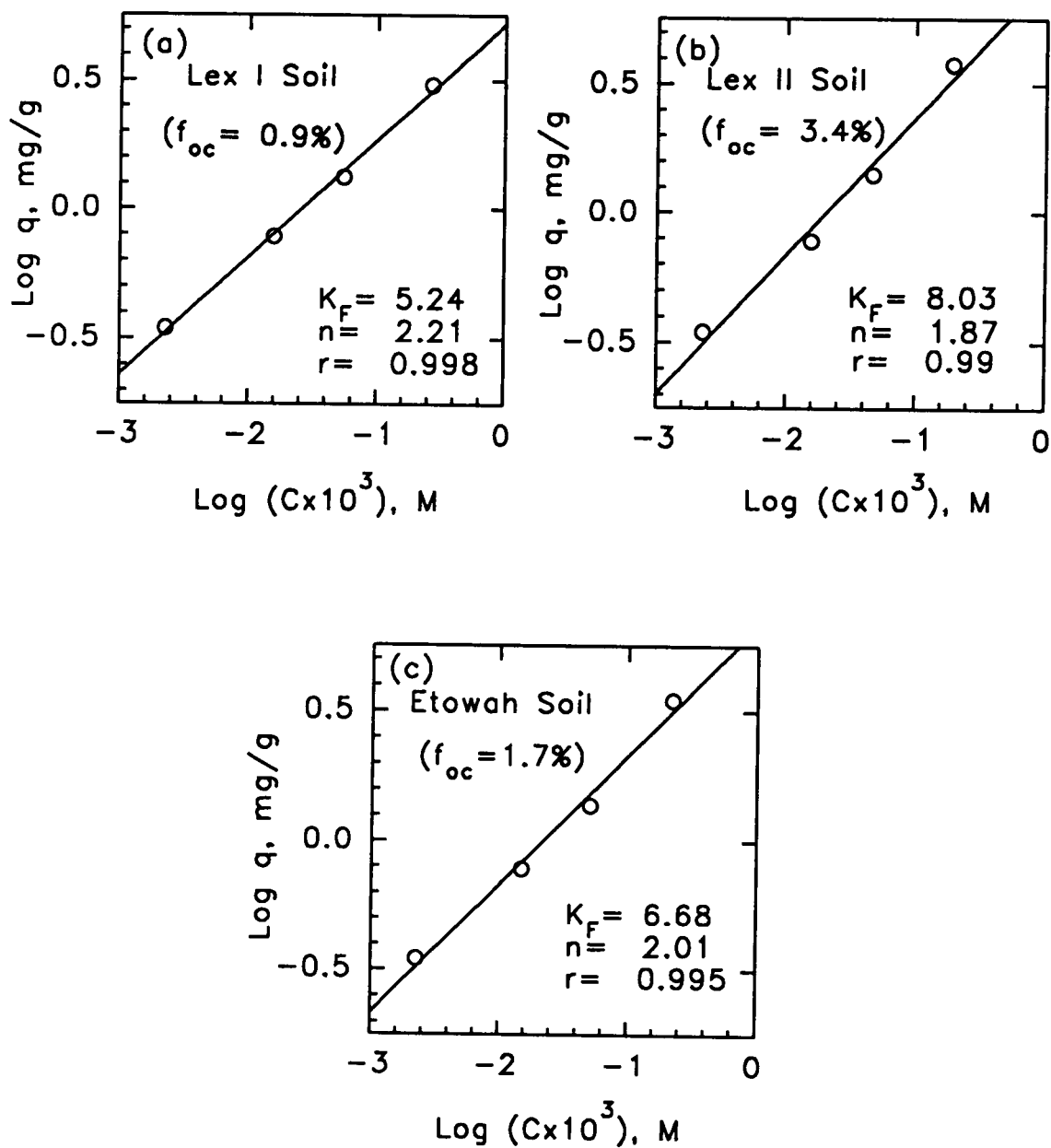


Figure 4.19 Freundlich isotherms for the sorption of Igepal CA-720 on different soils

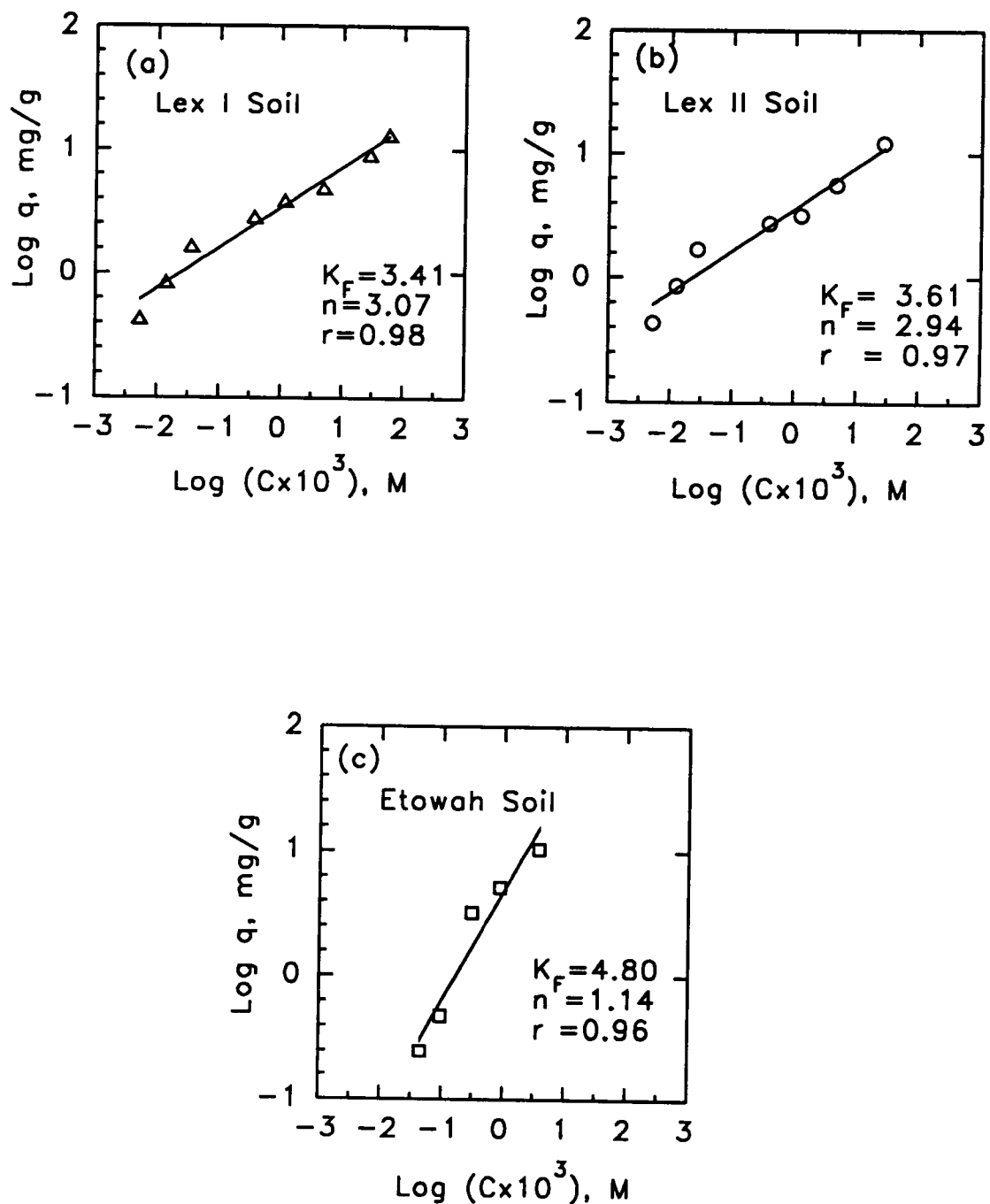


Figure 4.20 Freundlich isotherms for the sorption of Brij 30 on different soils

4.3.3 Surfactant-Enhanced Mobilization of PAH

The efficiency of solubilization of soil-bound naphthalene with Brij 30, and hence its desorption from the three natural soils are shown in Fig. 4.21. The soils were equilibrated to a 22.8 mg/L naphthalene solution for one day followed by washing with surfactant for one day. Insignificant desorption enhancement occurred at surfactant dosages below the CMC. At these dosages, a large fraction of the surfactant added was adsorbed on soil and, conceivably, was not available for solubilizing naphthalene. However, above the CMC dosage, desorption increased dramatically -up to 90 percent at a dose of 0.03 M; no further increase in desorption was evident beyond this dosage. The effectiveness of micellar and lamellar surfactants in mobilizing naphthalene are compared in Fig. 4.22. Though the micellar surfactant Igepal CA-720 mobilized naphthalene somewhat better than the lamellar Brij 30 at lower dosages, the desorption efficiencies were the same at high concentrations (>0.06 M). The effectiveness of a surfactant in mobilizing PAH is usually determined by the partitioning of the PAH between the micellar and aqueous pseudophases, given by the molar partitioning coefficient K_m (Eq. 2-23), and also by its sorption characteristics. Igepal has a higher K_m (Table 2.1) and lower sorptivity than Brij 30. Consequently, it showed better PAH-mobilization characteristics. However, the mobilization of the last traces (5 -10 percent) of soil-bound naphthalene may be

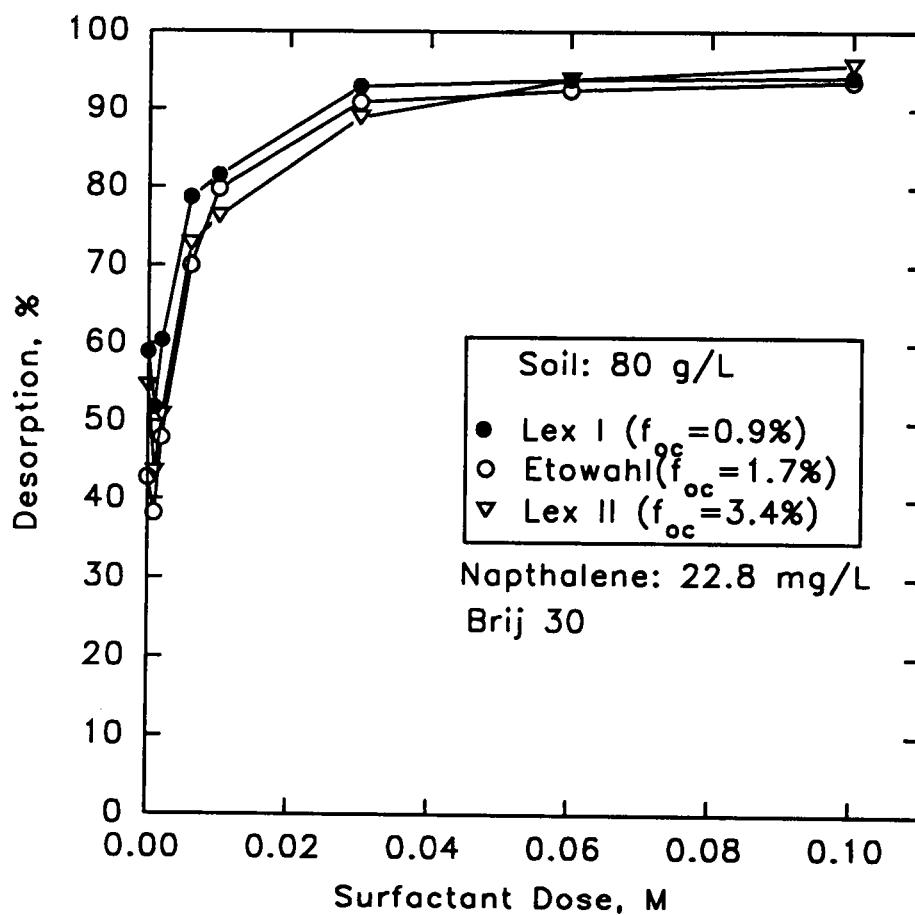


Figure 4.21 One-day desorption of naphthalene from soils using Brij 30

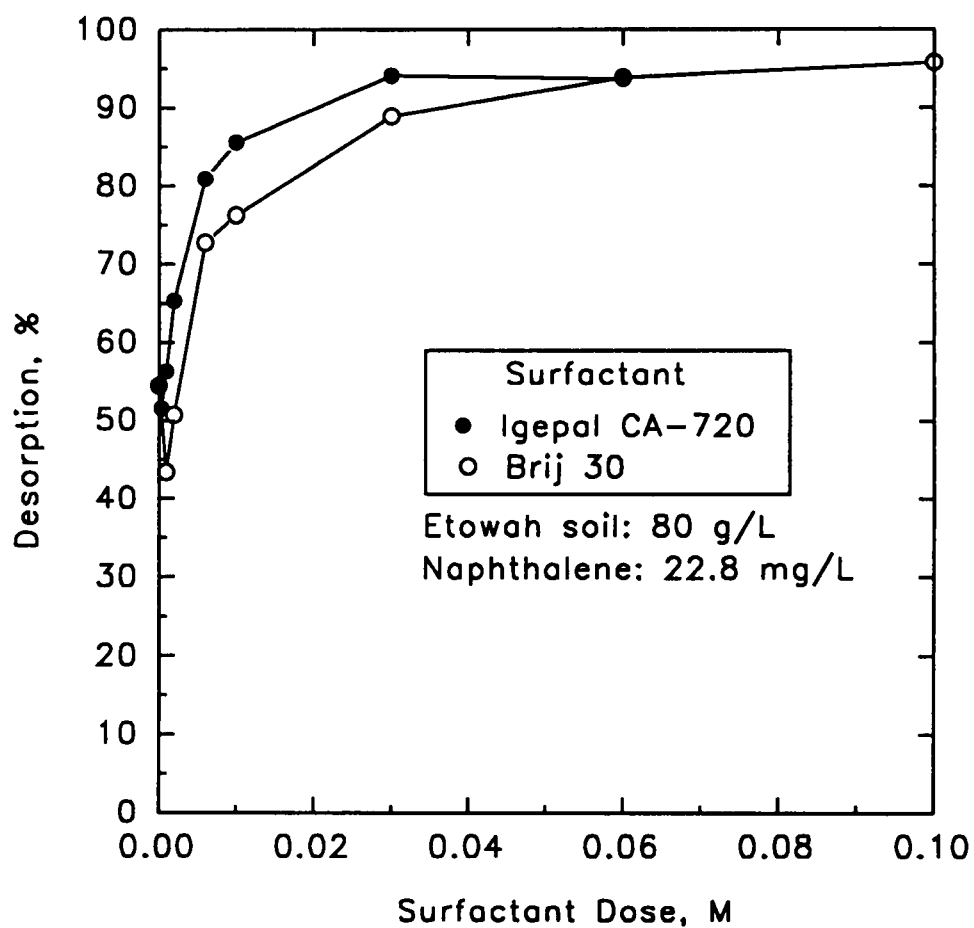


Figure 4.22 Desorption of naphthalene by two different types of nonionic surfactants

controlled by the slow diffusive mass transfer rather than the partitioning or sorption equilibria that are established very fast. It is reasonable to expect similar desorption behavior of the last traces of soil-bound PAHs regardless of the partitioning characteristics of the surfactants used. Suffice it to say that desorption of this fraction may depend to a large extent on the adsorption history of the PAH and the duration of the desorption period.

The results of batch experiments for desorbing phenanthrene from two Lexington soils using Brij 30 are shown in Fig. 4.23. As in naphthalene experiments, the soils were equilibrated to phenanthrene for one day followed by washing with surfactant for one day. A maximum desorption between 90-95% was obtained at a surfactant dosage of 0.3 M. Since the K_p of phenanthrene is much higher than that of naphthalene, phenanthrene would be more strongly associated with soil, mainly with soil organics. Therefore, the soil with higher f_{oc} (Lex II) displayed lower desorption of phenanthrene than that with lower f_{oc} (Lex I). Further, because of its higher f_{oc} Lexington II soil adsorbed a greater amount of the surfactant, making less of the surfactant available for mobilization of phenanthrene.

