3. ENVIRONMENTAL FATE AND TRANSPORT OF ORGANIC CONTAMINANTS IN SOILS AT WASTE DISPOSAL SITES

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ABSTRACT

Current approaches for describing the environmental dynamics of organic constituents in complex waste mixtures are reviewed. Factors controlling equilibrium and nonequilibrium sorption of organic contaminants from aqueous solutions are summarized, and extension of these concepts to predict the effects of mixed solvents are discussed. Presence of organic cosolvents increases solubility in a log-linear manner, leading to proportional decreases in sorption and retardation of nonpolar organic contaminants. Available data support the use of a log-linear cosolvency model and the UNIFAC model to predict the cosolvency effects. For predicting dissolution of aromatic hydrocarbons from multi-component organic liquid wastes, available data for gasolines, diesel fuels, and coal tars support the adequacy of approaches based on the assumption of ideal mixtures (Raoult's law). Examples are presented where the cosolvency model and the Raoult's law approach were applied for designing remediation of contaminated soils at industrial waste disposal/spill sites and for predicting the concentrations of aromatic hydrocarbons in the leachate from a source area.

3.1. INTRODUCTION

Environmental contamination problems at most industrial waste disposal sites or spill sites commonly involve wastes consisting of complex mixtures of organic and inorganic chemicals. Several researchers have made considerable efforts during the past decade to investigate the primary processes (e.g., solubility, sorption, transport) governing the environmental dynamics of organic chemicals in complex mixtures. Earlier efforts were usually limited to investigations of the behavior of single solutes in aqueous solutions, or to systems that were simple in composition relative to many waste mixtures found at or near disposal/spill sites. Complex mixtures are defined here as those systems comprising multiple organic solutes and multiple solvents. The solute mixtures of interest might consist of various combinations of nonpolar or hydrophobic organic chemicals (HOCs); hydrophobic, ionogenic organic chemicals (HIOCs); and ionic organic chemicals (IOCs). The solvent may be a mixture of water and one or more organic cosolvents (either completely- or partially-miscible in water). Solvent mixtures of interest may consist of water and cosolvents in a single, homogeneous liquid phase, or multi-phases that form at least two distinct liquid phases.

The release and migration of organic constituents from a waste disposal or spill source will produce a contaminant plume, either in the vadose zone or in the saturated zone or both. The contaminant plume composition will vary with time and distance as the plume size increases. For discussing solubility and sorption processes within the plume, three separate regions may be considered: a near-field region, a transition zone, and a far-field region. The basis for such a distinction is not the distance from the contaminant source. Rather, the criterion employed to designate these regions is the chemistry of the contaminant mixture within the plume as contrasted to the waste composition.

In the near-field region, corresponding to the source itself and its immediate vicinity, the composition and concentrations of most waste constituents are similar to that in the waste. There are usually two, possibly three, liquid phases in this region. This would be the case, for example, at waste disposal sites where we may find both "dense" and "light" organic immiscible liquids (OILs) and an aqueous phase as well as a vapor phase. In the transition zone, the solution phase is likely to be predominantly a single-phase, homogeneous liquid made up of water and varying amounts of cosolvents (if they were present in the near-field region). The concentration of one or more waste constituents may be sufficiently high such that approximations based on behavior in dilute aqueous solutions are found to be inadequate. Finally, the far-field region corresponds to that region of the contaminant plume in which the waste constituents are present in an aqueous solution. Most of these chemicals will be at concentrations well below their aqueous solubility limits. During migration of the contaminant plume through the vadose zone and the saturated zone, chromatographic separation of the waste constituents occurs due to their different mobilities. Furthermore, dilution resulting from hydrodynamic dispersion and attenuation resulting from abiotic and/or biotic transformations could decrease contaminant concentrations. Thus, high concentrations of multiple contaminants are less likely to be found as the distance from the source increases. Nevertheless, it is possible that these contaminant concentrations may be higher than the standards set by regulatory agencies.

This paper presents an overview of recent experimental and theoretical developments in describing: (1) solubility of HOCs in aqueous and mixed solvents; (2) sorption of HOCs and HIOCs by soils and other geologic media from water and mixed solvents; and (3) partitioning of HOCs from multi-component OILs into water. Applications of this information to definition, prediction, and remediation of soil and groundwater contamination problems will also be discussed.

3.2. SORPTION FROM AQUEOUS SOLUTIONS

Most of the available data and theories for predicting sorption and transport of organic chemicals may be successfully applied to predict contaminant behavior in the far-field region (i.e., dilute aqueous solutions). The following section will highlight the information available on equilibrium and nonequilibrium sorption of organic chemicals.

3.2.1. Equilibrium Sorption

Equilibrium sorption of HOCs by soils and sediments has been successfully predicted in many cases by the "solvophobic theory" and the use of linear free energy relationships (LFER). Excellent log-log, linear relationships have been reported between K_{oc}, the sorption coefficient normalized to the mass-fraction organic carbon content (OC) of the sorbent, and the octanol-water partition coefficient (K_{ow}) for several HOCs (c.f., Dzombak and Luthy 1984; Karickhoff 1981, 1984; Kenega and Goring 1980). Linear relationships have also been found between log K_{oc} and solute hydrophobic surface area (HSA) (Dzombak and Luthy 1984; Rao et al. 1985) and solute molecular connectivity (Sabljic 1984, 1987). The different slopes and intercepts found in these regression equations are predominantly determined by the characteristics of a group of compounds (i.e., class, degree of hydrophobicity, and structure) (see Gerstl 1990), while the sorbent properties other than OC appear to have only minor impact in most cases (Karickhoff 1981, 1984; Schwarzenbach and Westall 1985). The equations derived from LFER and experimental data obtained for only a few sorbents provide reasonable predictions of HOC distribution in diverse soil-water and sediment-water systems. However, the limitations of the K_{oc}concept have been pointed out by a number of authors (e.g., Green and Karickhoff 1990; Mingelgrin and Gerstl 1983). The two main concerns involve the contribution of adsorption on mineral constituents and the possibility of site-specific interactions between functional moieties of the solute and the sorbent.

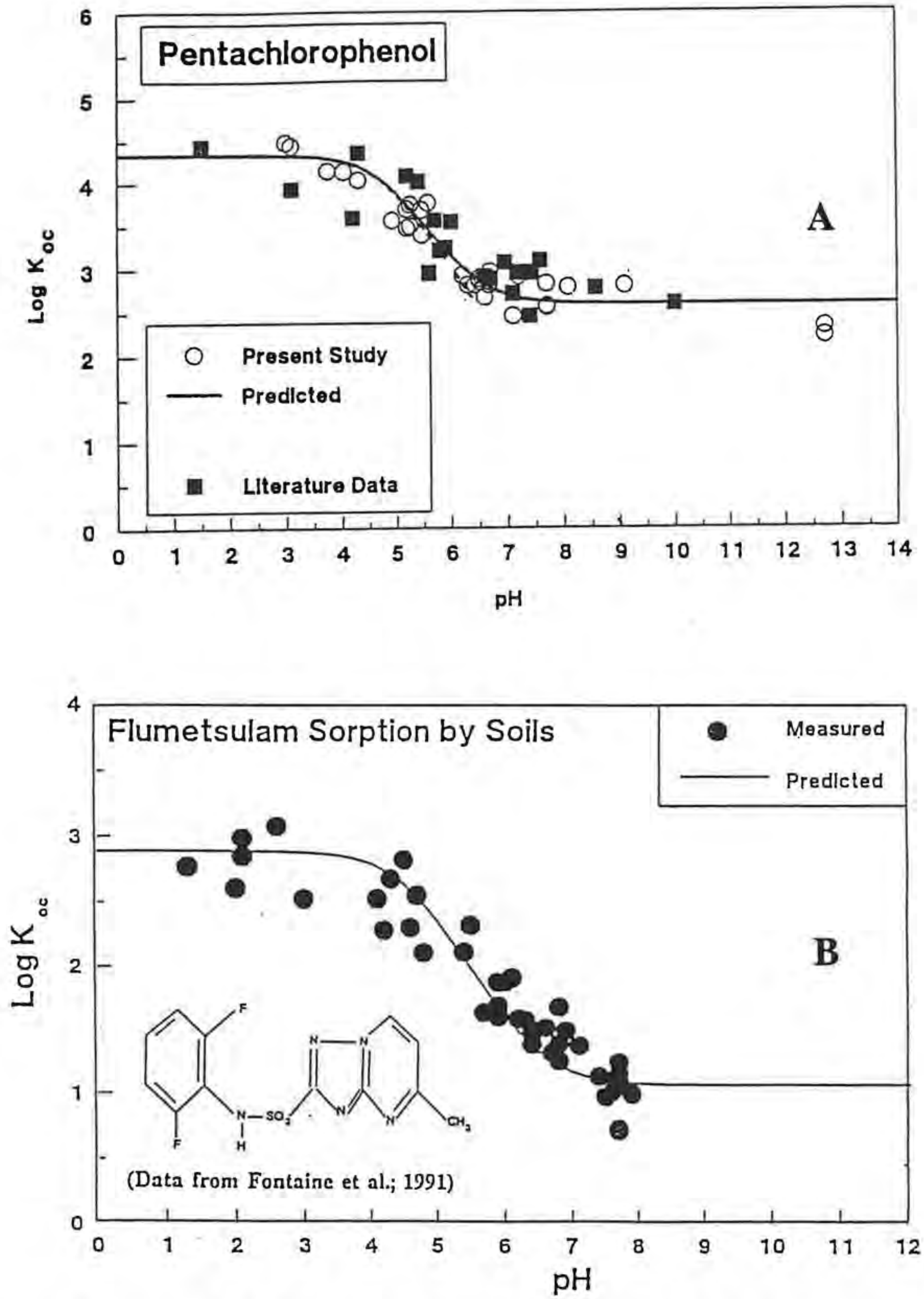
For HIOCs, predicting sorption from a single parameter becomes difficult due to additional processes that must be considered (i.e., speciation, ion-exchange, ion-associations, etc.). For example, on the basis of an analysis of a large data set for pentachlorophenol (PCP) sorption from aqueous solutions by several sorbents over a broad pH range (Figure 3-1A), Lee et al. (1990) showed that equilibrium sorption could be described by the following model:

$$K_{oc} = K_{oc,n}\,\phi_n + K_{oc,i}\,(1-\phi_n) \tag{1a}$$

where

$$\phi_n = (\,1 + 10^{pH-pKa}\,)^{-1} \tag{1b}$$

K is the measured distribution ratio for the sorbed- and solution-phase concentrations for sorption by a specific sorbent; K_{oc} =(K/OC) is the OC-normalized distribution ratio; OC is the soil organic carbon content (mass fraction); ϕ_n is the fraction of the neutral



1. Examples of pH-dependence of sorption of organic acids by soils from aqueous solutions. (A) Pentachlorophenol sorption by several sorbents, as reported by Lee et. al. (1992); (B) Flumetsulam herbicide sorption by several soils, based on data reported by Fontaine et. al. (1991) and interpreted by Lee (1993). The solid line in both cases is prediction based on eq (1a).

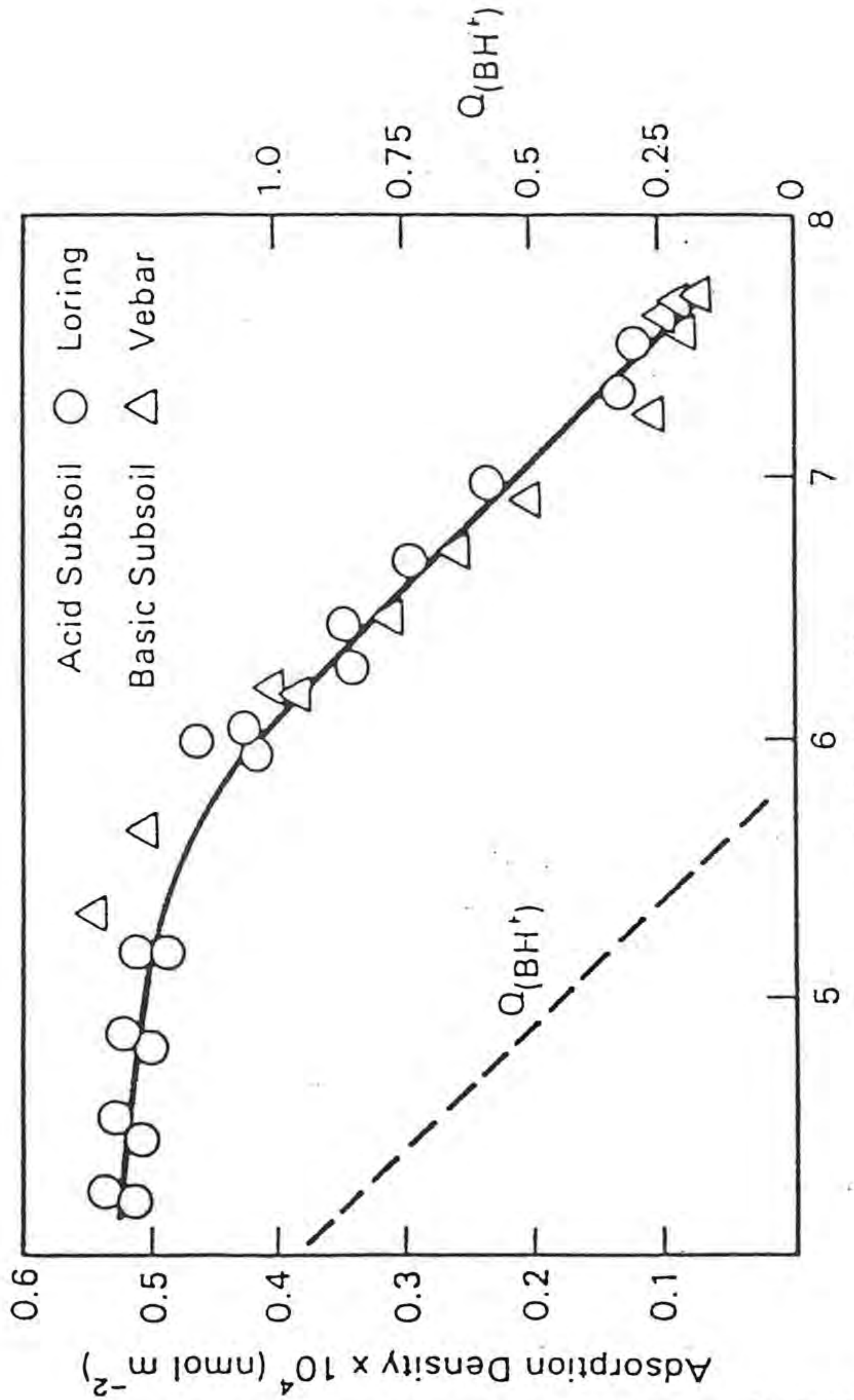
HIOC; the subscripts n and i refer to neutral and ionized species, respectively; and pK_a is the organic acid dissociation constant. Substantial deviations from eq (1a) suggest the predominance of specific sorption mechanisms (e.g., hydrogen bonding, ligand exchange). Lee (1993) applied eq (1a) to sorption data compiled from the literature for several other organic acids, and found that in most cases eq (1a) adequately described the sorption observed as a function of pH; Figure 3-1B shows an example of the agreement between the eq (1a) predictions and the reported pH-dependency of flumetsulam herbicide sorption by soils.

For sorption of organic bases, ion-exchange has been shown to be the controlling sorption mechanism even at pH values as much as two units greater than the solute pK_a (Ainsworth et al. 1987; Zachara et al. 1986, 1987, 1990). Figure 3.2 presents an example of the data reported by Zachara et al. (1986) for quinoline sorption by two subsoils. Note in Figure 3-2 that the observed change in quiniline sorption with bulk soil pH is not in direct response to the protonation of the organic base; enhanced protonation of quinoline at the soil-water interfaces accounts for the increased sorption (Zachara et al. 1986).