A series of batch experiments was conducted to study the solubilization of phenanthrene bound to soils of varying organic composition. The soil was equilibrated with

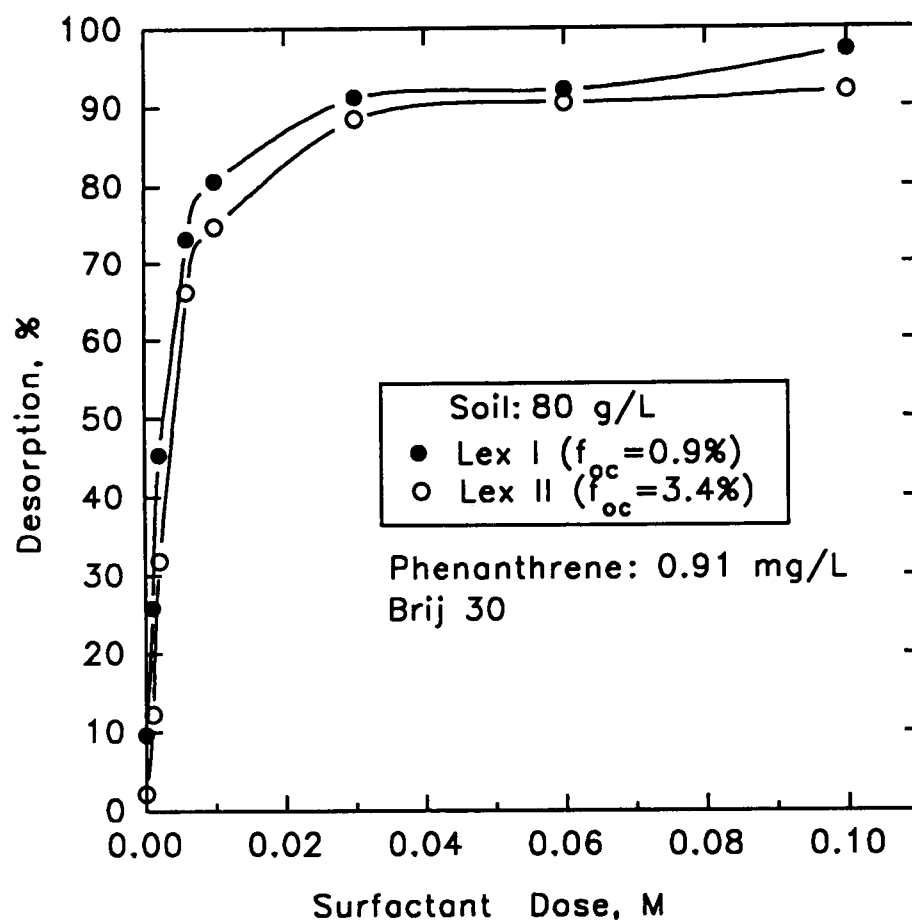


Figure 4.23 Desorption of phenanthrene from Lexington soils using Brij 30

phenanthrene solutions of varying concentrations for a period of 8 days (contamination age). It was then equilibrated with a 0.03 M solution of Brij 30 ($\text{CMC}=6.6 \times 10^{-5} \text{ M}$) for 1 day. The desorption isotherms obtained for the three soils, Lexington I, Etowah, and Lexington II, are shown in Fig. 4.24. The data could be fitted satisfactorily to a linear regression model. The slopes of the regression lines, a crude measure of the apparent partitioning coefficient, K_d , were 2.32, 2.77, and 3.1 (on mass per mass basis) for f_{oc} values of 0.9, 1.7, and 3.4%, respectively. It is reasonable to assume that, for a contamination age of 8 days, the desorption behavior of phenanthrene was almost identical despite the difference in the organic content of the test soils. However, in batch equilibrium studies of short duration - both adsorption and desorption cycles of one day duration- the distribution coefficient for the desorption of sorbed PAH depended on the organic content of soil, as shown in Fig. 4.25; the distribution coefficient normalized for the carbon content of soil was inversely related to f_{oc} and directly to the hydrophobicity of PAH. Regardless of the type of soil or PAH, reasonable desorption was obtained only at surfactant dosages much in excess of the CMC. Comparing Figs. 4.24 and 4.25, it may be inferred that in most cases of soil contamination- usually with contamination age of weeks or months- short-term mobilization of sorbed PAH is independent of the type of soil; surfactant dose is of critical importance

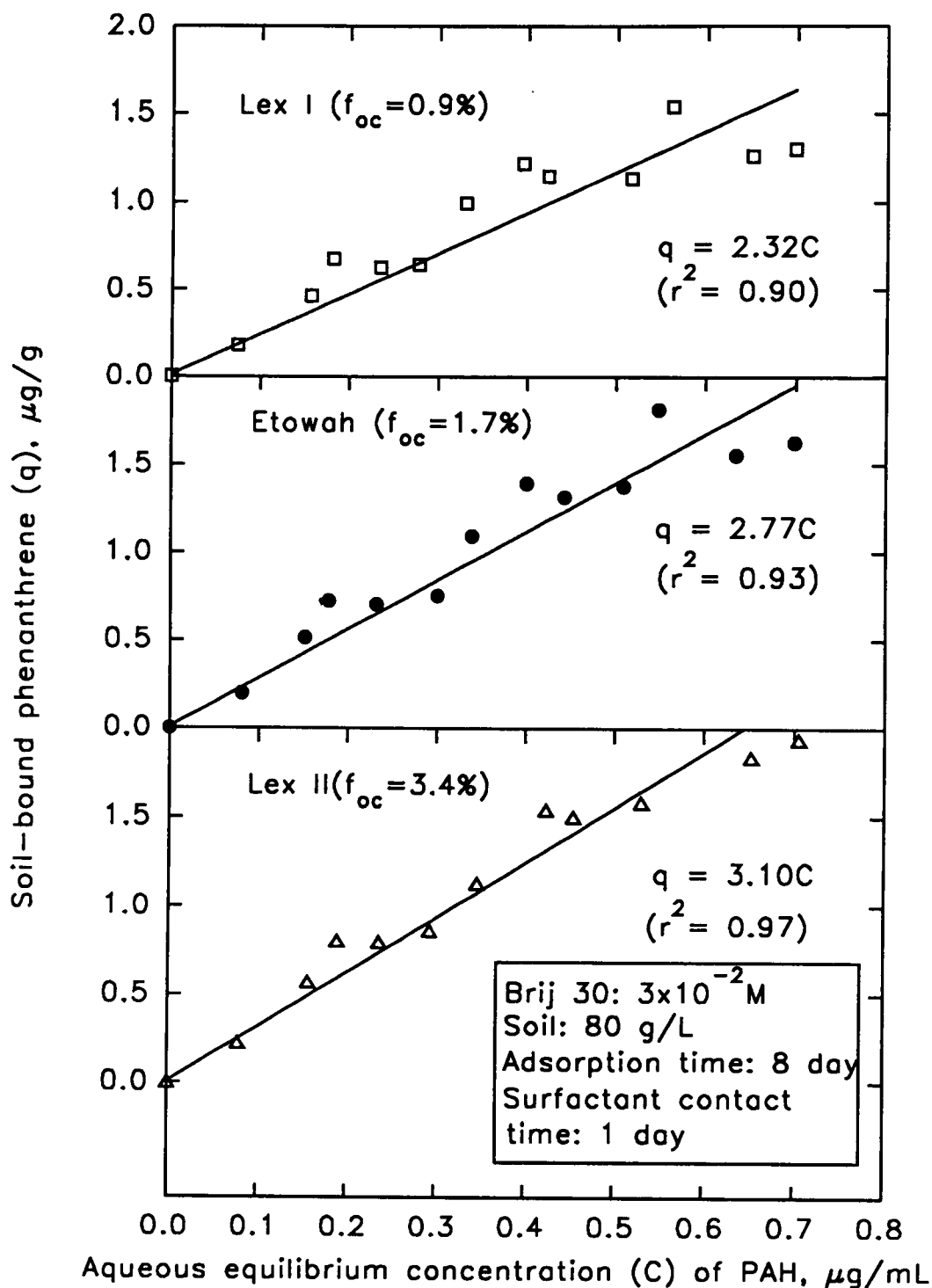


Figure 4.24 Isotherms for desorption of phenanthrene from various soils with 0.03 M Brij 30 (Soils were equilibrated for 8 days with 0.91 mg/L phenanthrene solution followed by desorption for 1 day only.)

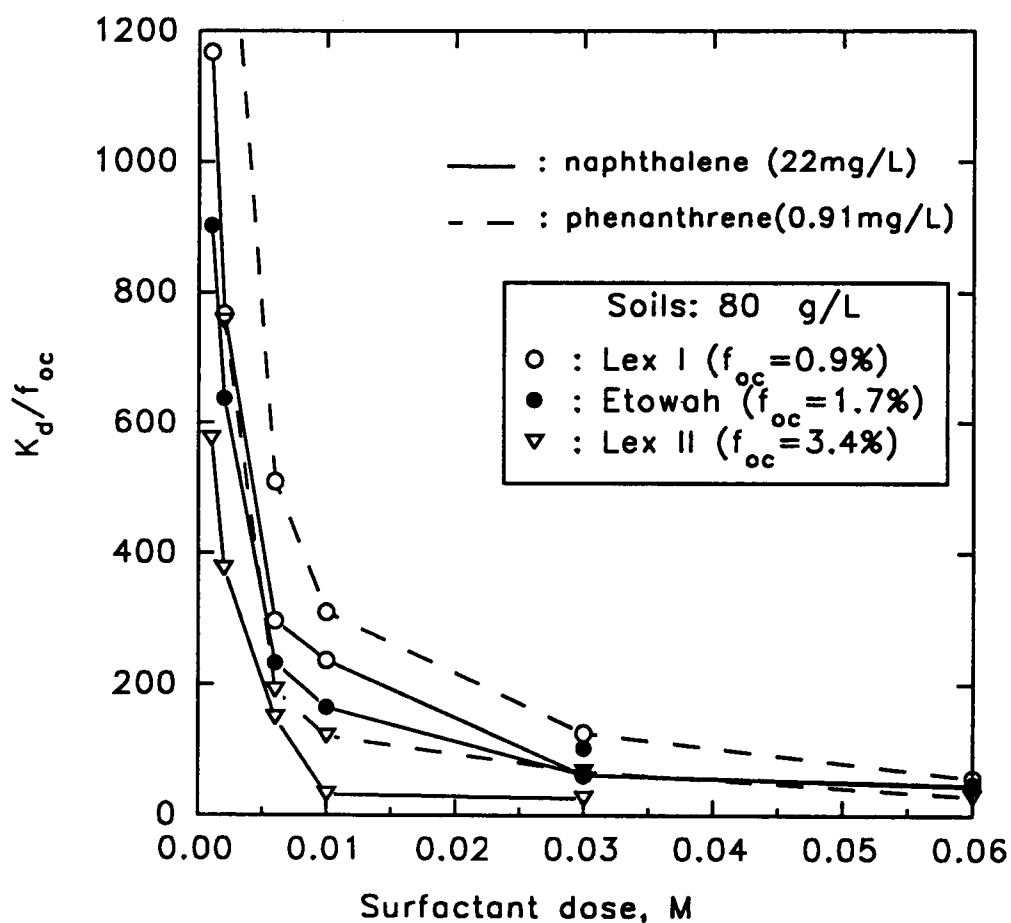


Figure 4.25 Normalized distribution of PAH desorption at various surfactant doses (soils were equilibrated with 22.8 mg/L naphthalene and 0.91 mg/L phenanthrene solutions for 1 day followed by desorption with Brij 30 for 1day.)

in achieving satisfactory desorption. However, slow, long-term release of contaminants, controlled by diffusive mass transfer, may hold the key to developing successful remediation strategies. Even for soils with a relatively short contamination age of 8 days, the difference in the distribution of desorbing PAH between water and soils of different values of f_{oc} was insignificant (Fig. 4.24). However, short-term (< 1 d) desorption kinetic studies are warranted to fully explore the relative significance of mass-transfer and equilibrium in the desorption of PAH from soil with long contamination ages.

4.3.4 Effect of Sorption Nonequilibrium

In desorbing soil-bound PAH with surfactants, it was observed that most of the PAH could be mobilized in a relatively short time. However, the last 5-10% of the contaminant showed a strong resistance to desorption regardless of the type and concentration of surfactant used. One possible explanation: occurrence of irreversible chemical reactions during adsorption. Irreversible sorption of certain fractions of the sorbate may also be responsible for the sorption-desorption hysteresis observed by some researchers (Karickhoff and Morris, 1985; Paviostathis and Jaglal, 1991). However, evidence supporting the view that the rates of sorption and desorption of chemicals in soils are controlled by diffusion is steadily increasing (Wu and Gschwend, 1986;

Brusseau et al., 1991). In the present study, 96 to 98 percent of the sorbed PAH was recovered by repeated surfactant washing, each one being of one-day duration. (Fig. 4.26). Depending on the period of adsorption of PAH on soil, defined as the "contamination age" in this study, a small but finite difference in the degree of PAH mobilization clearly exists. It is noteworthy that the amount of PAH mobilized per cycle of surfactant washing is somewhat misleading since, at the end of each 24-hr period, the "used" surfactant solution was replaced with a new one; cumulative desorption in this context merely gives the additive effect of several 1-day cycles. Essentially operated in a fill-and-draw mode, such a system hardly depicts a realistic scenario in developing remediation strategies. Nevertheless, desorption of PAH seems to be a two-step process: an initial fast step dictated primarily by partitioning coefficients, followed by a slow step controlled by diffusive mass-transfer as in the case of adsorption (Fig. 4.13a).

The efficiency of surfactant-enhanced desorption of PAH from soil may depend on the history of contamination - its contamination age, in particular. In batch experiments, soils with different organic carbon content and of different contamination ages ranging from 1 to 22 days were washed with a surfactant for 1 day and percent PAH desorbed measured. Both naphthalene and phenanthrene were used as contaminants but Brij 30 was used as the sole desorbent surfactant. Desorption

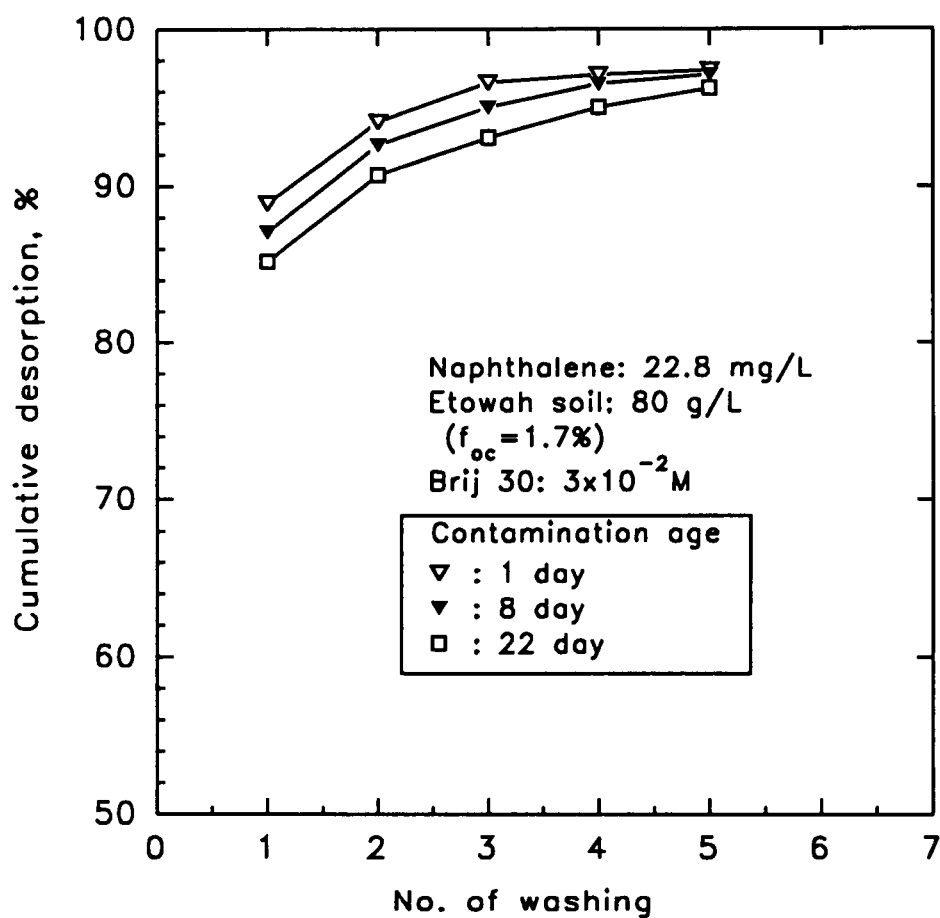


Figure 4.26 Recovery of naphthalene with repeated surfactant washings (Soils were equilibrated with naphthalene solutions for different time periods. Each washing cycle was of one-day duration.)

of phenanthrene from Lexington I soil with contaminations ages of 1, 8, and 22 days are shown as a function of surfactant dosage in Fig. 4.27. The effect of contamination age on the extent of attainable desorption is clear. Similar data for other PAH-soil systems are given in Appendix V (Figs. A.7 to A.10). Briefly, desorption decreased with increased contamination ages and was directly related to surfactant dose; the effect of contamination age was more pronounced at large surfactant dosages. Also, as expected, the more hydrophobic (less soluble) the PAH the greater the effect of contamination age on desorption.

An attempt was made to study kinetics of desorption over a 30-day period using a soil contaminated with phenanthrene (Etowah soil equilibrated to 0.91 mg/L phenanthrene solution for 22 days) and Brij 30 as the desorbent surfactant. The results are shown in Fig. 4.28. Unfortunately, no data were collected during the first 24-hr period of desorption. Almost 65% of the phenanthrene was desorbed in one day. But desorption continued, albeit slowly, for the entire 30-day study period reaching 78% on the 30th day. This is clear evidence of a rate-limited nonequilibrium desorption process which may control the release of phenanthrene from soil over a long period.

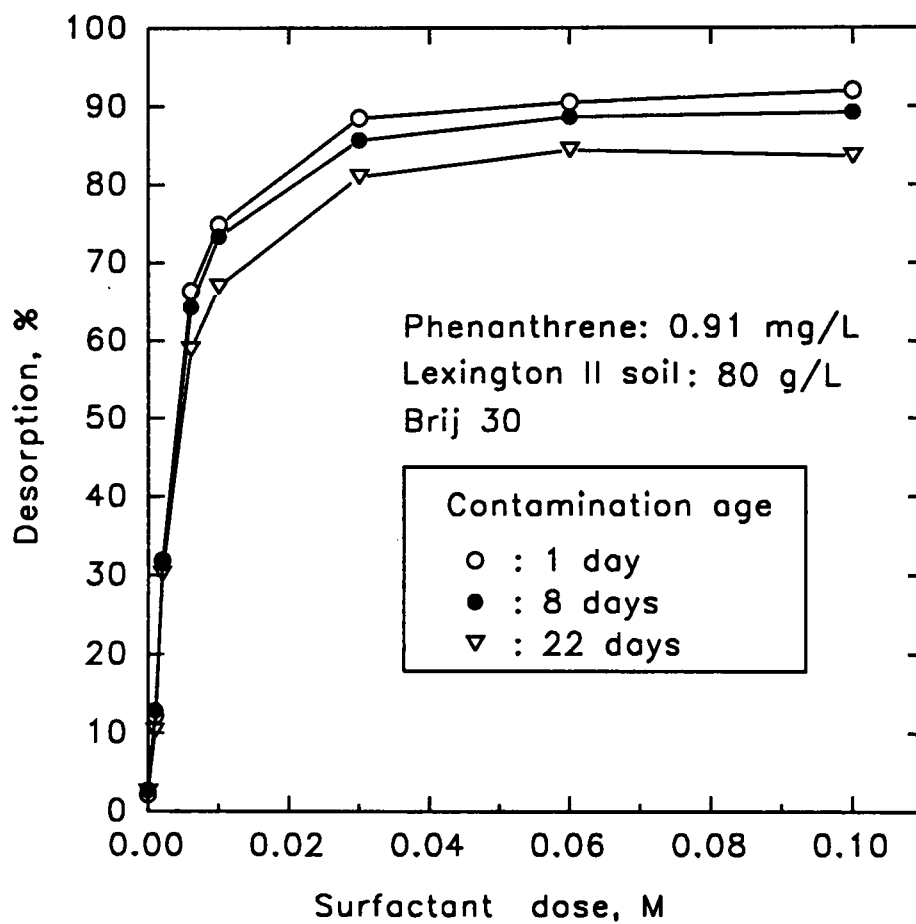


Figure 4.27 One-day desorption of phenanthrene from Lexington II soil with different contamination ages

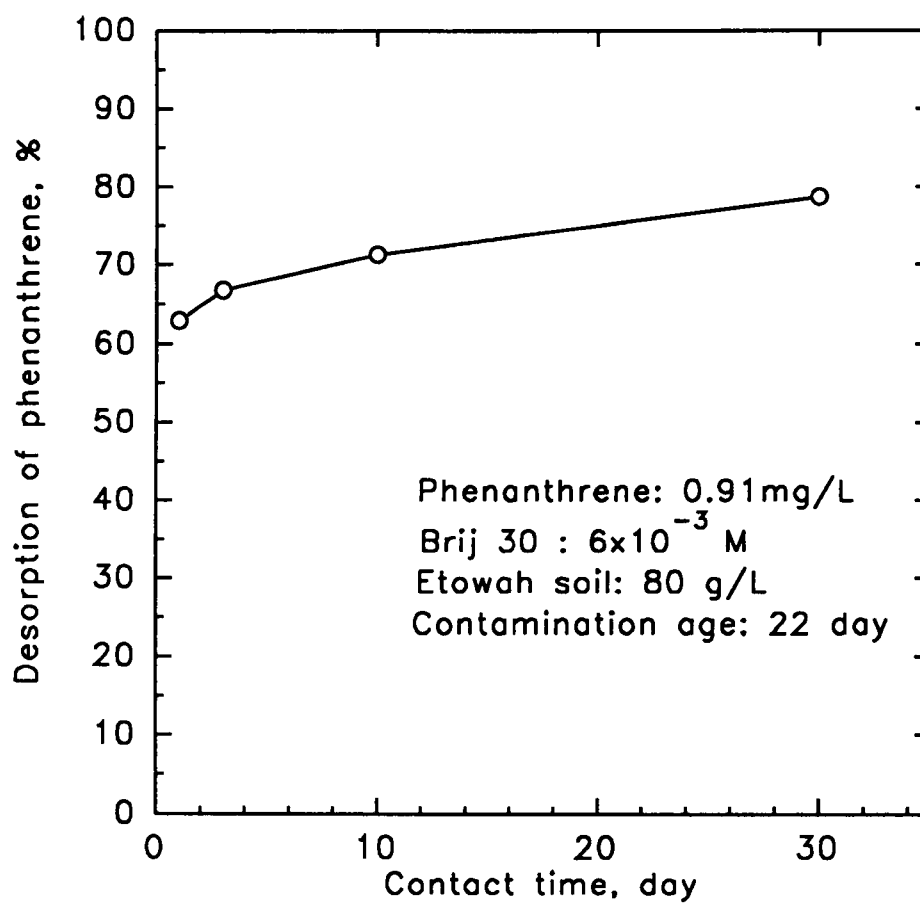


Figure 4.28 Effect of contact time on desorption of phenanthrene from Etowah soil with Brij 30

4.4 MODELING OF PAH DESORPTION

To date, most quantitative models for describing distribution of PAH compounds in various environmental compartments have considered only equilibrium partitioning. However, in the face of mounting evidence that the distribution of most hydrophobic organic compounds in the environment may be controlled by diffusive mass-transfer, attention has been shifted to kinetic models. An attempt was made to evaluate some existing models for both equilibrium partitioning and diffusive mass transfer in the light of the experimental results obtained in the present study.

4.4.1 Equilibrium Partitioning Model

The model proposed by Edwards et al. (1991b) was used to describe equilibrium partitioning of PAH in aqueous suspension of PAH-contaminated soil and surfactant (section 2.3.3). The primary assumptions involved in this model are:

- (a) complete reversibility of solute partitioning between soil, aqueous pseudophase, and micellar phase,
- (b) relatively fast attainment of equilibrium,

In this model, the distribution of PAH between phases are described by partitioning coefficients. The values of K_m , the coefficient describing partitioning between aqueous pseudophase and micelle phase for the PAH-surfactant combinations tested, were taken from the literature (Table

2.1). The partitioning coefficient (K_p) between soil and aqueous pseudophase at a given surfactant dosage was determined separately. First, contaminated soil was mixed with surfactant at a dosage of CMC_{eff} (CMC of surfactant in soil-water system) for a period equal to the time used in a given desorption experiment (one day in most cases). $K_{p,cmc}$ was then determined from the measured concentration of PAH in aqueous pseudophase. $K_{p,cmc}$ value was further corrected for $f_{oc,cmc}$ and f'_{oc} , the modified soil organic carbon content at a surfactant dosage of CMC_{eff} and at a given surfactant dosage, obtained from Table 4.3. From these values, the partitioning coefficient (K_p) of PAH in soil-water-surfactant system, at a given surfactant dosage, was calculated:

$$K_{p,cmc}' = K_{p,cmc} [f'_{oc}/f_{oc,cmc}] \quad (4.1)$$

From Eqs. 2.33 and 2.34, the PAH concentration in aqueous pseudophase and the percent desorption of PAH, respectively, were calculated for each surfactant dose. The experimental results for desorption of phenanthrene and naphthalene after one day of contact with Brij 30 are compared with model predictions in Figs. 4.29 and 4.30, respectively. For phenanthrene, satisfactory correspondence between measured and predicted values were obtained, at least in soils of recent contamination history (1 day). In such soils, most of the sorbed PAH is readily amenable to desorption; therefore, the

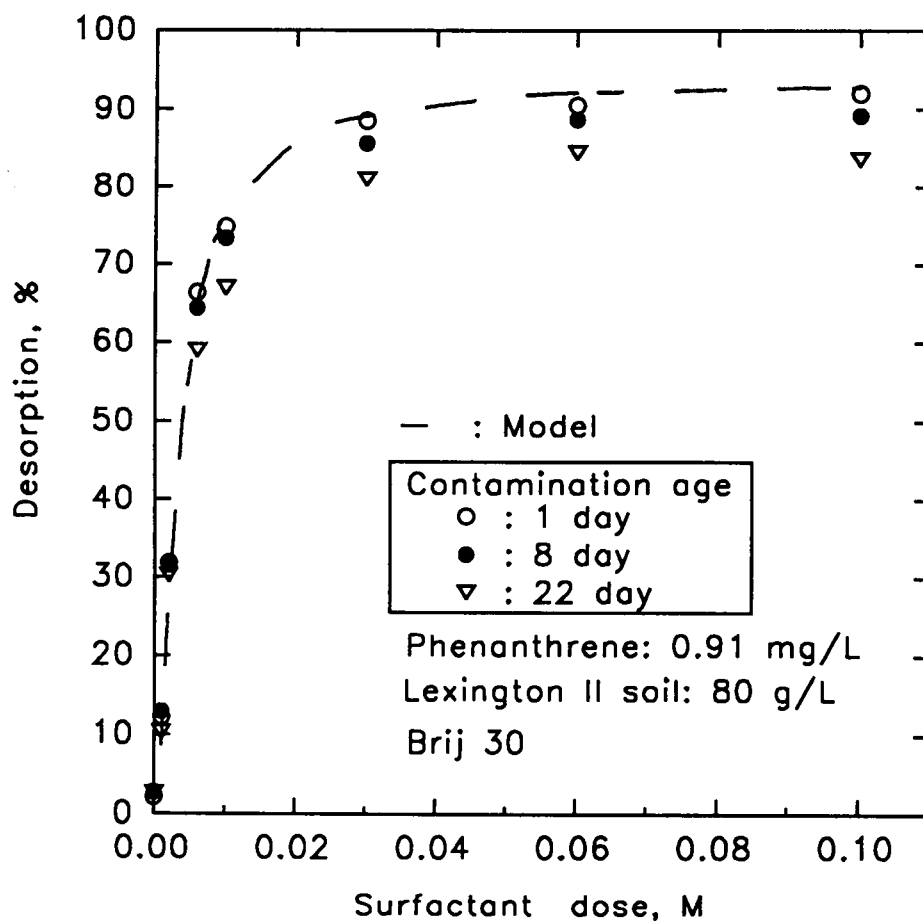


Figure 4.29 Comparison of theory and experiment using equilibrium model (contaminated soil equilibrated to Brij 30 for 1 day only)

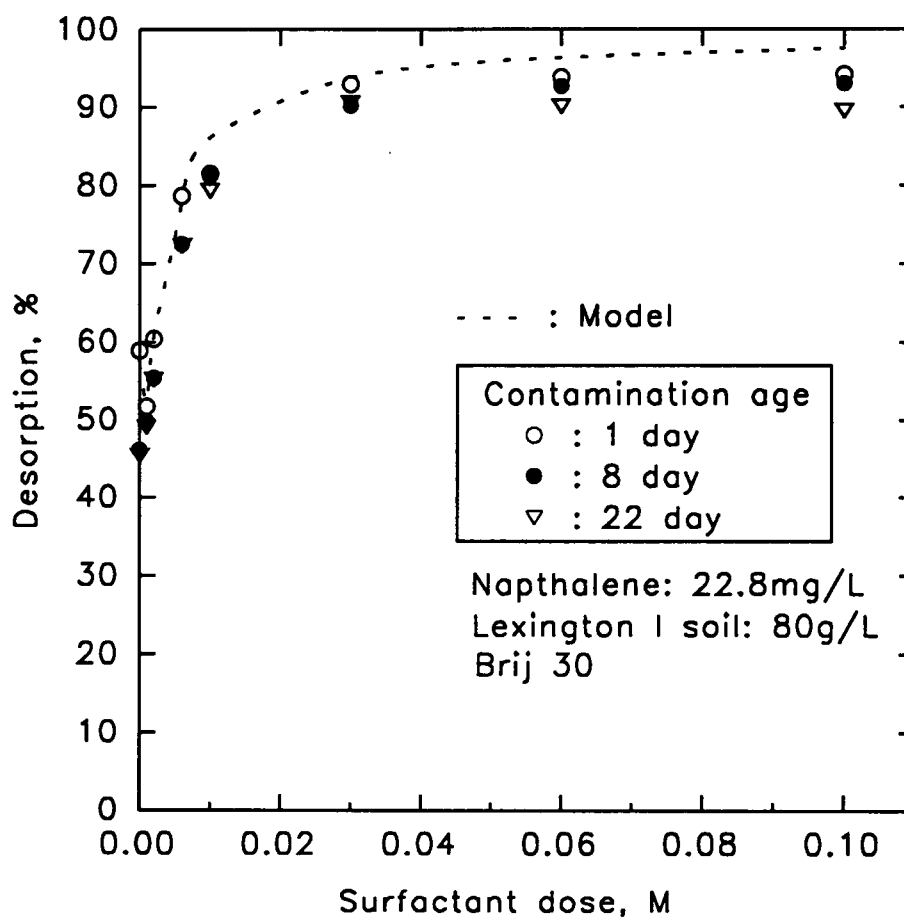


Figure 4.30 Comparison of theory and experiment using equilibrium model (contaminated soil equilibrated to Brij 30 for 1 day only)

basic assumption - fast attainment of equilibrium - is valid. Clearly, as the contamination age increases, equilibrium model overestimates the performance of surfactant, especially at high surfactant dosages - almost by 10 percent at a dosage of 0.1 M in soils contaminated 22 days since. The effect of nonequilibrium is most pronounced for desorption of the last traces of phenanthrene. Further as shown in Fig. 4.28, phenanthrene desorption after one day of washing with 0.06 M surfactant solution represents no more than 80 % of the expected equilibrium value. Obviously, the model can not appropriately estimate the desorption efficiency for relatively short periods of surfactant-washing of soils with contamination ages; conceivably, measured desorption could approach predicted values after a long period. Additional studies are needed to underscore the kinetics of desorption over long periods of time. Nonetheless, mass transfer limitations could cause significant retardation of desorption while remediating sites with a contamination age of months or years; the equilibrium partitioning model would most often overestimate desorption even when chemicals are used for soil washing.