Competitive sorption in multi-component mixtures has been observed for N-heterocyclic compounds when pH is low enough that protonated form is the dominant species (Felice et al. 1985; Zachara et al. 1987). In contrast, for HOCs and neutral HIOCs competition has been rported to be minimal (Chiou et al 1983; Karickhoff et al. 1979; MacIntyre and deFur 1985; Rao et al. 1986; Schwarzenbach and Westall 1981; Zachara et al. 1987). The predominance of ion-exchange in the sorption of organic bases suggests the use of a sorption coefficient normalized to the cation exchange capacity of the sorbent as a first approximation, analogous to the use of K_{oc} for describing sorption of HOCs.

3.2.2. Sorption Nonequilibrium

The importance of accurately describing the effective travel time and recovery of a contaminant plume has stimulated the characterization of sorption nonequilibrium processes for organic chemicals. Brusseau and Rao (1989a) have



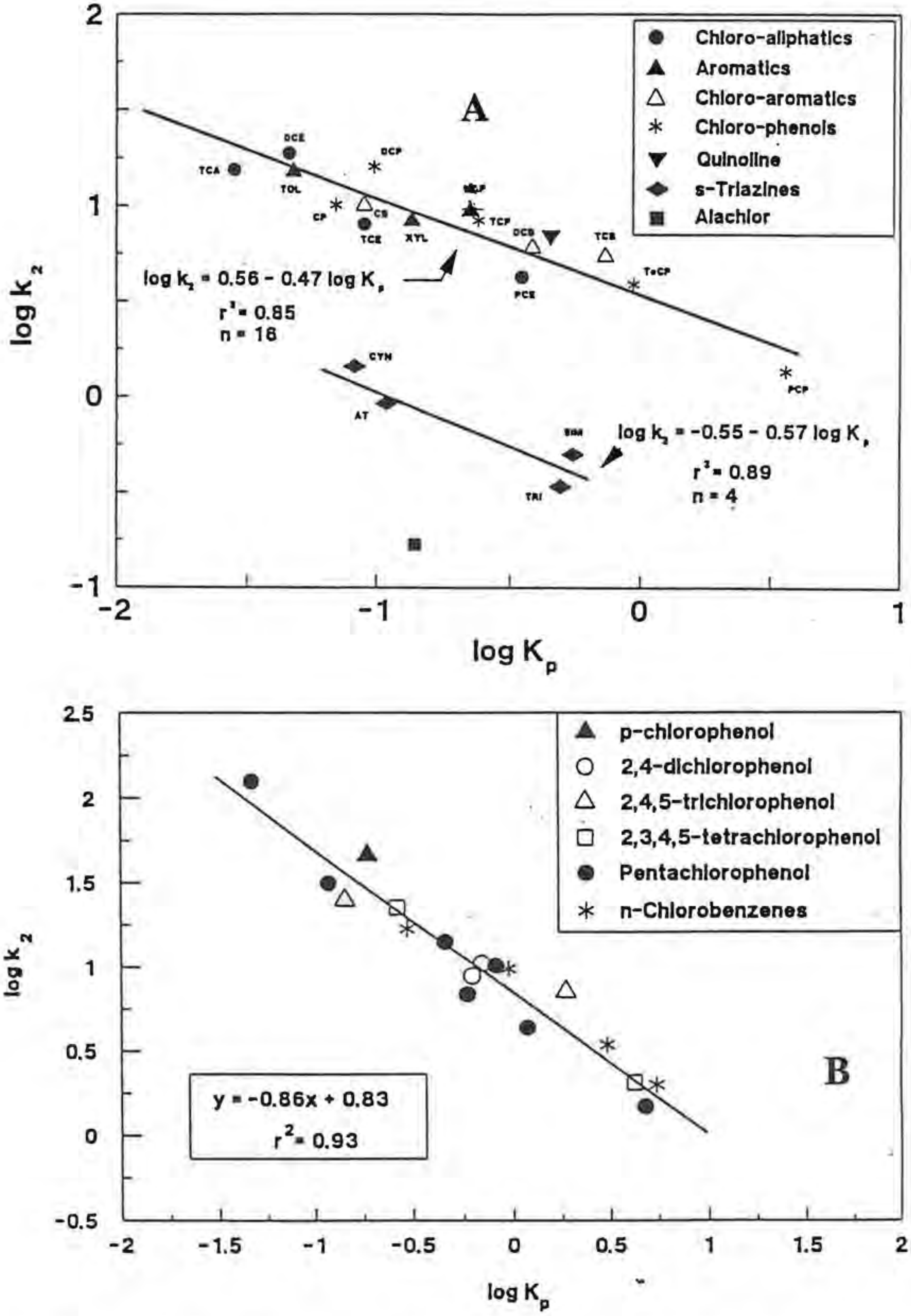
2. Examples of pH-dependence of quinoline sorption by two subsoils from aqueous solutions. The dashed line shows the fraction of total quinoline present as the quinolinium cation. Taken from Zachara et al. (1986).

compiled and analyzed an extensive data base for sorption nonequilibrium; they noted an inverse log-log linear relationship between sorption rate coefficients (k_2, h^{-1}) and corresponding equilibrium sorption constants (K_p, mL/g). This inverse relationship has been confirmed by data collected from more recent studies (Brusseau et al. 1990, 1991a,c); see Figure 3-3A for an example of the sorption data compiled for several classes of organic solutes. Brusseau and Rao (1989a) postulated that the sorption nonequilibrium observed with HOCs in soils was due to intra-organic matter diffusion (i.e., diffusion into the organic matter matrix). Other researchers have proposed intra-granular (i.e., retarded diffusion within the pores of mineral particles) as the predominant mechanism for sorption nonequilibrium, especially for aquifer materials (Ball and Roberts 1991a,b). A detailed discussion on the processes affecting nonequilibrium sorption and transport is given by Brusseau and Rao (1989b).

Lee et al. (1991) also noted a single log-log inverse relationship between the k_2 and K_p for several chlorophenols (regardless of ionization status) and for a series of chlorobenzenes (Figure 3-3B). This k_2-K_p relationship was also similar to that observed by Brusseau and Rao (1989a) for HOCs suggesting that the processes controlling nonequilibrium soroption for chlorophenols are similar to those experienced by HOCs. For other classes of organic acids (e.g., carboxylic and phenoxy-acetic acids) and for organic bases (e.g., N-heterocyclic compounds), sorption nonequilibrium may be significantly influenced by pH and chemical nonequilibrium processes (i.e., rate-limited interactions between the solute and specific sites on the sorbent; chemisorption) (Brusseau and Rao 1989a; Brusseau et al. 1991c); however, limited data prevents any further assessment of their behavior.

3.3. COSOLVENCY

The effects on solubility and sorption (hence, on transport) of organic chemicals upon addition of one or more organic cosolvents to an aqueous solution are defined here as cosolvency. This section will focus on the most significant interactions affecting solubility and sorption of both HOCs and HIOCs. Such interactions include solute-cosolvent, cosolvent-cosolvent, and cosolvent-water



3. Examples of log-log inverse relationship between the sorption mass-transfer rate coefficient (k_2, hr^{-1}) and equilibrium sorption coefficient (K_p, mL/g). (A) Taken from Brusseau and Rao (1991); (B) Taken from Lee et al. (1993).

interactions for solubility; for sorption, solvent-sorbent interactions must also be considered.

3.3.1. Solubility in Mixed Solvents

The log-linear cosolvency model and the UNIFAC model are among the theoretical approaches that have been used to examine cosolvent effects on solubility (Fu and Luthy 1986a; Pinal et al. 1990). The log-linear cosolvency model (Yalkowsky and Roseman 1981) is based on the central assumption that the logarithm of the solute solubility in a mixed solvent is given by the weighted-average of the logarithms of solubilities in the component solvents in the mixture; the weighing coefficient is taken to be the volume fraction of each solvent component. Thus,

$$\log S_m = \Sigma f_i \log S_i \qquad (2)$$

where S is solubility (mg/L), f is volume fraction of the solvent, and the subscript m denotes mixed solvent and i the i-th cosolvent. Note that averaging the logarithms of solubilities is equivalent to averaging the free energies of solution in different solvents in the mixture. The UNIFAC model (Fredenslund et al. 1975) is a group-contribution scheme for calculation of the activity coefficients. This model is based on the UNIQUAC model (Abrams and Prausnitz 1975) and the solution-of-group concept (Wilson and Deal 1962). In this model, a mixture of different chemicals is treated as a mixture of the functional groups constituting the components in solution.

In many cases the UNIFAC model may be preferred over the log-linear model because: (1) it has a more sound theoretical basis, (2) activity coefficients in mixtures can be calculated given only pure component data, and (3) all possible interactions among the components in the mixture are explicitly considered. A limitation of the UNIFAC model, however, is that although the group interaction parameters required to estimate the solute activity coefficients are continuously reviewed and updated, their values are not available for a number of systems of interest here. Furthermore, the UNIFAC model provides poor estimates of HOC solubility in predominantly aqueous solutions (Fu and Luthy 1986a).

A convenient measure of the impact of a cosolvent on the solubility of an organic chemical is the cosolvency power (σ), which is defined as:

$$\sigma = \log [S_c / S_w] \qquad (3)$$

where the subscripts c and w refer to neat cosolvent and pure water, respectively. HOC solubility in organic solvents is larger than that in water, thus $\sigma > 0$. Larger values of σ indicate a greater solubilizing power of the solvent for a specific solute.

Rubino and Yalkowsky (1987a) and Pinal et al. (1990) have shown that σ values can be viewed as being equivalent to hypothetical partition coefficients for the HOC between a cosolvent and water. Morris et al. (1988) have shown that σ values can be correlated to HOC octanol-water partition coefficient (K_{ow}) as follows:

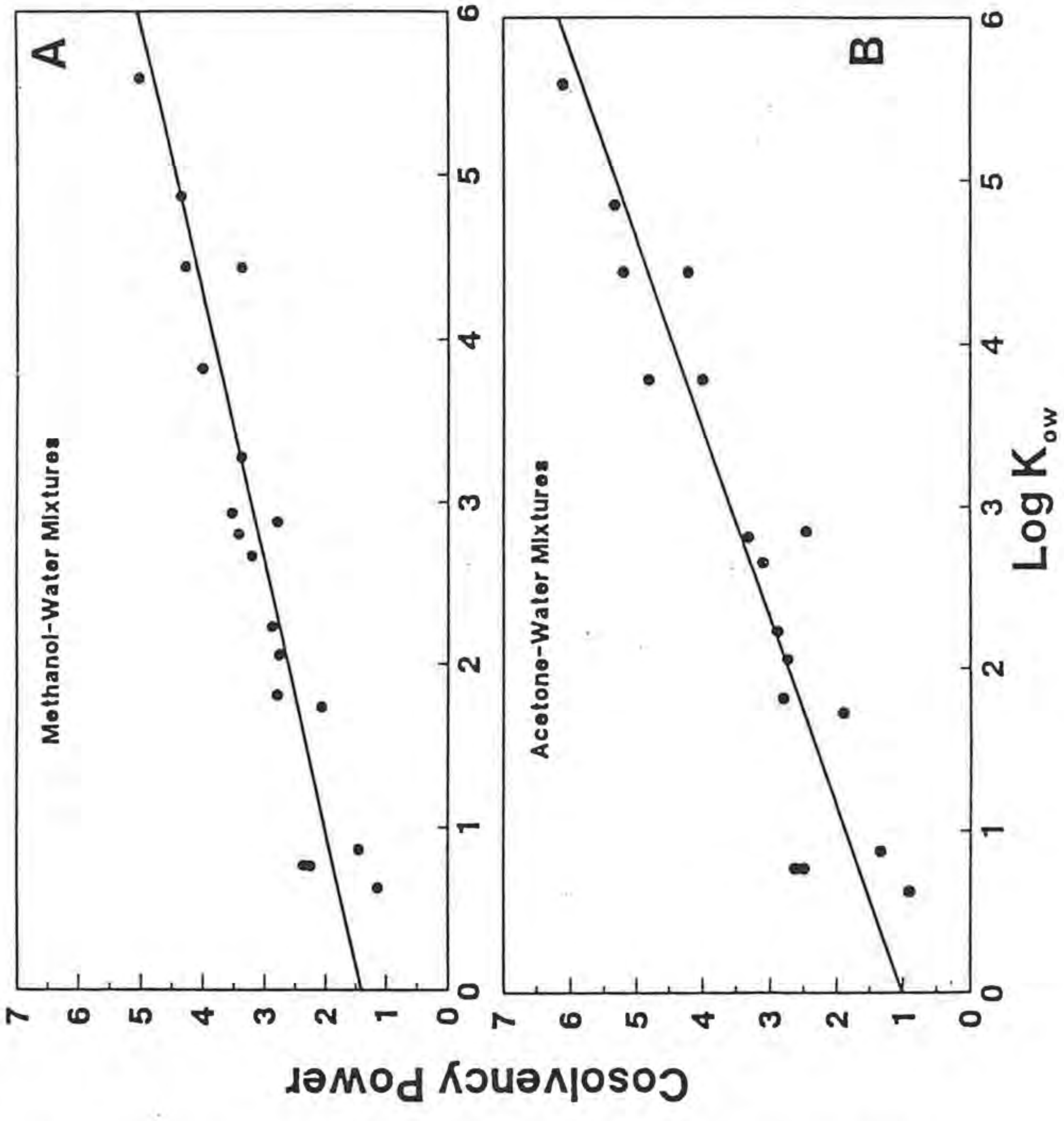
$$\sigma = a \log K_{ow} + b \qquad (4)$$

where a and b are empirical constants unique for a given cosolvent. Figure 3-4 presents a plot of eq (4), where the σ values were estimated from HOC solubility profiles measured in methanol-water and acetone-water mixtures. It should be noted that other cosolvent and solute properties may also be used to estimate σ values (Morris et al. 1988; Rubino and Yalkowsky 1987a,b).

Although both eqs (3) and (4) provide useful first-order approximations of the cosolvency power of a solvent for a solute, measured HOC solubility profiles in solvent mixtures often exhibit deviations from the expected log-linear behavior primarily due to solvent-cosolvent interactions. The observed cosolvency in a binary mixed solvent can be more generally defined as,

$$\log S_m = \log S_w + \beta \sigma_c f_c \qquad (5)$$

where β is an empirical constant that accounts for water-cosolvent interactions. Note that $\beta = 1$ implies the absence of water-cosolvent interactions. Equation 5 provides only a reasonable approximation of the expected cosolvency effects, because solvent-solvent interactions are not constant over the entire f_c range. Pinal et al. (1991) proposed a modified log-linear model for estimating the solubility of HOCs in nonideal solvent mixtures which used the UNIFAC model to estimate expected deviations due to solvent nonideality as a function of f_c.



4. Relationship between cosolvency power (σ) and log octanol-water coefficient (K_{ow}) for several hydrophobic organic chemicals. Data compiled for solubility in methanol-water mixtures (A), and acetone-water mixtures (B) are shown. Taken from Rao et al. (1991).