For naphthalene, the model predicts higher desorption even in soils with only one-day old contamination. This discrepancy may be attributed to the volatilization loss of naphthalene during preparation of contaminated soil; the actual amount of sorbed naphthalene at the start of desorption

experiment might have been smaller than calculated.

4.4.2 Radial Diffusion Model

Mathematical models developed to date for describing the rate of sorption of HOC on soils fall in two different categories: diffusion and mass-transfer. Though the rate-limiting mechanisms are different for these models - intraparticle diffusion in the former and intraorganic matter diffusion in the latter, the mathematical forms of the models remain unchanged. Despite their differences, congruence of experimental results with either of the two types of models may not shed any light on the exact mechanism. A brief comparison of these models were made earlier (section 2.1.2). Arguably, intraparticle diffusion models (Karickhoff and Morris, 1985; Wu and Gschwend, 1986) appear to be somewhat more realistic, assumptions notwithstanding. The radial diffusion model of Wu (1986) (Appendix VI) was used in the present study to evaluate the kinetics of PAH transport in soil; only the results of phenanthrene adsorption and desorption were analyzed. Developed for hydrophobic solutes in soil-water systems, the model has been used in the present study to describe both adsorption and surfactant-enhanced desorption of PAH; appropriate estimates of effective diffusivity (D_{eff}) of phenanthrene in the soil-water-surfactant milieu was used.

In this model, the soil particles are assumed to be

spherical and the transport of hydrophobic solute is described by radial diffusion through spherical aggregates. The distribution of solute (sorbate) in soil (sorbent) is given by $S(r)$, its local volumetric concentration in soil as a function of radial distance r from the center of the aggregate. The effective diffusivity (D_{eff}) of solute in soil micropore is a function of several parameters (Eq. 2.12): molecular diffusivity in aqueous solution (D_m), intra-aggregate porosity (n), dry soil density (ρ_s), and soil-water partitioning coefficient (K_p). Since size of test soil particles spanned one to two orders of magnitude (1-150 μm), particle size distribution (PSD), instead of a representative size, was used.

Adsorption of phenanthrene

In performing numerical analysis of adsorption, it was found that grid size, incremental distance in the aggregate, had a significant effect on the outcome of analysis during early period of adsorption (< 1 hr); large grid sizes produced erroneously high values. However, for times greater than 1 hr, the grid size did not make any substantial difference in program output. Depending on the required accuracy and the specific time of adsorption, grid size can be adjusted. Since, in this study, phenanthrene adsorption data were collected for times as small as minutes, a relatively large number of grid (40) was used. Fig. 4.31 shows a comparison of the model with

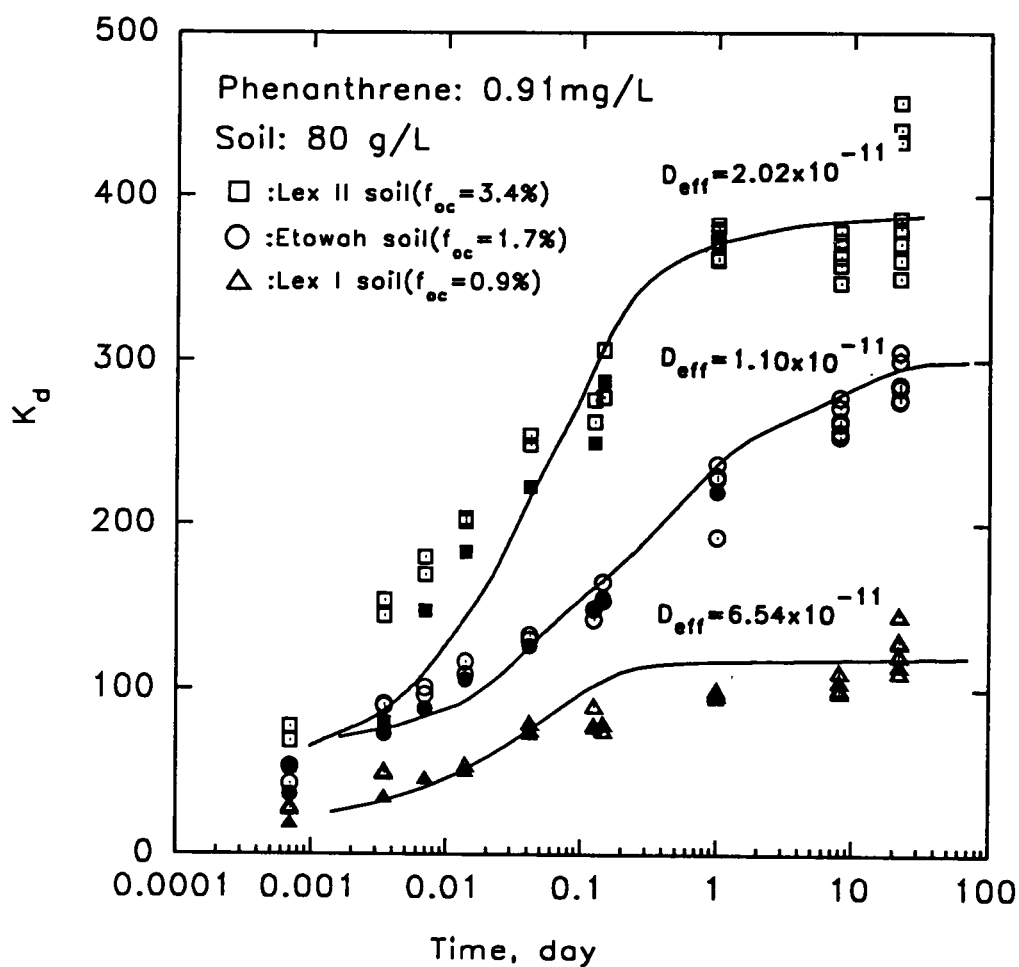


Figure 4.31 Comparison of experiment and model prediction of partitioning during adsorption using radial diffusion model

(● ▲ ■ : results obtained by filtration,
○ △ □ : results obtained by centrifugation)

experiment; a satisfactory correspondence was obtained. The effective diffusivity, D_{eff} , was the only fitting parameter used for model calibration; the calibrated value of D_{eff} was 6.54×10^{-11} , 1.1×10^{-11} , and 2.02×10^{-11} cm/sec for Lexington I, and Etowah, and Lexington II soils, respectively. Etowah soil showed the highest retardation although its f_{oc} values were less than that of Lexington II soil. Intraparticle porosities (n) were calculated from D_{eff} values using Eq. 2.12 to estimate retardation of solute transport due to soil geometry. The molar diffusivity (D_m) of phenanthrene was calculated using the Wilke-Chang equation (Wilke and Chang, 1955) and found to be 5×10^{-6} cm/sec for phenanthrene. Apparent distribution coefficient (K_d) of phenanthrene after 22-day of adsorption (Fig. 4.13) was taken as the first estimate of the equilibrium partitioning coefficient (K_p). Interestingly, it was found to be 0.06 for both Lexington soils, regardless of their much different organic carbon contents, and 0.04 for the Etowah soil. These values are quite low compared to those reported by Wu and Gschwend (1986): 0.07-0.17. Given the paucity of geophysical data available, no immediate explanation can be given for the observed difference. Possibly, this was due to high microscale retardation caused by the specific geometry of soil micropore other than n .

Surfactant-mediated desorption of phenanthrene

In analyzing data for desorption of phenanthrene using

Brij 30, a modified value of partitioning coefficient ($K_{p,sur}$) was used for the partitioning of the PAH between soil and bulk solution. $K_{p,sur}$ is defined by independently measurable parameters: K_{oc} , f_{oc} , K_m and micelle concentration (C_M), as shown in Eq. 4.2 (Jafvert, 1991b):

$$K_{p,sur} = K_{oc}f_{oc}/[1.0 + K_m(C_M)] \quad (4.2)$$

It should be noted that f_{oc} and hence $K_{p,sur}$ were corrected for the adsorption of surfactant. The effect of surfactant on D_{eff} is not obvious: n and/or D_m may decrease in the presence of surfactant monomers. On the other hand, a significant increase in D_{eff} may result from solubility enhancements. No method could be found to quantify these effects satisfactorily. D_{eff} was used as a fitting parameter in fitting kinetic data for surfactant-enhanced desorption. Since, in this study, all desorption data were obtained for a reaction time of one day or larger, a grid number of only 10 was used for model calibration. Etowah soil contaminated with 0.91 mg/L phenanthrene was washed with 0.03 M solution of Brij 30 for 30 days and the amount of phenanthrene desorbed measured as a function of time. The corresponding values of the apparent distribution coefficient (K_d) plotted as a function of desorption time are compared with that predicted by the model in Fig. 4.32. The model fits the results well. D_{eff} in this system was found to be 1.35×10^{-10} cm/sec, one

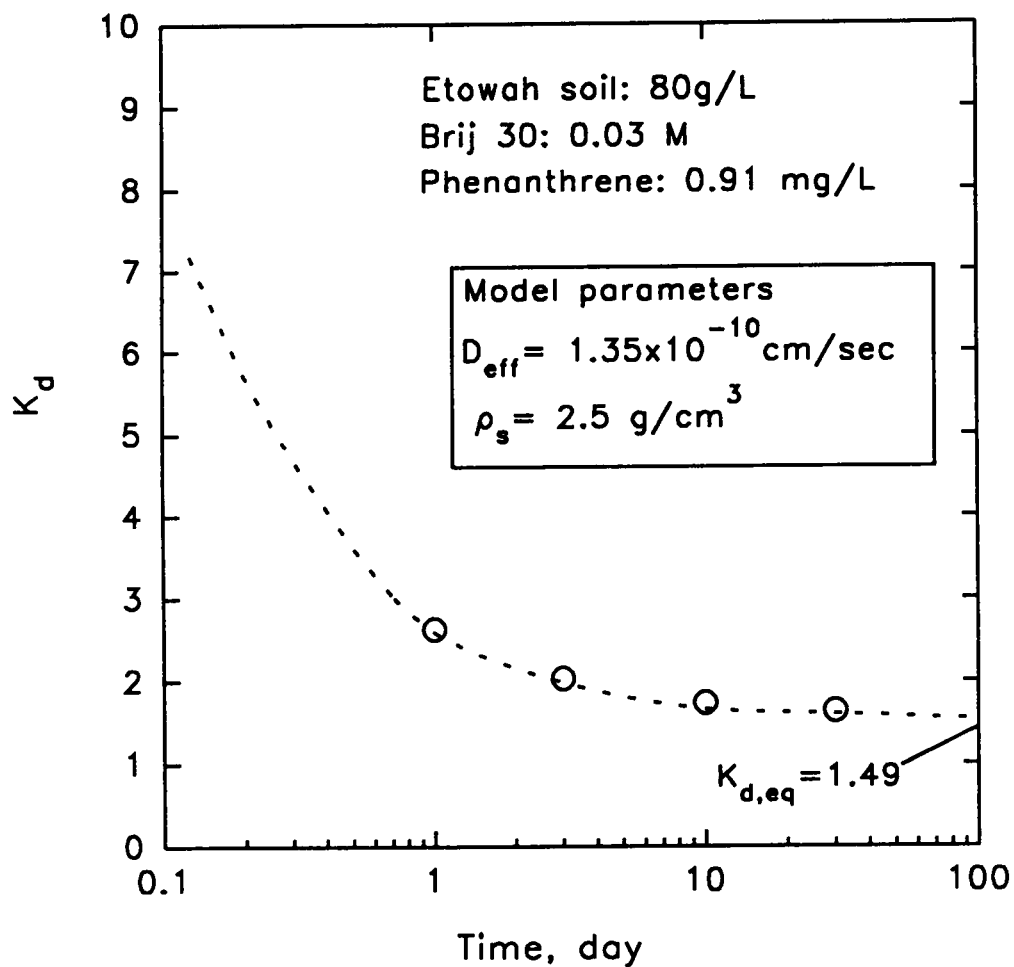


Figure 4.32 Comparison of experiment with model prediction during desorption using radial diffusion model

order magnitude higher than that in system without surfactant. Though experimental data are missing for shorter detention periods (<1 day), model predictions for reasonably long desorption periods look promising.

To analyze the desorption efficiency as a function of surfactant dose, the model was run separately for each surfactant dosage with appropriate values for $K_{p,sur}$ and n . Lexington I soil contaminated with 0.91 mg/L phenanthrene for various periods (1, 8, and 22 days) was used as the test soil in different desorption experiments with Brij 30 employed at various dosages. While $K_{p,sur}$ was calculated by Eq. 4.2 for each surfactant dose, n values were interpolated from their values determined previously: 0.04 without surfactant and 0.01 at 0.03 M surfactant solution, assuming that the decrease in n is proportional to aqueous surfactant concentration. Though not attempted in this study, the efficiency of the model may be improved by adding a recursive algorithm for calculation of $K_{p,sur}$ and D_{eff} values for each surfactant dose. Then, additional inputs such as range of surfactant dose, number of data points, amount of surfactant sorption, and corrected n values will be required. The model prediction of one-day desorption of phenanthrene from Lexington I soil, contaminated with 0.91 mg/L phenanthrene for 22 days, was excellent (Fig. 4.33). For soils with long contamination history, good correspondence of model with experimental data results from the equilibrium boundary condition of the model: at

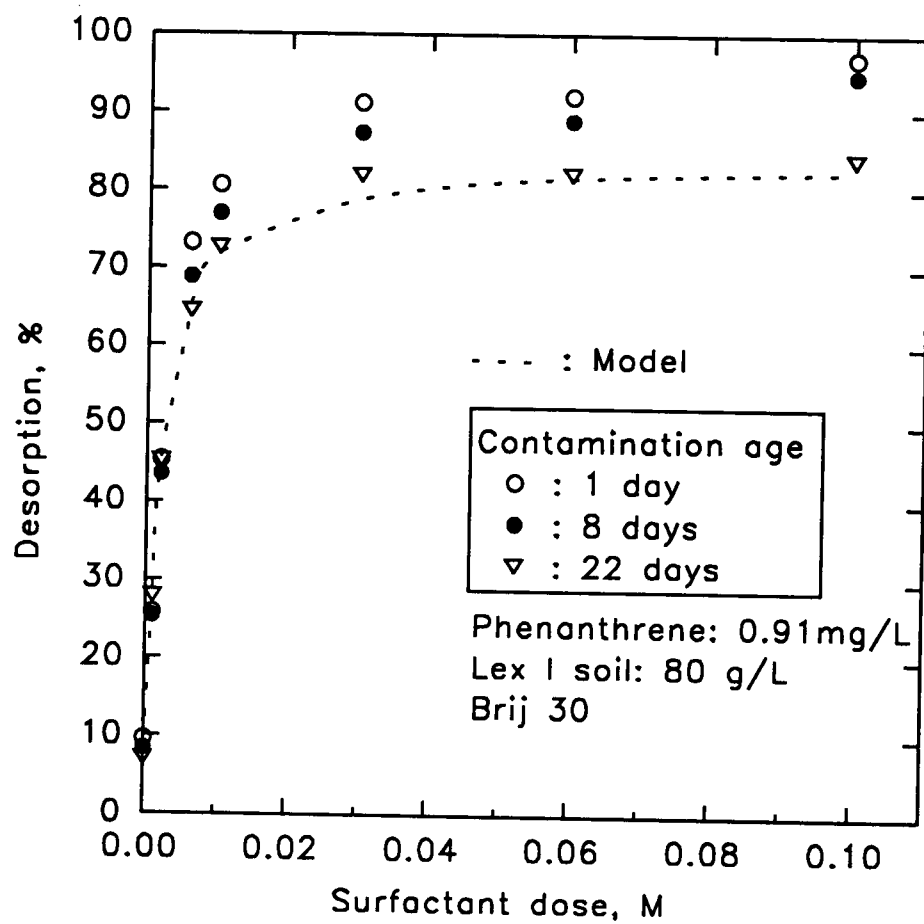


Figure 4.33 Comparison of theory and experiment using radial diffusion model (contaminated soil equilibrated to Brij 30 for 1 day only)

equilibrium, the model assumes a uniform distribution of solute on soil. Therefore, best congruence may be expected where the solute is at or near equilibrium with soil at the beginning of desorption. As shown earlier (Fig. 4.31), phenanthrene was at equilibrium with Lexington soils after about 22 days, and hence, its distribution on the soils was uniform.