3.3.2. Equilibrium Sorption from Mixed Solvents

3.3.2.1. Hydrophobic Organic Chemicals (HOCs)

A log-linear cosolvency model describing the decrease in sorption of HOCs with increasing f_c in a binary solvent is given by (Fu and Luthy 1986b; Rao et al. 1985):

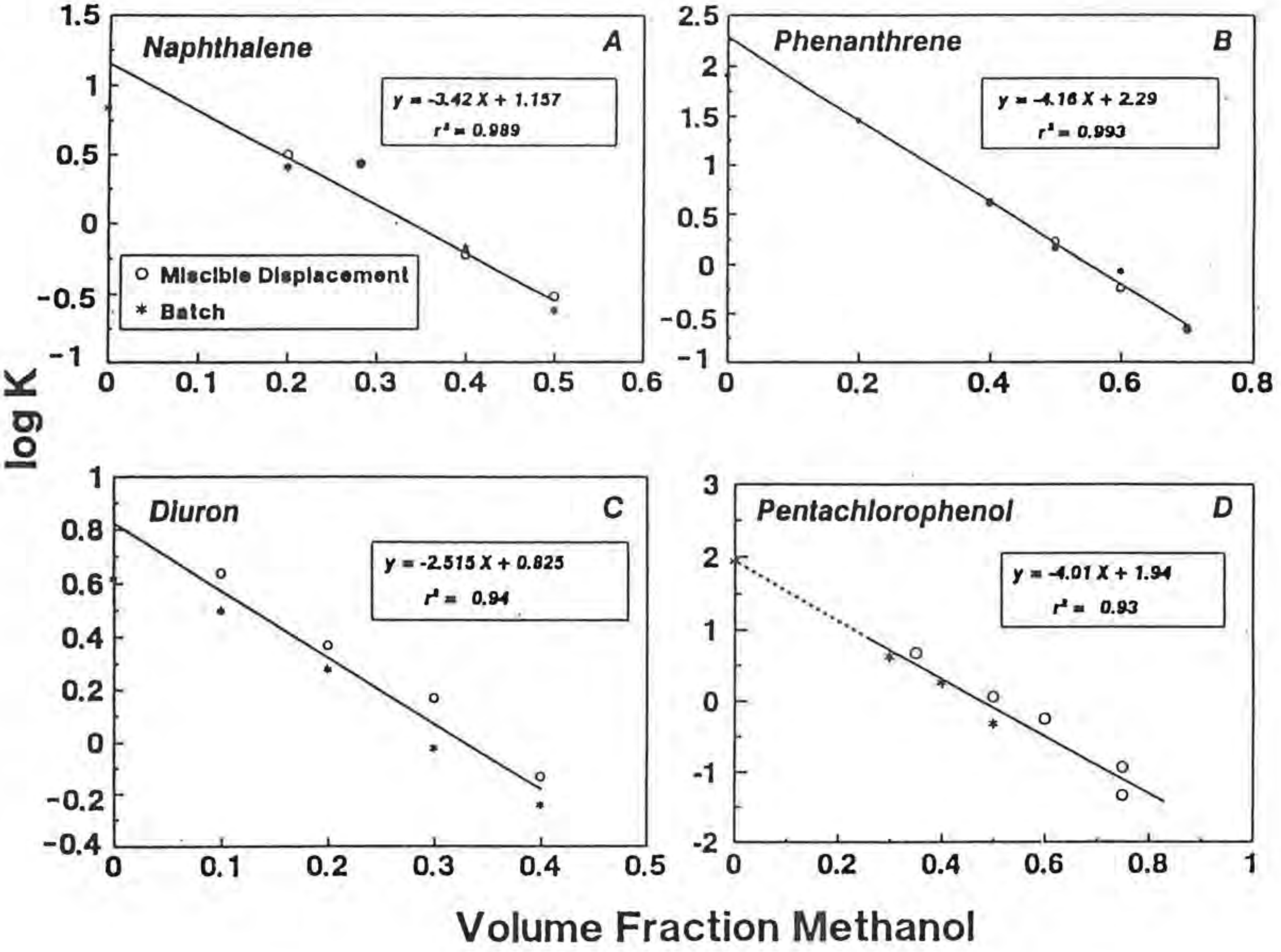
$$\log K_b = \log K_w - \alpha \beta \sigma_c f_c \qquad (6)$$

where K is the equilibrium sorption coefficient (mL/g), α and β are empirical constants for describing solvent-solvent and solvent-sorbent interactions, and the subscript b stands for binary mixed solvent. For a mixture of water and multiple cosolvents, eq (6) may be extended as follows (Rao et al. 1985; Rao and Lee 1987; Woodburn et al. 1986):

$$\log K_m = \log K_w - \Sigma \alpha_i \beta_i \sigma_i f_i \qquad (7)$$

where the subscript m denotes mixed solvent and the other terms are as defined earlier.

An extensive amount of data has shown that in binary mixed solvents, HOC solubility increases and sorption decreases in a log-linear manner as the volume fraction of the organic cosolvent increases (Fu and Luthy 1986a,b; Nkedi-Kizza et al. 1985, 1987, 1989; Rao et al. 1985, 1986, 1989, 1990; Rubino and Yalkowsky 1985, 1987a,b,c; Walters and Guissepi-Ellie 1988; Woodburn et al. 1986; Yalkowsky 1985, 1987). Examples of the log-linear decrease in sorption of several organic solutes are presented in Figure 3-5. These experimental findings are consistent with the predictions of both the UNIFAC model and the log-linear cosolvency model. The successful application of the log-linear model to describe solubility and sorption in ternary and quinary mixed solvents has also been demonstrated (Rao and Lee 1987; Rubino et al. 1984; Rubino and Yalkowsky 1985; Yalkowsky and Rubino 1984). Lane and Loehr (1992) measured the dissolution/desorption of several polycyclic aromatic hydrocarbons from tar-contaminated soils. They successfully applied the log-linear cosolvency model to predict the aqueous phase concentrations by extrapolating from data collected in a few binary solvents mixtures.



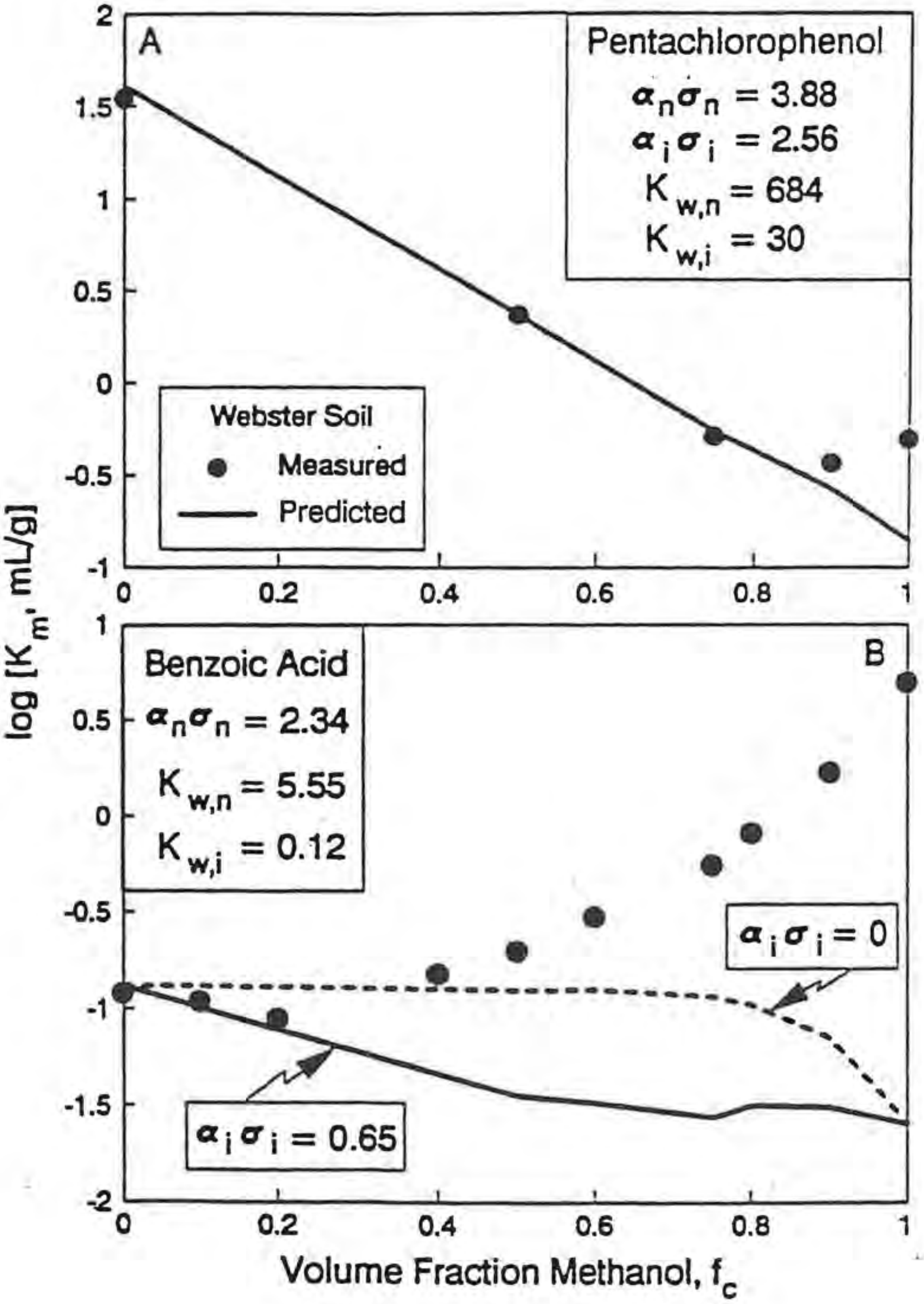
5. Log-linear decrease in equilibrium sorption coefficient (K, mL/g) and volume fraction methanol for sorption of several organic solutes. Taken from Rao et al. (1991).

3.3.2.2. Hydrophobic Ionogenic Organic Chemicals (HIOCs)

For hydrophobic ionogenic compounds (HIOCs) of environmental interest, data on solubility, sorption, and transport in mixed solvents are limited. However, pharmaceutical literature contains solubility data for several drugs spanning a wide polarity range. Yalkowsky and Roseman (1981) observed that as solute polarity increases relative to the solvent, the solubilization curves become increasingly more parabolic in shape until an inverse relationship occurs (i.e., decreased solubility with cosolvent additions). Such behavior is explained on the basis of the solute-solute and solute-cosolvent interactions.

The sorption of HIOCs from mixed solvents has received little research attention to date. For several HIOCs of environmental relevance (log $K_{ow} > 1.0$), solubility does increase with increasing f_c, thus a decrease in sorption is expected. However, prediction of HIOC sorption from mixed solvents is confounded by a number of indirect effects resulting from cosolvent-induced phenomena occurring either in the solution phase or on the sorbent. For an organic acid in solvents of low dielectric constants (e.g., methanol, acetone, dimethylsulfoxide) an alkaline shift in the solute pK_a results in an increase in the fraction of neutral species.

Zachara et al. (1988) evaluated the sorption of quinoline by a clay isolate and montmorillonite in methanol/water solutions over a range of 0 to 60 volume per cent methanol, but the log-linear relationship was confirmed only up to 40% methanol by volume. In soil thin-layer chromatography studies (Hassett et al. 1981), dicamba (3,6-dichloro-2-methoxybenzoic acid) moved with the solvent front in both aqueous and 50/50 (v/v) ethanol/water solutions, but was strongly retained by soil with neat ethanol as the mobile phase. The greater retention of dicamba in neat ethanol over that in aqueous solutions was attributed to solute-solvent interactions. Lee et al. (1993) investigated the sorption by soils of several substituted phenols and carboxylic acids in methanol/water solutions. As shown in Figure 3-6A, they successfully described the cosolvency behavior of the substituted phenols by a model incorporating both speciation and cosolvent effects (i.e., summation of eqs 1 and 6). However, large positive deviations from the proposed model were observed for the



6. Comparison of measured (data points) and predicted (dashed and solid lines) impacts of methanol on equilibrium sorption coefficient (K_m) for sorption of pentachlorophenol (A) and benzoic acid (B) from methanol-water mixtures. Taken from Lee et. al. (1993).

sorption of benzoic acid (Figure 3-6B), especially at high cosolvent contents, suggesting the role of some type of cosolvent-enhanced surface complexation mechanism(s). Further investigation is needed to better understand the impacts of cosolvents on HIOC interactions with soils.

3.3.3. Sorption Nonequilibrium in Mixed Solvents

Cosolvents have been shown to influence the rate at which sorption equilibrium is attained. The inverse log-log relationship between the sorption rate constant (k_2) and the equilibrium sorption coefficient (K_w) for aqueous systems, and the inverse, log-linear relationship between sorption coefficient and volume-fraction cosolvent (f_c) suggests that k_2 would increase in a log-linear fashion with increasing f_c:

$$\log k_{2,m} = \log k_{2,w} + A \alpha \beta \sigma_c f_c \tag{8}$$

where A is an empirical coefficient, and other parameters are as defined previously. Figure 3-7 presents a compilation of experimental data from column studies confirming eq (8). Brusseau et al. (1991b) suggested that as the cosolvent content increases, the polymeric organic matter swells; this leads to enhanced rates of solute permeation and is reflected in faster intra-organic matter diffusion rates (i.e., increased k_2 values).

3.3.4. Cosolvency and Contaminant Transport

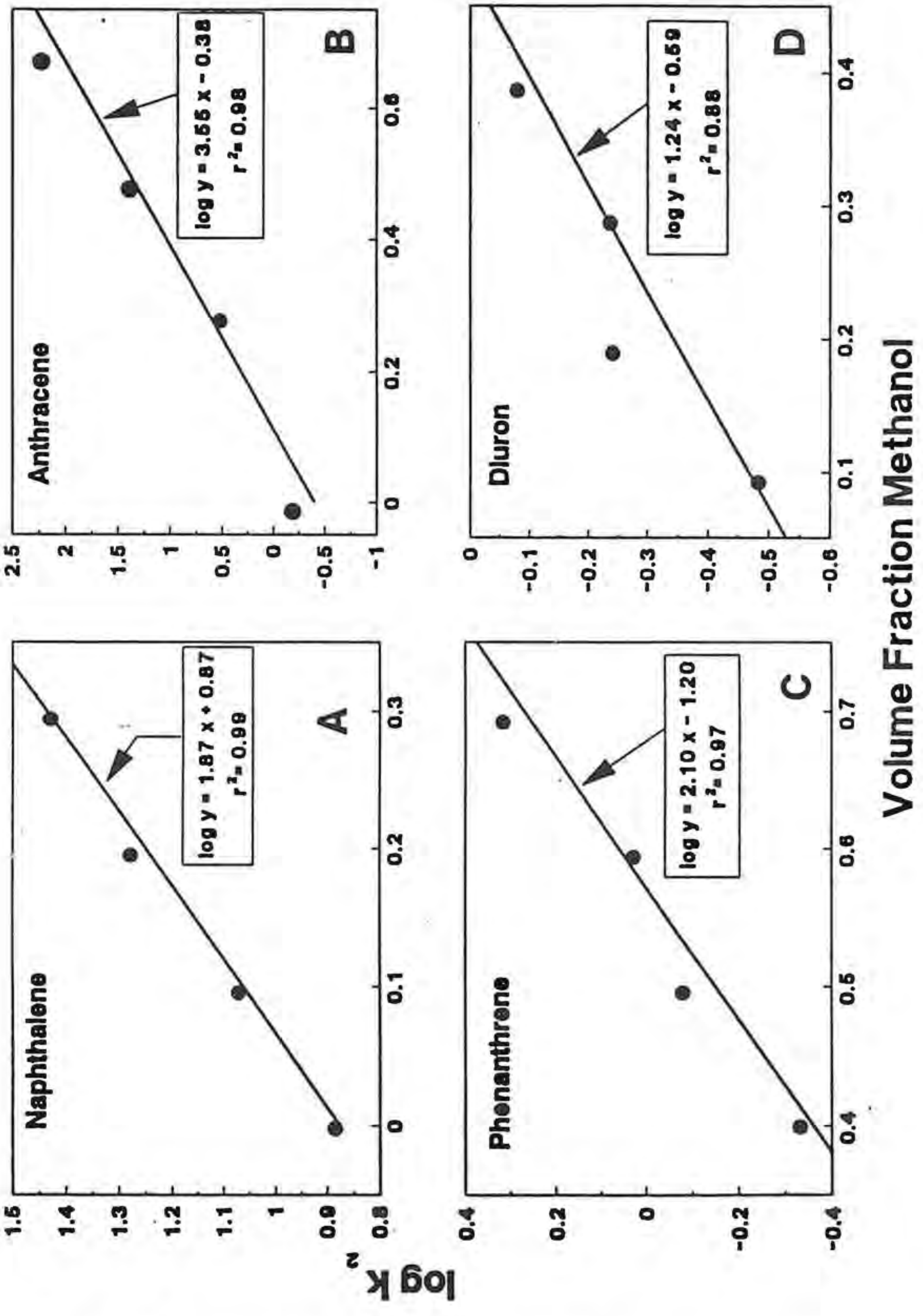
Sorption effects on contaminant transport can be conveniently expressed using the retardation factor (R) defined as follows:

$$R_w = [\,1 + (\rho K_w/\theta)] \tag{9}$$

where ρ is the soil bulk density, K_w is equilibrium sorption coefficient (for sorption from aqueous solutions), and θ is the volumetric soil-water content. Note that for a nonsorbed solute, $R=1$ since $K_w=0$. Equation (9) can be modified to account for cosolvent effects by substituting eq. (6) for K_w in eq (9), and rearranging, to give:

$$\log (R_m - 1) = \log (R_m - 1) - \alpha \beta \sigma_c f_c \tag{10}$$

Therefore, an increase in solubility upon cosolvent addition is reflected in a decrease in sorption and retardation. Nkedi-Kizza et al. (1987) and Wood et al. (1990) have demonstrated the validity of eq (10) with experimental data collected from soil column



7. Log-linear dependence of sorption mass-transfer rate coefficient (k_2, hr^{-1}) and volume fraction methanol. Taken from Rao et al. (1991).

studies with several organic contaminants under conditions of isocratic elution (i.e., f_c was time invariant).

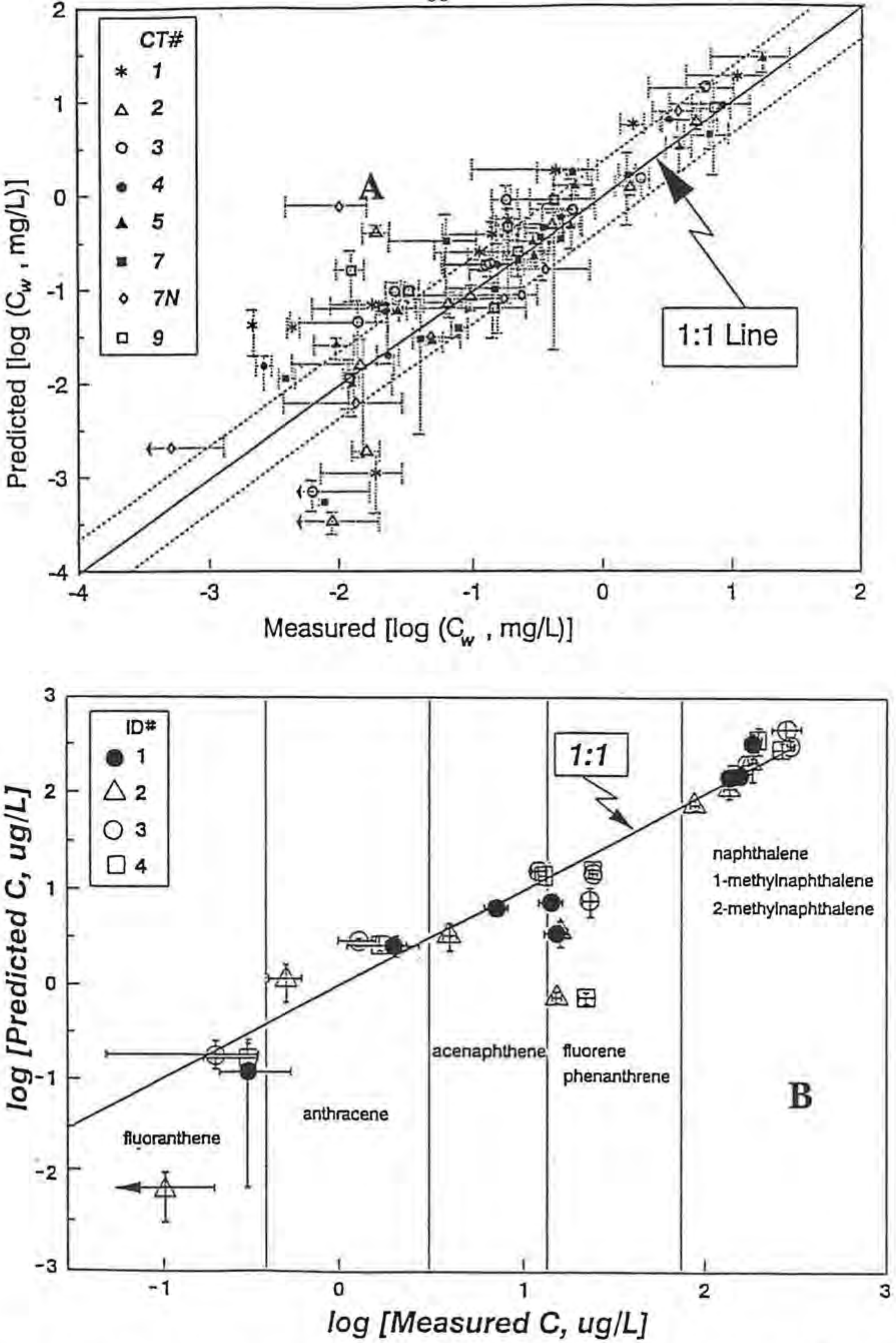
3.4. PARTITIONING FROM MULTI-PHASIC LIQUIDS

An understanding of solubility (or partitioning) of HOCs from complex liquids is essential for predicting contaminant release from mixtures such as fuels (e.g., gasoline, diesel, kerosene) and industrial wastes (coal tar, creosote). The solubility of a given component in a mixture may be altered by other components that may act as cosolutes or cosolvents. According to the model based on Raoult's law, the concentration of an organic constituent in the aqueous phase (C_w) in equilibrium with an "ideal" organic mixture is equal to the product of the mole fraction (X_o) of that constituent in the organic phase and the pure compound solubility (S_l, moles/L) in its liquid phase (i.e., $C_w = X_o S_l$). Note that for solids, S_l is the solubility of a hypothetical super-cooled liquid. Examining the ideality of the entire system in a single, graphical representation is made feasible by considering the liquid-liquid partition coefficient (K_D). Application of Raoult's law and the assumption of ideal behavior yields the following relationship (Cline et al. 1991; Lee et al. 1992b):

$$\log K_D = -\log S_l - \log \bar{V}_o \qquad (11)$$

where $\bar{V}_o$ is the molar volume of the organic phase which can be estimated by the ratio of the average molecular weight ($\underline{MW}_o$, g/mole) and the density of the organic phase (ρ). It is evident from eq (11) that a linear inverse relationship exists between log K_D and log S_l where the slope is negative one and the intercept is dependent on the molar volume ($\bar{V}_o$) of the particular organic mixture. Using this relationship, the assumption of ideal behavior can be conveniently assessed for a complex mixture with minimal number of easily obtained parameters.

Cline et al. (1991) and Lee et al. (1992a,b) presented data for liquid-liquid partitioning of hydrocarbons from several gasolines, diesel fuels, and coal tars. As indicated by the data shown in Figure 3-8, their analysis suggests that deviations from ideal behavior (Raoult's law) are within a factor-of-two or less in most cases. Agreement between the model predictions based on Raoult's law and measured liquid-



8. Comparison of measured and predicted aqueous-phase concentrations of several polycyclic aromatic hydrocarbons partitioning from coal tars (A) and diesel fuels (B) into water. The predictions were based on eq (12) with the assumption that ideal behavior is valid. Taken from Lee (1993).