A comparison of equilibrium partitioning and radial diffusion models, as illustrated in Figs. 4.29 and 4.33, respectively, reveals that, while the former describes the upper limit of surfactant-mediated desorption, the latter describes the lower limit of the same. Neither model, however, can singly describe desorption from soils with different contamination histories in a comprehensive manner. It may be appropriate to use radial diffusion model in surfactant-aided remediation of field sites which, by and large, have long contamination ages.

In spite of satisfactory prediction obtained with the limited amount of data available, further work is warranted to evaluate the diffusion model, especially for short adsorption/desorption periods; factors affecting high retardation of desorption during initial periods need to be determined; assumptions involved in the estimation of model parameters such as D_{eff} or n in the presence of surfactant need to be verified.

CHAPTER 5. CONCLUSIONS

The effectiveness of nonionic surfactants in mobilizing PAH compounds bound to soils were examined in this study; the effect of nonequilibrium kinetics of PAH sorption/desorption was also examined. Only a preliminary analysis of rates of PAH binding and desorption in soil systems could be made with the limited amount of data available. Further research on kinetics of PAH adsorption and surfactant-induced desorption over extended periods of time (up to months) at various surfactant concentrations is needed to understand the nature of kinetically limited mass transfer and partitioning equilibrium in these systems. Moreover, to accurately estimate the effect of particle size on rate, desorption of PAH with surfactants should be investigated in more detail using soils of different geometric mean particle size (GMD), and a narrow particle size distribution (PSD).

Other important issues concerning the use of surfactant in aquifer restoration include the bioavailability of solubilized PAH and the toxicity of surfactants. If surfactants are used in bioremediation of contaminated aquifers, their optimum dosage must be based on several parameters - toxicity, solubilization efficiency, and extent of sorption on soil, among others. Biodegradation of mobilized PAH increases the complexity of the system and

requires the construction of more complicated models to evaluate the net effect of surfactant dose on environment. Conceivably, several separate models namely, intra-aggregate diffusion of PAH, solubilization of PAH by surfactant, surfactant sorption, and biodegradation of solubilized PAH, may be combined to develop a general purpose model.

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

1. The sorption of humic acid (AHA) on hematite, a low-porosity mineral, can be explained by ligand exchange between carboxylic groups on the humic acid and hydroxylic groups on the mineral. Over the mass percent carbon range of 0.008-0.455%, the sorption of naphthalene on the AHA-coated mineral varied directly with the amount of sorbed AHA. The corresponding K_{oc} value for naphthalene compares well with those reported in the literature. The CMC of surfactant in aqueous solution increased in the presence of AHA-coated hematite indicating adsorption of surfactant on soil. Both naphthalene and nonionic surfactants were poorly adsorbed on hematite. Seventy-five percent of the naphthalene sorbed on AHA-coated hematite could be washed off with DI water. Of the remainder, 45% could be desorbed with surfactants.

2. Nonionic surfactants could mobilize 90% or more of the soil-bound PAHs in a relatively short time (< 1 day); but, surfactant dosages much in excess of CMC were required. At low dosages (<0.01 M), PAH desorption increased dramatically with increasing surfactant concentration. However, additional surfactant could improve desorption by no more than 10-15%.
3. The micellar surfactant (Igepal CA-720) desorbed more of the soil-bound PAHs than the lamellar surfactant (Brij 30). However, at concentrations greater than 0.06 M, the performance of these two surfactants was nearly equal.
4. The apparent distribution coefficient (K_d) for the desorbing PAH in a surfactant-mediated system strongly correlated with the f_{oc} of soil. The organic carbon-normalized distribution coefficient K_{oc} decreased as f_{oc} increased with increasing surfactant dose.
5. Desorption of PAH seems to proceed in two steps: a fast equilibrium partitioning followed by slow mass-transfer presumably by intra-aggregate diffusion. Short-term desorption (< 1 day) was inversely related to the contamination age of soil. The last 10-20% of the adsorbed PAH is the most difficult to desorb. Desorption

of this fraction depends strongly on the period of adsorption during the contamination phase and also the period of desorption.

6. The efficiency of surfactant-mediated desorption of PAH from soil cannot be satisfactorily described by equilibrium partitioning models, especially during initial periods, in soils with long contamination ages. Radial diffusion model seems to better predict such processes.

REFERENCES

REFERENCES

- Abdul, A. S. and Gibson, T. L. (1991). Laboratory Studies of Surfactant-Enhanced Washing of Polychlorinated Biphenyl from Sandy Material. Environ. Sci. Technol., 25, 665.
- Alexander, M. (1981). Biodegradation of Chemicals of Environmental Concern. Science, 221, 132.
- American Society of Agronomy. (1965). Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties. ASA, Inc., Madison, Wis.
- Aronstein, B. N., Calvillo, Y. N. and Alexander, M. (1991). Effect of Surfactants at Low Concentrations on the Desorption and Biodegradation of Sorbed Aromatic Compounds in Soil. Environ. Sci. Technol., 25, 1728.
- Aston, J. R., Lane, J. E. and Healy, T. W. (1989). The Solution and Interfacial Chemistry of Nonionic Surfactants Used in Coal Flotation. Min. Process. and Extract. Metallurgy Review, 5, 229.
- Atwood, D. and Florence A.T. (1983). Surfactant Systems: Their Chemistry, Pharmacy and Biology, Chapman and Hall, Inc., New York, NY.
- Ball, W. P. (1989). Ph. D. Dissertation, Stanford University, Stanford, CA.
- Ball, W. P. and Roberts, P. V. (1985). Rate-limited Sorption of Halogenated Aliphatics onto Sandy Aquifer Material-Experimental Results and Implications for Solute Transport. ES, 66, 894.
- Ball, W. P. and Roberts, P. V. (1991a). Long-Term Sorption of Halogenated Organic Chemicals by Aquifer Material. 1. Equilibrium. Environ. Sci. Technol., 25, 1223.
- Ball, W. P. and Roberts, P. V. (1991b). Long-Term Sorption of Halogenated Organic Chemicals by Aquifer Material. 2. Intraparticle Diffusion. Environ. Sci. Technol., 25, 1237.
- Benedouch, D., Chen, S-H. and Koehler, W. C. (1983). Structure of Ionic Micelles from Small Angle Neutron Scattering. J. Phys. Chem., 87, 153.
- Brusseau, M. L., Jessup, R. E. and Rao, P. S. C. (1991). Nonequilibrium Sorption of Organic Chemicals: Elucidation of Rate-Limiting Processes. Environ. Sci. Technol., 25, 134.

Brusseau, M. L. and Rao, P. S. C. (1989). Sorption Nonideality During Organic Contaminant Transport in Porous Media. CRC Crit. Rev. Environ. Control, 19, 33.

Carroll, B. J. (1981). The Kinetics of Solubilization of Nonpolar Oils by Nonionic Surfactant Solutions. J. Colloid Interface Sci., 79, 126.

Chin, Y. P. and Weber, Jr. W. J. (1989). Estimating the Effect of Dispersed Organic Polymers on the Sorption of Contaminants by Natural Solids. 1. A Predictive Thermodynamic Humic Substance-Organic Solute Interaction Model. Environ. Sci. Technol., 23, 978.

Chiou, C. T., Peters, L. J. and Freed, V. H. (1979). A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds. Science, 206, 831.

Chiou, C. T., Kile, D. E., Brinton, T. I., Malcolm, R. L. and Leenheer, J. A. (1987). A Comparison of Water Solubility Enhancements of Organic Solutes by Aquatic Humic Materials and Commercial Humic Acids. Environ. Sci. Technol., 21, 1231.

Clunie, J. S. and Ingram, B. T. (1983). Adsorption of Nonionic Surfactants. In Adsorption from Solution at the Solid/Liquid Interface, Parfitt, G. D. and Rochester, C. H., Eds. Academic Press, Inc., London, pp105-152.

Compeau, G. and Mahaffey, W. D. (1990). Full-scale Bioremediation of Contaminated Soil and Water. Presented at the Symposium on Environmental Biotechnology. Knoxville, TN.

Curtis, G. P., Roberts, P. V. and Reinhard, M. (1986). A Natural Gradient Experiment on Solute Transport in a Sand Aquifer. IV. Sorption of Organic Solutes and Its Influence on Mobility. Water Resour. Res., 22, 2059.

DiToro, D. M., Dodge, L. J. and Hand, V. C. (1990). A Model for Anionic Surfactant Sorption. Environ. Sci. Technol., 24, 1013.

Edwards, D. A., Luthy, R. G. and Liu, Z. (1991a). Solubilization of Polycyclic Aromatic Hydrocarbons in Micellar Nonionic Surfactant solutions. Environ. Sci. Technol., 25, 127.

Edwards, D. A., Liu, Z. and Luthy, R. G. (1991b). Surfactant-Enhanced Solubility of Hydrophobic Organic Compounds in Water and in Soil-Water Systems. In Organic Substances and Sediments in Water: vol.2. Processes and Analytical., Baker, R. A. Eds. Lewis Publishers, Inc., Chelsea, MI. pp.383-405.

Freeze, R. A. and Cherry, J. A. (1979). Groundwater, Prentice Hall, Inc, Englewood Cliffs, NJ.

Ghosh, M. M. and Yuan, J. R. (1987). Adsorption of Inorganic Arsenic and Organoarsenicals on Hydrous Oxides. Env. Prog., 6, 150.

Halle, B. and Carlstrom, G. (1981). Hydration of Ionic Surfactant Micelles from Water Oxygen-17 Magnetic Relaxation. J. Phys. Chem., 85, 2142.

Hasset, J. J., Means, J. C., Barnwart, W. L. and Wood, S. G. (1980). Sorption Properties of Sediments and Energy-Related Pollutants. U.S. Environmental Protection Agency, No. EPA-600/3-80-041.

Hayase, K. and Hayano, S. (1977). Bull. Chem. Soc. Japan. 50, 83.

Hunter, R. J. (1987). Foundation of Colloid Science, Clarendon Press, Inc., Oxford, Vol. 1.

Jafvert, C. T. (1991a). Sediment- and Saturated-Soil-Associated Reactions Involving an Anionic Surfactant (Dodecylsulfate). 1. Precipitation and Micelle Formation. Environ. Sci. Technol., 25, 1031.

Jafvert, C. T. (1991b). Sediment- and Saturated-Soil-Associated Reactions Involving an Anionic Surfactant (Dodecylsulfate). 2. Partitioning of PAHs. Environ. Sci. Technol., 25, 1039.

Karickhoff, S. W. (1980). Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments., Vol. 2, Baker, R. A., Eds., Ann Arbor Science, Inc., Ann Arbor, MI., chap. 11.

Karickhoff, S. W. (1981). Semi-empirical Estimation of Hydrophobic Pollutants in Natural Sediments. Chemosphere. 10, 833.

Karickhoff, S. W. (1984). Organic Pollutant Sorption in Aquatic Systems. J. Hydraulic Engr. ASCE. 110, 707.

Karickhoff, S. W., Brown, D. S. and Scott, T. A. (1979). Sorption of Hydrophobic Pollutants on Natural Sediments. Water Res., 13, 241.

Karickhoff, S. W. and Morris, K. R. (1985). Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions. Environ. Tox. Chem., 4, 469.

Kile, D. E. and Chiou, C. T. (1989). Water Solubility Enhancement of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration. Environ. Sci. Technol., 23, 832.

Kummert, R. and Stumm, W. (1980). The Surface Complexation of Organic Acids on Hydrous $\gamma\text{Al}_2\text{O}_3$. J. Colloid Interface Sci., 75, 373.

Leo, A., Hansch, C. and Elkins, D. (1971). Partitioning Coefficients and Their Uses. Chemical Reviews, Vol. 71, No. 6, 525.

Liu, Z., Edwards, D. A. and Luthy, R. G. (1991a). Sorption of Nonionic Surfactants onto Soil. Unpublished.

Liu, Z., Laha, S. and Luthy, R. G. (1991b). Surfactant Solubilization of Polycyclic Aromatic Hydrocarbon Compounds in Soil-Water Suspensions. Wat. Sci. Technol., 23, Kyoto, 475.

Mackay, D. and Shin, W-Y. (1974). The Aqueous Solubility and Air-Water Exchange Characteristics of Hydrocarbons Under Environmental Conditions. Chemistry and Physics of Aqueous Gas Solutions., American Society Testing Materials, Philadelphia, Pa., pp.104-108.

McDermont, J. B. et al. (1989). Two Strategies for PCB Soil Remediation: Biodegradation and Surfactant Extraction. Env. Prog., 8, 46.

Mitchell, D. J., Tiddy, G. J. T., Waring, L., Bostock, T. and McDonald, M. P. (1983). Phase Behavior of Polyoxyethylene Surfactants with Water. J. Chem. Soc. Faraday Trans. 1. 79, 975.

Mueller, J. B., Chapman, P. J., Pritchard, P. H. (1989). Environ. Sci. Technol., 23, 1197.

Murphy, E. M., Zachara, J. M. and Smith, S. C. (1990). Influence of Mineral-Bound Humic Substances on the Sorption of Hydrophobic Organic Compounds. Environ. Sci. Technol., 24, 1507.

Oliver, B. G. (1985). Desorption of Chlorinated Hydrocarbons from Spiked and Anthropogenically Contaminated Sediments. Chemosphere, 14, 1087.

Ogram, A. V., Jessup, R. E., Ou, L. T. and Rao, P. S. C. (1985). Effect of Sorption on Biological Degradation Rates of (2,4-Dichlorophenoxy) Acetic Acid on Soils. Appl. Env. Micro., 49, 582

- Pavlostathis, S. G. and Jaglal, K. (1991). Desorptive Behavior of Trichloroethylene in Contaminated Soil. Environ. Sci. Technol., 25, 274.
- Pennell, K. D. and Rao, P. S. C. (1992). Comment on "The Surface Area of Soil Organic Matter". Environ. Sci. Technol., 26, 402.
- Partyka, S., Zaini, S., Lindheimer, M. and Brun, B. (1984). The Adsorption of Nonionic Surfactants on a Silica Gel. Colloids Surf., 12, 255.
- Robinson, K. G., Farmer, W. S. and Novak, J. T. (1990). Availability of Sorbed Toluene in Soils for Biodegradation by Acclimated Bacteria. Water Res., 24, 345.
- Rosen, M. J. (1989). Surfactants and Interfacial phenomena, 2nd Ed. John Wiley & Sons, Inc., New York, NY.
- Saito, S. (1967). Solubilization Properties of Polymer-Surfactant Complexes. J. Colloid Interface Sci., 24, 227.
- Schwarzenbach, R. P. and Westall, J. C., (1981). Transport of Non-Polar Organic Compounds from Surface Water to Groundwater. Environ. Sci. Technol., 15, 1360.
- Tanford, C. (1980). The Hydrophobic Effect: Formation of Micelles and Biological Membranes, 2nd Ed., John Wiley & Sons, Inc., New York, NY.
- Tipping, E. (1981). The Adsorption of Aquatic Humic Substances by Iron Oxides. Geochim. Cosmochim. Acta., 45, 191.
- Tipping, E. (1982). The Effect of Adsorbed Humic Substances on the Surface Charge of Goethite (α -FeOOH) in Fresh Waters. Geochim. Cosmochim. Acta., 46, 75.
- Tokiwa, F. (1968). Solubilization Behavior of Sodium Dodecylpolyoxy -ethylene Surfactants. J. Phys. Chem., 72, 1214.
- Urano, K., Saito, M. and Murata, C. (1984). Adsorption of Surfactants on Sediments. Chemosphere, 13, 293.
- Valsaraj, K. T. and Thibodeaux, L. J. (1989). On the Estimations of Micelle-Water Partition Constants for Solutes from Their Octanol-Water Partition Constants, Normal Boiling Point, Aqueous solubilities, and Group and Bond Contribution Schemes. Water Res., 23, 183.

Valsaraj, K. T. and Thibodeaux, L. J. (1990). Relationship between Micelle-Water and Octanol-Water Partition Constants for Hydrophobic Organics of Environmental Interest. Sep. Sci. Technol., 25, 369.

Vigon, B. W. and Rubin, A. J. (1989). Practical Considerations in the Surfactant-Aided Mobilization of Contaminants in Aquifers. Jour. Water Poll. Control Fed., 61, 1233.

Westall, J. C. (1987). Adsorption Mechanisms in Aqueous Surface Chemistry. In Aquatic Surface Chemistry, Stumm, W. Eds., John Wiley & Sons, Inc., New York, NY.

Wu, S-C. (1986). Transport of Hydrophobic Organic Compounds Between Water and Natural Sediments. Ph.D. Dissertation. Department of Civil Engineering, Massachusetts Institute of Technology, Boston, MA.

Wu, S-C. and Gschwend, P. M. (1986). Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils. Environ. Sci. Technol., 20, 717.

Wu, S-C. and Gschwend, P. M. (1988). Numerical Modeling of Sorption Kinetics of Hydrophobic Compounds in Soil and Sediment Particles. Water Resour. Res., 24, 1372.

APPENDICES

Appendix I. Preparation of PAH stock solution

1. Preparation of non-labeled PAH solution

One gram of non-labeled PAH compound was added to 2 L of DI water in an 2-L Erlenmeyer flask with a screw cap, the suspension stirred for 24 hours, and filtered through a 0.22 μm sterile nylon membrane filter to remove undissolved crystals. The sterilization of the solution was also achieved by this procedure. The concentration of non-labeled stock solution was measured by a HPLC (Waters Co.) using a column from Vydac Co. (Model 201TP54) and a fluorescence detector (Waters Co.). PAH standard solutions (5 for each PAH) were prepared in methanol and standard curves obtained. The final concentrations of PAH in "saturated" solutions so defined were 22.6 mg/L and 764 $\mu\text{g/L}$ for naphthalene and phenanthrene, respectively. These concentrations are somewhat less than the reported solubilities of the compounds; presumably, the time allowed for dissolution was insufficient; also, some loss might have occurred because of binding of PAH to filter material.

2. Preparation of PAH stock solution

Labeled PAH compounds were supplied as solids by the vendor. One hundred microcurie of each PAH compound was dissolved in 20 mL of methanol. An appropriate amount (4-5 mL) of ^{14}C -labeled PAH solution was added to 2 L non-labeled PAH

solution prepared earlier to give a solution activity of about 30,000 DPM/mL. The solution was mixed thoroughly on a shaker and the final concentration of the stock PAH solution and its activity-concentration ratio were calculated by measuring the activity of the composite solution with LSC.

$$[\text{PAH}]_{\text{stock}} = [\text{PAH}]_{\text{non}} + [\text{DPM}_{\text{stock}} \times 1000 / \Phi] M_w / A_{\text{sp}} \quad (\text{A.1})$$

$$R' = \text{DPM}_{\text{stock}} / [\text{PAH}]_{\text{stock}} \quad (\text{A.2})$$

$[\text{PAH}]_{\text{stock}}$ = concentration of PAH stock solution ($\mu\text{g/L}$)

$[\text{PAH}]_{\text{non}}$ = concentration of nonlabeled PAH solution ($\mu\text{g/L}$)

$\text{DPM}_{\text{stock}}$ = activity of PAH stock solution (DPM/mL)

M_w = molecular weight of PAH compound (g/mole)

A_{sp} = specific activity of radiolabeled PAH (mCi/mmol)

R' = activity-concentration ratio

The final concentrations obtained were 22.8 mg/L for naphthalene and 908 $\mu\text{g/L}$ for phenanthrene, about 65 to 75% of their respective aqueous solubilities. The activity-concentration ratio, R' , was used to convert measured DPM values to gravimetric concentration of PAH. The volume percent of methanol in the PAH stock solution was below 0.25% and was assumed not to affect the sorption/desorption behavior of PAH (Edward et al., 1990). The stock solution was used immediately

after preparation to minimize volatilization losses. When the solution was stored for some time, the activity of the stock solution was measured just prior to sampling and the PAH concentration was corrected for any volatilization losses.

3. PAH solutions for isotherm experiment

Non-labeled PAH stock solution was diluted with DI water.

PAH solutions of various concentrations were prepared in 200-mL Erlenmeyer flasks with screw caps, then 0.4 mL of ^{14}C -labeled PAH solutions added. The final concentration of each PAH solution was calculated using Eq. A.1.

Appendix II. Volatilization loss of PAH compounds

1. Volatilization loss due to head space partitioning and/or air-leakage

Volatilization losses of only naphthalene, the more volatile of the two PAHs used in this research, were investigated. Naphthalene stock solution, 5, 10, 15, 20 and 25 mL, were added in test tubes, and the activity of solution measured before and after addition. The activity applied to each tube was determined by interpolation from these two measured values. Each tube, sealed by a screw cap lined with aluminum foil and backed by Teflon septa, was equilibrated in a rotary mixer for 2 and 30 days and the activities of solutions measured. In calculating losses, Henry's law constant of naphthalene was taken as 4.25×10^{-4} atm/(mol/m³) (Mackay and Shin, 1974). For a system of h mL headspace and v mL solution,

P_{NAP} (partial pressure of naphthalene)

= Henry's constant $\times$ (naphthalene concentration in aqueous phase)

= 4.25×10^{-4} atm/(mol/m³) $\times$ [NAP]_{aq}

= 4.25×10^{-4} [NAP]_{aq} atm

[NAP]_{air} = 4.25×10^{-4} [NAP]_{aq} mol/22.4L

= 1.897×10^{-2} [NAP]_{aq} mol/m³

Percent loss

$$\begin{aligned} &= ([\text{NAP}]_{\text{air}}h) / ([\text{NAP}]_{\text{air}}h + [\text{NAP}]_{\text{aq}}V) \\ &= (1.897 \times 10^{-2} [\text{NAP}]_{\text{aq}}h) / (1.897 \times 10^{-2} [\text{NAP}]_{\text{aq}}h + [\text{NAP}]_{\text{aq}}V) \\ &= 1.897 \times 10^{-2} (h/v) = 1.897 (h/v) (\%) \end{aligned}$$

The measured losses are compared with those calculated in Fig. A.1. The volatilization losses of naphthalene were well within those calculated by Henry's law constant. Considering the fact that the samples used in sorption/desorption test have at most 3 mL of headspace atop 25 mL aqueous solution, and that a good portion of solute PAH compound adsorbs on soil before liquid-air partitioning occurs, it is concluded that the volatilization loss due to headspace partitioning was not significant (<0.1%), even for relatively long period of time (1 month). It is also obvious that PAH losses due to other factors such as air-leakage, biodegradation, and sorption on glass wall or lining material, were negligible.

2. Volatilization loss during sampling or transferring

Collection and transfer of samples were conducted under a hood. Since the PAH stock solution was exposed to fresh air during consecutive pipettings of 25-mL samples, volatilization of PAH from the stock solution was unavoidable. A 6.3% loss of stock naphthalene solution was found to occur in 5 minutes from an open 2-L Erlenmeyer flask with a volatilization surface area of 0.025 cm²/mL. From this data and other

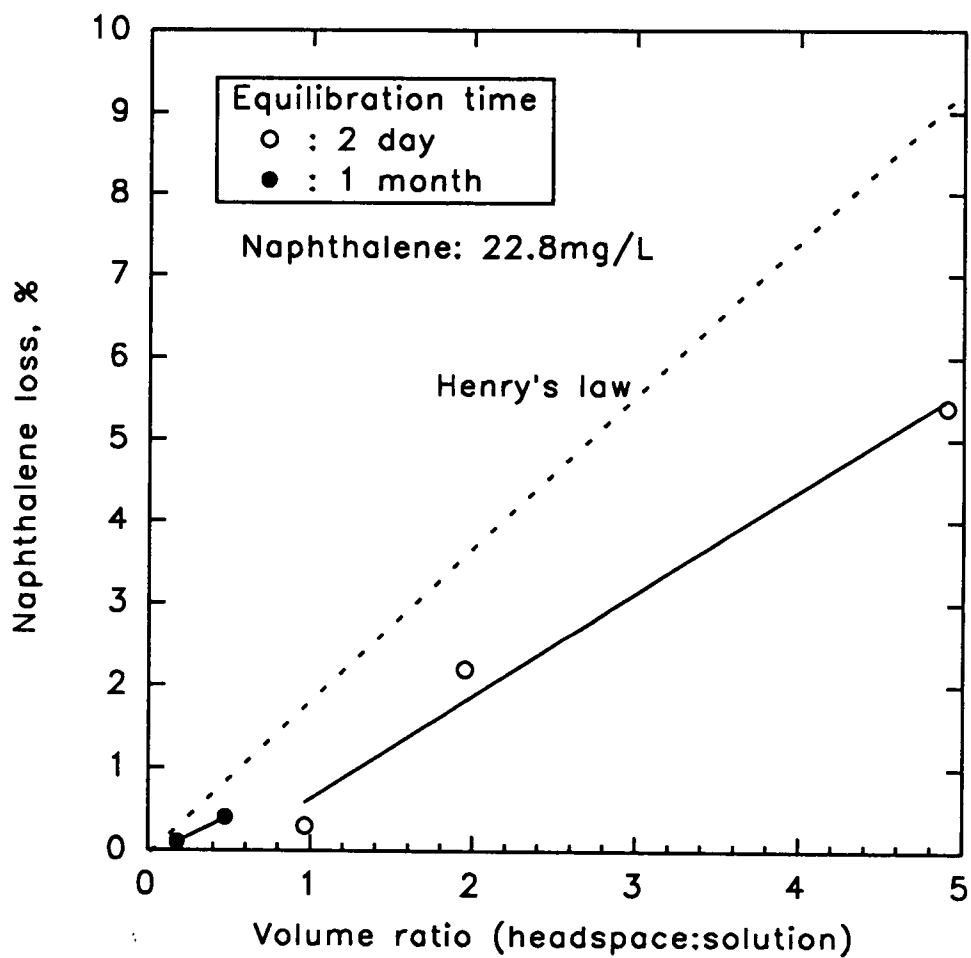


Figure A.1 Percent loss of naphthalene by volatilization into headspace in 25-mL centrifuge tube

similar observations, it seemed inappropriate to use only one value of activity as the reference for all samples collected during tens of minutes of testing. Instead, the activity of solution was measured after every five pipettings of stock solution and the activity of each sample determined by interpolation.

The volatilization of PAH during preparation of samples for scintillation counting was also investigated. Relatively insignificant losses, a maximum 0.8% and 0.1% for naphthalene and phenanthrene, respectively, were observed. The experimental data were not corrected for this loss unless the sample tube remained open for more than 20 seconds. When surfactant solution was applied, no detectable volatilization loss of PAH was observed during preparation of LSC samples, presumably because most of PAH molecules were trapped in surfactant micelles and the concentration of free PAH in aqueous pseudophase was very low.

Appendix III. Correction of results from desorption studies

1. Solution residue in soil after solid separation

When preparing contaminated soil for desorption experiments, solid separation was performed by centrifugation. Even after the supernatant was decanted, there still remained a small amount of residual solution trapped in soil pores or glass wall. This well increase the liquid phase radioactivity when surfactant solution is applied, thus biasing the results in favor of the efficiency of surfactant washing. To correct the desorption data, the amount of solution residue was estimated. Soil suspensions (80 g/L) were prepared with DI water in 25-mL glass centrifuge tube and shaken for 24 hours, followed by centrifugation at 5000×g for 40 minutes. After decanting the supernatant, the tubes were weighed, correct to 4 decimal points, and then oven-dried for 1 hour at 103°C. The amount of solution residue was determined from the difference in weight of the tube (Table A.1). This was replicated using five samples and the average value taken.

Table A.1. Percent solution residue after solid separation from various soil suspensions

	Etowah ($f_{oc}=1.68\%$)	Lexington I ($f_{oc}=0.9\%$)	Lexington II ($f_{oc}=3.4\%$)
range	4.6 - 5.3 %	4.4 -4.7 %	5.5 - 6.6 %
average	4.8 %	4.5 %	5.8 %

The activity (DPM) in bulk surfactant solution due to only enhanced desorption of soil-bound PAH was determined by;

$$[\text{DPM}]_{\text{corrected}} = [\text{DPM}]_{\text{measured}} - (\% \text{ solution residue}) [\text{DPM}]_s \quad (\text{A.3})$$

where $[\text{DPM}]_s$ is the activity of the decanted supernatant.

Appendix IV. Graphical Determination of CMC in Soil-Water System

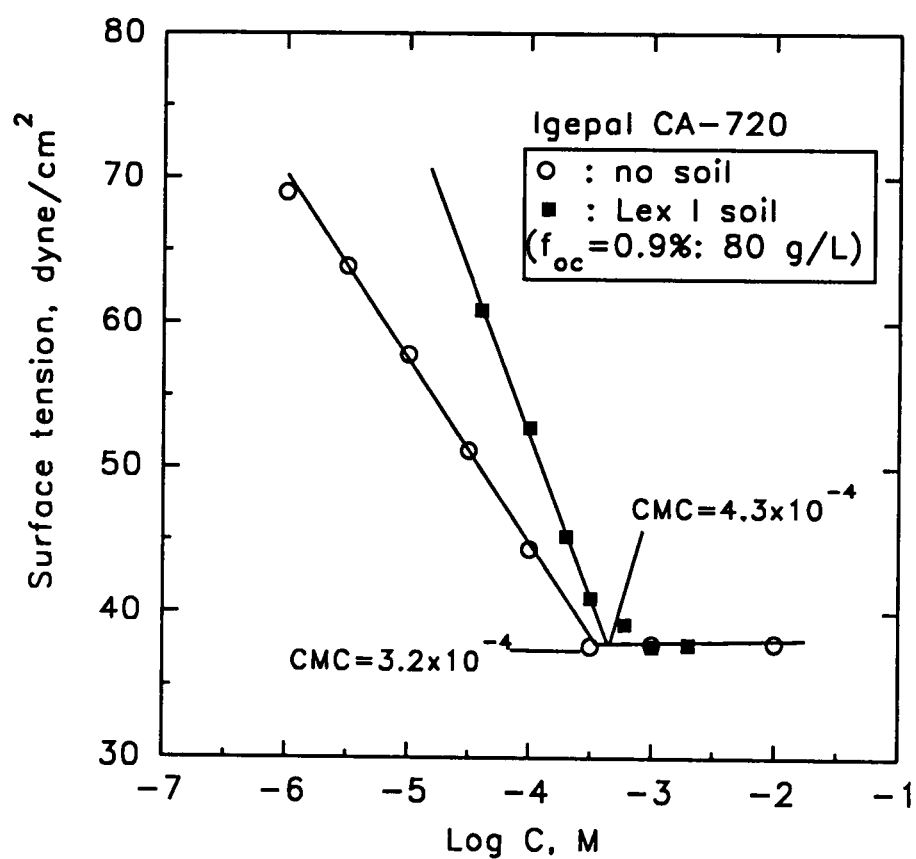


Figure A.2 Determination of CMC of Igepal CA-720 in the presence of Lexington I soil

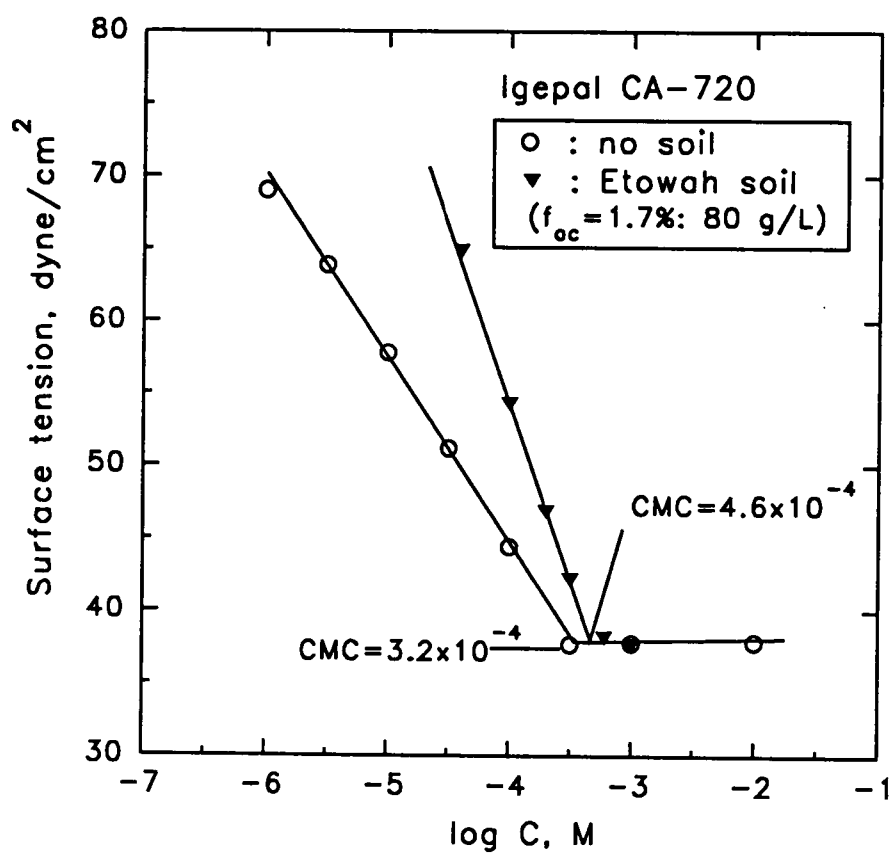


Figure A.3 Determination of CMC of Igepal CA-720 in the presence of Etowah soil

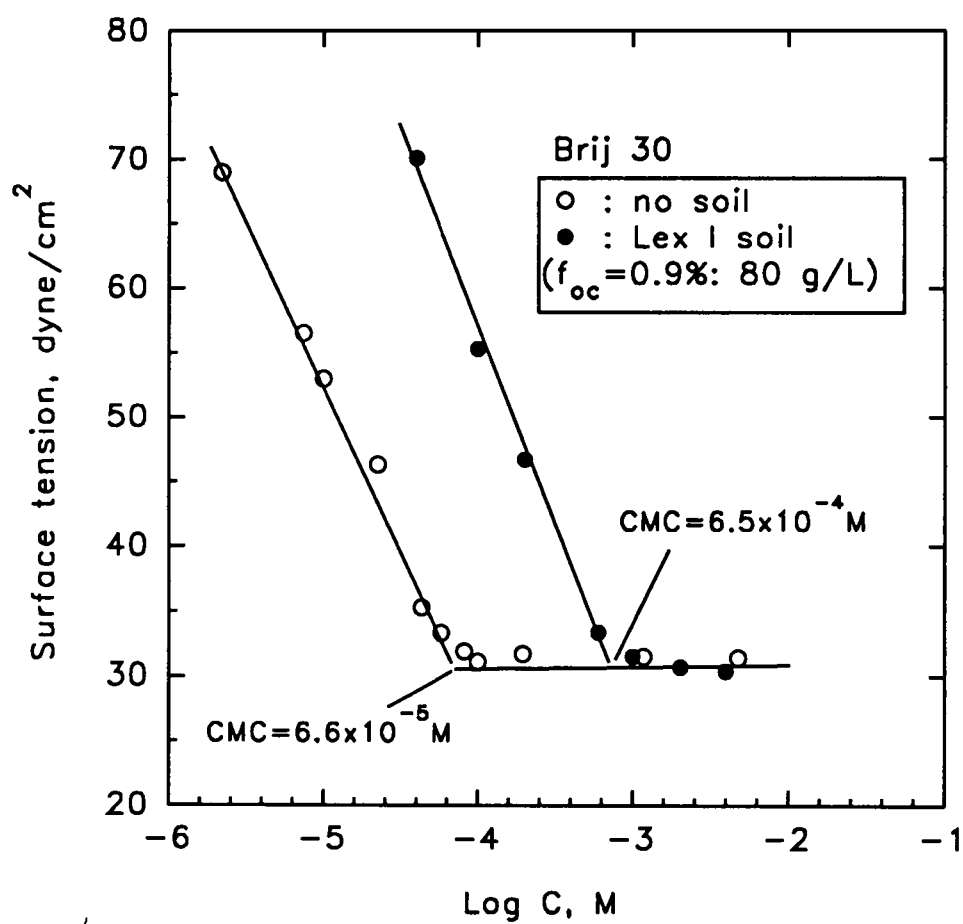


Figure A.4 Determination of CMC of Brij 30 in the presence of Lexington I soil

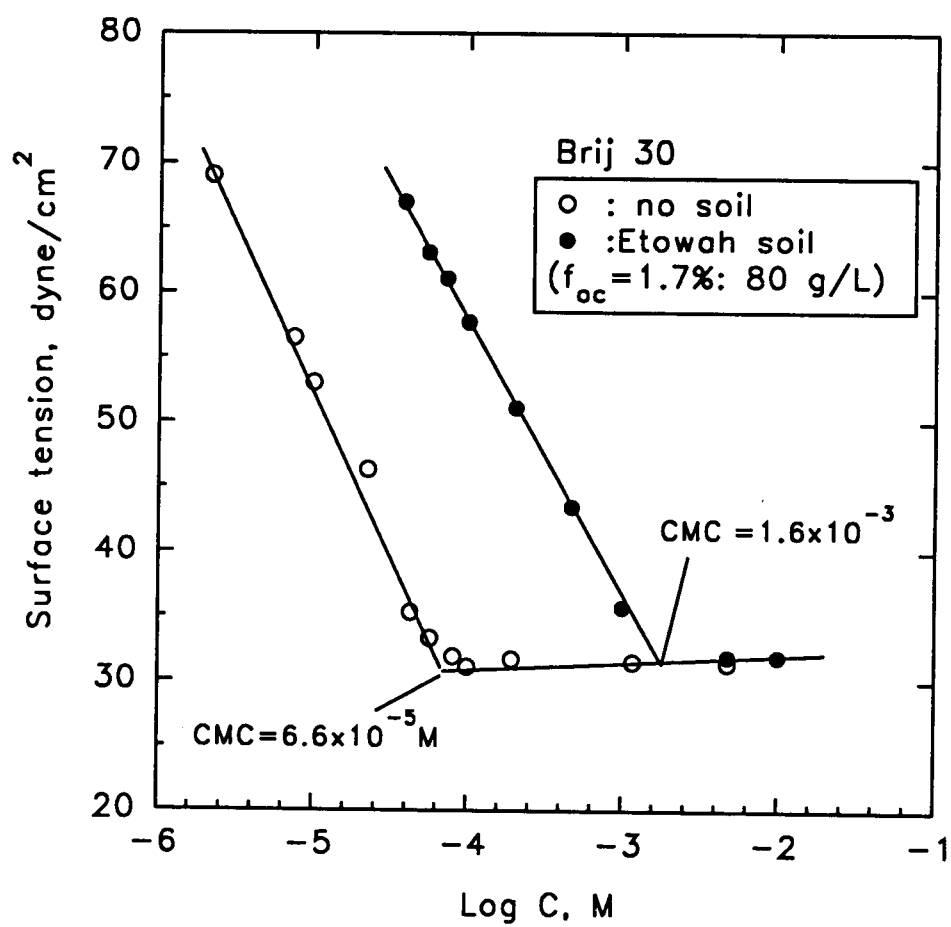


Figure A.5 Determination of CMC of Brij 30 in the presence of Etowah soil

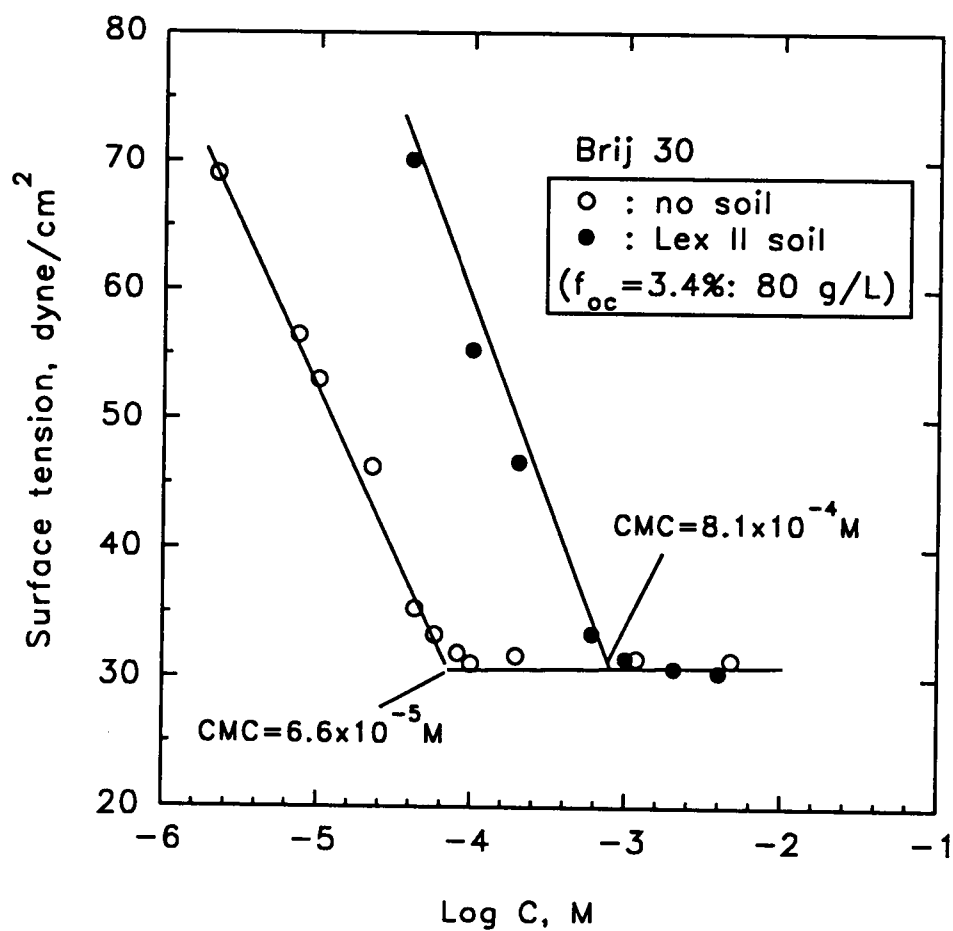


Figure A.6 Determination of CMC of Brij 30 in the presence of Lexington II soil

Appendix V. Desorption of PAH from Soil Using Surfactant

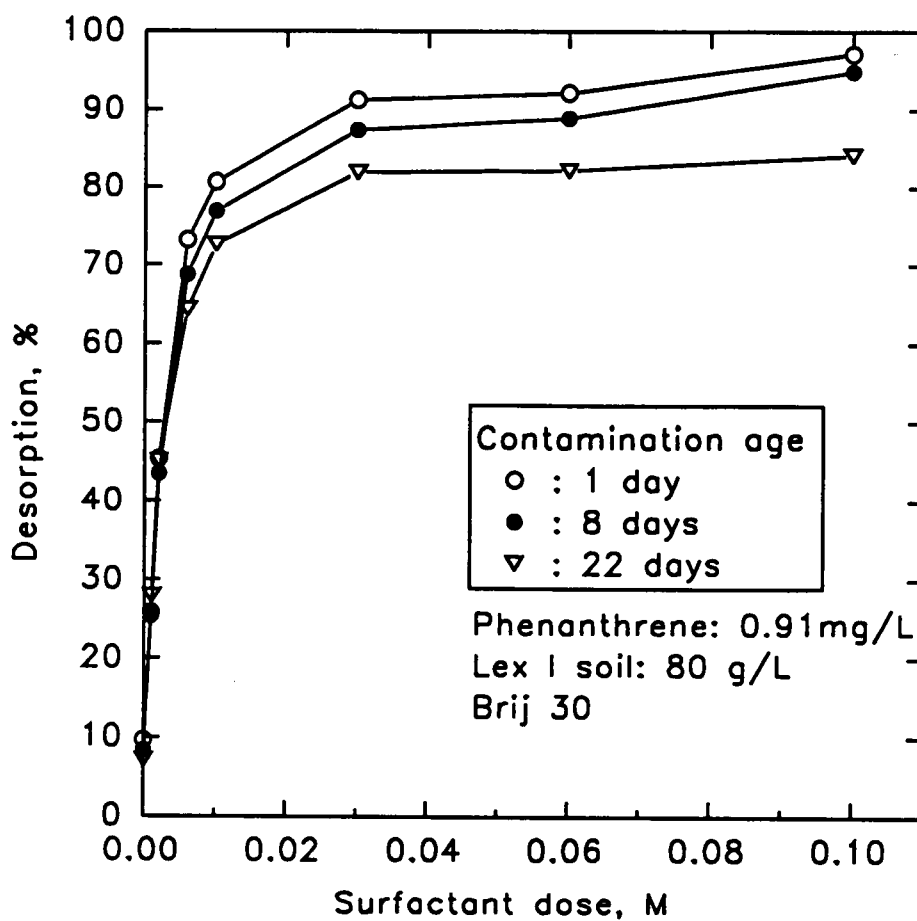


Figure A.7 One-day desorption of phenanthrene from Lexington I soil using Brij 30

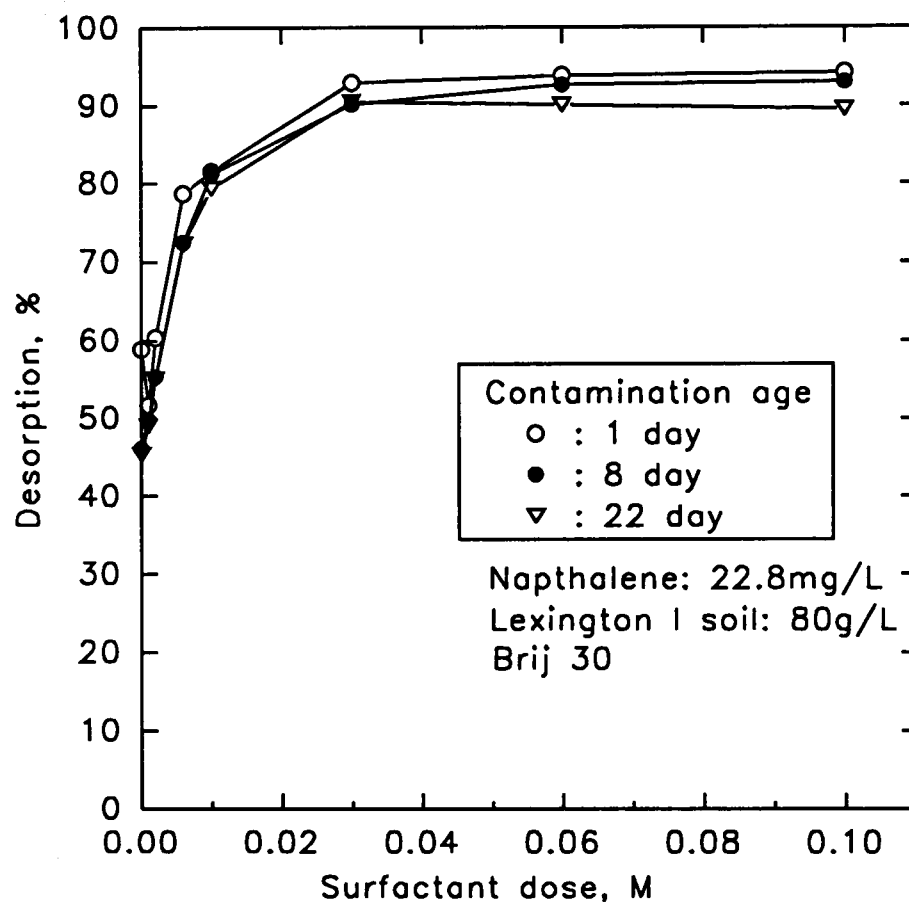


Figure A.8 One-day desorption of naphthalene from Lexington I soil using Brij 30

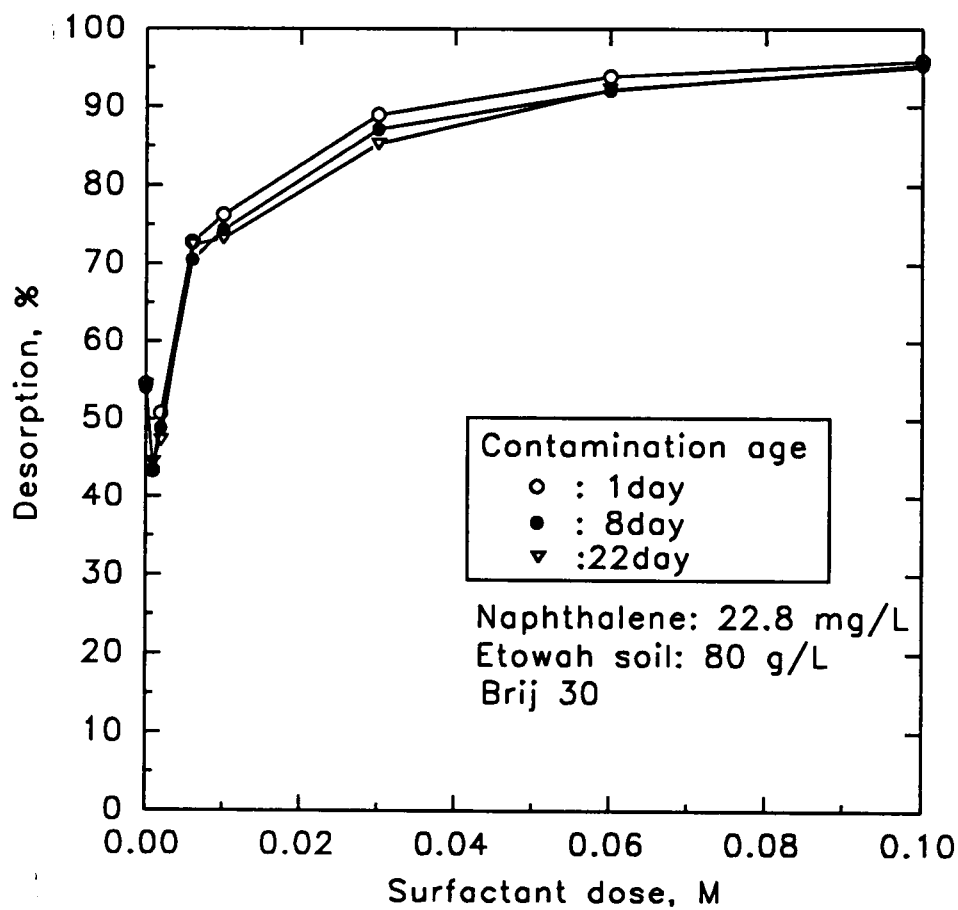


Figure A.9 One-day desorption of naphthalene from Etowah soil using Brij 30

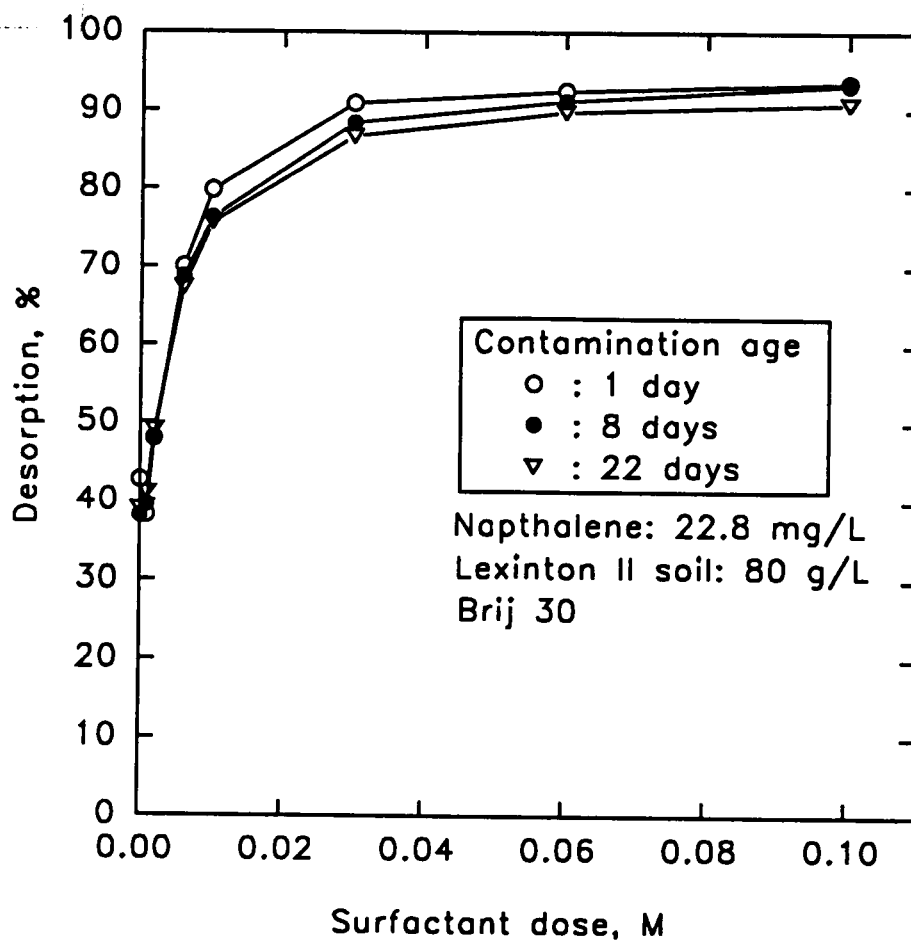


Figure A.10 One-day desorption of naphthalene from Lexington II soil using Brij 30

Appendix VI. Radial Diffusion Model (After Wu, 1986)

```

C *****
C The following program was originally proposed by S.C. Wu as a
C BASIC program by S. C. Wu, and recoded in Fortran 77 by J. R.
C Mihelcic, Department of Civil Engineering, Carnegie Mellon
C University.
C *****
CHARACTER*1 changeC, knoDeff
DOUBLE PRECISION one, two, zero, ca, ssp, t1
INTEGER ngrid(10), num(20)
c INTEGER ngrid(10), num(10)
REAL fs(10), rad(10), u(10,201), g(10)
REAL dx(10), h(10), ut(10,201), gridsize(10), te(20), co(20)
REAL sl(10), kl(10), Kow, tmint, Kp, Koc, Kow, foc
one=1
zero=0
two=2
OPEN(UNIT=10, FILE='des.out', STATUS='unknown')
WRITE(*,4)
4 FORMAT('Please enter environmental parameters.',/)
WRITE(*,5)
5 FORMAT('Enter the number of particle classes ', $)
READ(*,*) ng
DO 9 n=1, ng
WRITE(*,6)
6 FORMAT('Enter fraction ', $)
READ(*,*) fs(n)
WRITE(*,7)
7 FORMAT('Enter particle radius in cm ', $)
READ(*,*) rad(n)
WRITE(*,8)
8 FORMAT('Enter gridsize of class #, cm ', $)
READ(*,*) gridsize(n)
9 CONTINUE
WRITE(*,11)
11 FORMAT('Initial concentration of solid (mole/g) ? ', $)
READ(*,*) so
WRITE(*,12)
12 FORMAT('Simulation starting time (minute) ? ', $)
READ(*,*) te(0)
WRITE(*,14)
14 FORMAT('Printing time step size (minute) ? ', $)
READ(*,*) Timestep
ncycle=0
15 CONTINUE
ncycle=ncycle+1
WRITE(*,16)
16 FORMAT('Ending time (minute) ? ', $)
READ(*,*) te(ncycle)
17 CONTINUE
WRITE(*,18)
18 FORMAT('Concentration in aqueous phase (mol/ml) ? ', $)
READ(*,*) co(ncycle)
WRITE(*,20)
20 FORMAT('Do you want to change concentration in aqueous phase? ', $)
READ(*,*) changeC
IF(changeC .EQ. 'Y' .OR. changeC .EQ. 'y') THEN
GOTO 15

```

```

      END IF
      WRITE(*,22)
22      FORMAT('Sorbent concentration (g/ml) ? ', $)
      READ(*,*)solid
      WRITE(10,200)rad
200      FORMAT('radius (cm)=' ,1PE10.4)
      WRITE(10,205)gridsize
205      FORMAT('gridsize (cm)=' ,1PE11.5)
      WRITE(10,210)so
210      FORMAT('initial aqueous conc. in solid (mole/g)=' ,1PE10.4)
      WRITE(10,216)co
216      FORMAT('initial aqueous conc. (mole/ml)=' ,1PE8.2)
      WRITE(10,220)solid
220      FORMAT('sorbent concentration (g/ml)=' ,0PF8.4)
      GO to 376
25      CONTINUE
      GO TO 585
170      P=1.5
      GOTO 640
175      CONTINUE
      GOTO 720
185      ts=te(0)
      Do 187 n=1, ng
      Do 188 ni=1, ngrid(n)
      u(n,ni)=dx(n)*(ni-1)*so*ps*(1-poro)
188      CONTINUE
187      CONTINUE
      Do 190 n1=1, ng
      s1(n1)=so
      k1(n1)=(10.56*solid*Kp+22.7)*d/rad(n1)**2
190      CONTINUE
      sss1=so
      GOTO 760
340      CONTINUE
      GOTO 375
375      CONTINUE
376      continue
      WRITE(*,377)
377      FORMAT('What is known? Kp=1, Ce=2, Koc=3 or Kow=4 ', $)
      READ(*,*)k
      IF (k .EQ. 1) THEN
      GOTO 395
      ELSE IF(k .EQ. 2) THEN
      GOTO 405
      ELSE IF(k .EQ. 3) THEN
      GOTO 425
      ELSE IF(k .EQ. 4) THEN
      GOTO 445
      END IF
395      WRITE(*,397)
397      FORMAT('Enter Kp (cm^3/g) ', $)
      READ(*,*)Kp
      GOTO 550
405      WRITE(*,407)
407      FORMAT('Reenter Co [moles/ml] ', $)
      READ(*,*)co(1)
      WRITE(*,410)
410      FORMAT('Enter Ce [moles/ml] ', $)
      READ(*,*)ce
      Kp=(co(1)+(solid*so)-ce)/(solid*ce)
      GOTO 550
425      WRITE(*,427)

```

```

427  FORMAT('Enter Koc(cm^3/g)  ', $)
      READ(*,*)Koc
      WRITE(*,428)
428  FORMAT('Enter foc(g/g)  ', $)
      READ(*,*)foc
      Kp=Koc*foc
      GOTO 550
445  continue
      WRITE(*,446)
446  FORMAT('Enter Kow  ', $)
      READ(*,*)Kow
      WRITE(*,447)
447  FORMAT('Which equation do you want to use',/)
      WRITE(*,448)
448  FORMAT('eq.q: log Koc=log Kow - 0.21  or',/)
      WRITE(*,449)
449  FORMAT('eq.2: log Koc=0.72 log Kow +0.49 ?  ', $)
      READ(*,*)eq
520  IF (eq .EQ. 1) THEN
      GOTO 535
      ELSE IF(eq .EQ. 2) THEN
      GOTO 537
      END IF
C535  CONTINUE
535  Koc=10**(LOG10(Kow)-0.21)
      GOTO 545
537  CONTINUE
      Koc=10**(0.72LOG10(Kow)+0.49)
545  WRITE(*,547)
547  FORMAT('Enter foc  ', $)
      READ(*,*)foc
      Kp=Koc*foc
550  continue
      ce=(co(1)+solid*so)/(solid*Kp+one)
      WRITE(10,560)Kp
560  FORMAT('Kp=',1PE12.4)
      GOTO 25
585  continue
      WRITE(*,587)
587  FORMAT(' Do you know the value of Deff?  ', $)
      READ(*,*)knoDeff
      IF (knoDeff .EQ. 'N' .OR. knoDeff .EQ. 'n')THEN
      GOTO 615
      END IF
      WRITE(*,610)
610  FORMAT('Enter Deff (cm^2/s)  ', $)
      READ(*,*)DinSecond
      d=DinSecond*60
      GOTO 170
615  CONTINUE
      WRITE(*,617)
617  FORMAT('Enter the intraparticle porosity  ', $)
      READ(*,*)poro
      WRITE(*,618)
618  FORMAT('Enter the solid dry density  ', $)
      READ(*,*)ps
      WRITE(*,619)
619  FORMAT('Enter the molecular diffusivity (cm^2/sec)  ', $)
      READ(*,*)Dm
      d=Dm*poro**2/Kp/(1-poro)/ps*60
      WRITE(10,625)poro
625  FORMAT('intraparticle porosity=',1PE12.4)

```

```

        WRITE(10,635)ps
635    FORMAT('solid dry density=',1PE12.4)
        WRITE(10,636)Dm
636    FORMAT('molecular diffusivity=',1PE15.4)
        WRITE(10,637)
        FORMAT(' ')
        WRITE(10,638)
638    FORMAT('The following columns are time, aqu conc., sorbed conc.')
        WRITE(10,642)
642    FORMAT('aqu conc. in units of moles/ml and sorbed in moles/gram')
        WRITE(10,639)
639    FORMAT(' ')
        GOTO 170
640    CONTINUE

```

```

        tmin=TimeStep
        DO 692 n=1, ng
            ngrid(n)=1.0 +INT((rad(n)/gridsize(n)/2))*2
c        ngrid(n)=1.0 +INT((rad(n)/gridsize(n)/2)**2
            tmint=(rad(n)**2/d/(ngrid(n)-1)**2)/2

            IF (tmin .GT. tmint) THEN
                tmin=tmint
            END IF
            dx(n)=one/(ngrid(n)-1)
            h(n)=fs(n)*solid*dx(n)**2/(ps-ps*poro)
692    CONTINUE
            GOTO 175
720    continue
        DO 735 n=1, ng
730        g(n)=d*tmin/(rad(n)*dx(n))**2
735    CONTINUE
        GOTO 185

760    continue
        DO 965 nc=1, ncycle
            c=co(nc)
            num(ncycle)=INT((te(nc)-te(nc-1))/TimeStep)
            DO 960 nk=1, num(ncycle)
785    continue
                aa=zero
                bb=zero
                DO 835 ni=1, ng
                    sumj=zero
                    DO 823 nj=2, ngrid(ni)-1
                        ut(ni,nj)=u(ni,nj)+g(ni)*(u(ni,nj+1)-two*u(ni,nj)+u(ni,nj-1))
                        sumj=sumj+(3+(-1)**nj)*(nj-1)*(ut(ni,nj)-u(ni,nj))
823    CONTINUE
                    aa=aa+h(ni)*(sumj-(ngrid(ni)-1)*u(ni,ngrid(ni)))
                    bb=bb+h(ni)*(ngrid(ni)-1)*Kp*ps*(1-poro)
835    CONTINUE
                    ct=(c-aa)/(one+bb)
                    ts=ts+tmin
                    c=ct
                    DO 880 n1=1, ng
                        DO 870 nm=1, ngrid(n1)-1
                            u(n1,nm)=ut(n1,nm)
870    CONTINUE
                            u(n1,ngrid(n1))=Kp*ps*(1-poro)*c
880    CONTINUE
                    IF (ts .LT. te(nc-1)+TimeStep*nk) THEN

```

```

GOTO 785
END IF
ss=zero
DO 925 ni=1, ng
    sumk=zero
    DO 915 nj=2, ngrid(ni)-1
        sumk=sumk+(3+(-1)**nj)*(nj-1)*ut(ni,nj)
915    CONTINUE
        ss=ss+fs(ni)*dx(ni)**2*(sumk+(ngrid(ni)-1)*u(ni,ngrid(ni)))
925    CONTINUE
    ca=c
    ssp=ss/(ps-ps*poro)
    t1=ts
    WRITE(*,955)t1,ca,ssp
955    FORMAT('1PE11.5,'          ',1PE11.5,'          '1PE11.5)
    WRITE(10,958)t1,ca,ssp
958    FORMAT(1PE11.5,'      '1PE11.5,'      '1PE11.5)
960    CONTINUE
965    CONTINUE
END

```

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 receive 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 entered The University of Tennessee, Knoxville and in December, 1992 received a Master of Science degree in Civil Engineering.

He is presently a graduate student seeking for Doctor of Philosophy in Civil Engineering, at The University of Tennessee, Knoxville.