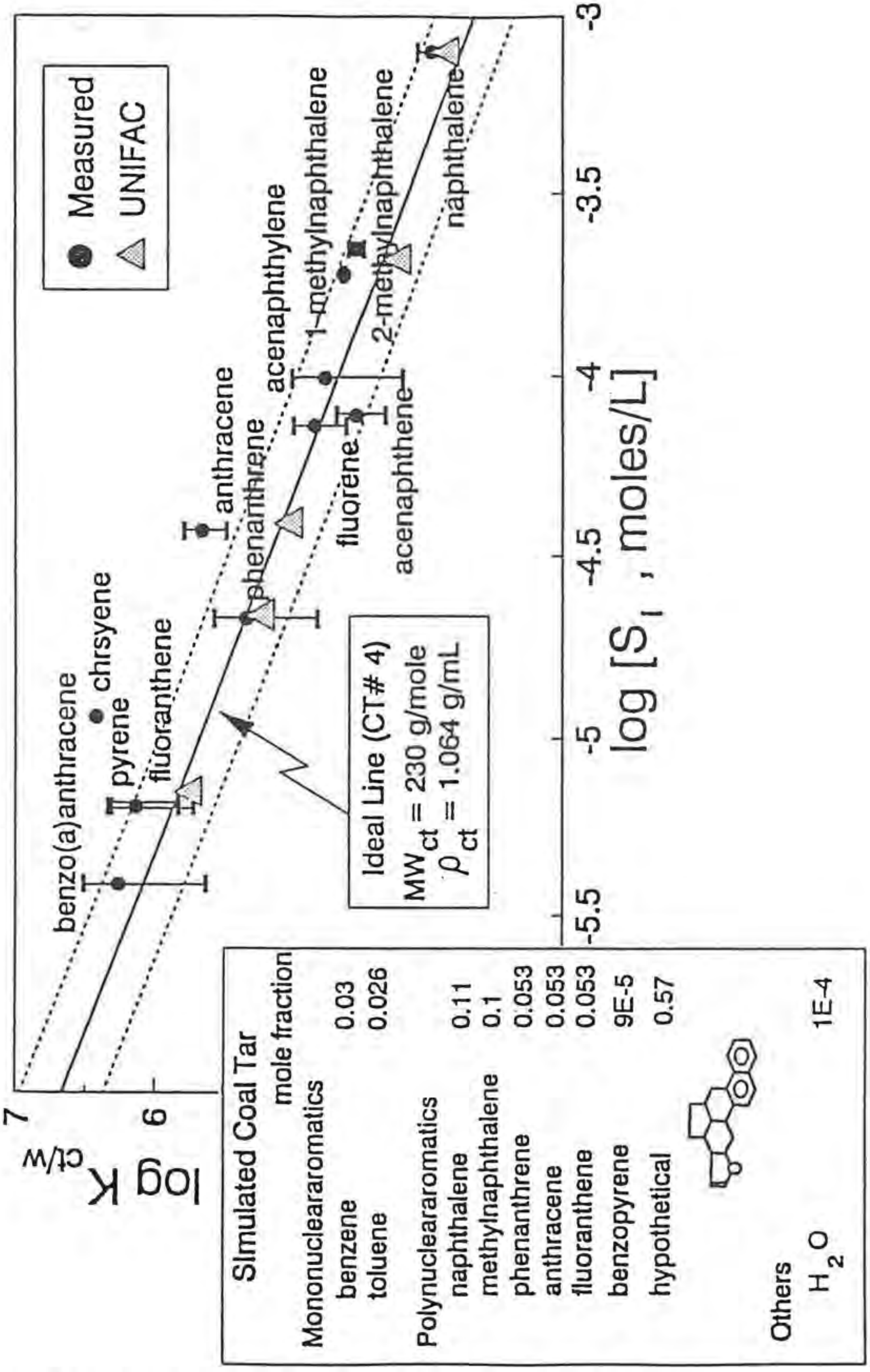
liquid partitioning data is not to be taken as evidence that complex organic wastes are indeed ideal mixtures. Rather, the assumption of ideal behavior might suffice for practical considerations in providing first-order estimates for maximum contaminant concentrations likely to be found in groundwater leaving such a waste source.

The magnitude of the deviations from solute-solute interactions that might lead to nonideal partitioning behavior for complex liquid mixtures may be evaluated using the UNIFAC model. Two problems are encountered in such attempts. First, it is extremely difficult to characterize (either qualitative or quantitative) the composition of these wastes. For example, no more than about 60% of the coal tar constituents can be identified and quantified using sophisticated chromatographic techniques. Second, even if the compositional information were available, the necessary UNIFAC model parameter values may not always be available in existing compilations. Thus, it is often necessary to replace the complex mixture with a simpler, hypothetical mixture comprising of fewer compounds, as was done by Lee et al. (1992a,b) in analyzing the data for gasolines and diesel fuels. A comparison of the UNIFAC model predictions with measured tar-water partition coefficients is shown in Figure 3-9.

Peters (1992) investigated the dissolution of coal tar in binary mixed solvents. She evaluated the feasibility of representing coal tar as a single "psuedo" component in order to evaluate an approach based on ternary phase diagrams. Parameter estimation techniques for describing the tar/solvent/water system was successful. However, Peters (1992) concluded that the predictive power of the model is currently limited by a lack of accurate binary data and the need to use several tie lines.

3.5. ENVIRONMENTAL APPLICATIONS

The likely presence of organic cosolvents at waste disposal/spill sites will result in higher concentrations of organic contaminants in pore water, since an increase in the concentration of organic cosolvents is reflected in decreased sorption. Decreased sorption, in turn, will lead to organic contaminants being transported farther than predicted from aqueous-based transport data. While this manifestation of cosolvency can exacerbate environmental problems, judicious application of the



9. Comparison of measured (solid circles) tar-water partition coefficients and predictions based on the UNIFAC model (triangles) and the Raoult's law approach (solid and dashed lines). The assumed composition of the coal tar, used in UNIFAC model calculations, is shown in the inset. Taken from Lee (1993).

principles of cosolvency can assist in alleviating existing problems. For example, removal of contaminated soils from a disposal/spill site and extraction with solvent mixtures (so-called "solvent washing") is one remediation technique that is receiving considerable attention.

3.5.1. Magnitude of Cosolvent Effects

A variety of organic cosolvents may be expected at and near waste disposal sites, especially if codisposal of a number of wastes had been practiced. However, protocols for site investigations usually do not call for monitoring of organic cosolvents in groundwater. Site-specific information on concentrations and types of cosolvents that may be present can be surmised only if waste composition is known. Thus, estimating the magnitude of cosolvent impacts in enhancing solubility and decreasing sorption/retardation is often difficult. Although direct field-scale evidence for cosolvency is lacking, anecdotal evidence from site investigations suggests that organic cosolvents are present and may have contributed to facilitated transport of organic contaminants at waste disposal facilities. Our data and model calculations suggest that solubility enhancement for most organic contaminants is likely to be small (< 20% increase) as long as cosolvent concentrations in pore water are < 2% by volume (or about 20,000 mg/L). Thus, dramatic alterations of chemodynamic properties are to be expected only in close proximity to a disposal site (i.e., the "near-field" region) where high concentrations of cosolvents are likely. With increasing distance from the site, cosolvent effects should diminish in proportion to decreasing cosolvent concentrations.

3.5.2. Dissolution of Multi-Component OIL Constituents

Available data (Cline et al. 1991; Lee et al. 1992a,b) indicate that Raoult's law can be used to provide reliable estimates of organic contaminant concentrations in groundwater in contact with multi-component OILs, such as gasolines, diesel fuels, and coal tars. Even though these wastes are complex liquid mixtures, the nonideality resulting from interactions with other constituents is apparently sufficiently small to be neglected for most practical applications. Equilibrium or maximum concentration of a multi-component OIL constituent in groundwater, C_w (mg/L), can be estimated as follows:

$$C_w = M_o \underline{MW}_o S_l \qquad (12)$$

where M_o is the concentration (mg/g) of a specific constituent in the organic phase, $\underline{MW}_o$ is average molecular weight of the organic mixture (g/mole), and S_l is the super-cooled liquid solubility (moles/L).

Table 3.1 summarizes the range of likely maximum concentrations of selected hydrocarbons in groundwater which is in contact with some multi-component OILs. Equation (12) was used along with information on the composition of the waste mixtures (Cline et al. 1991; Lee et al. 1992a,b; Millner et al. 1992). Equilibrium for liquid-liquid phase partitioning was assumed in calculating the values in Table I. The range in calculated C_w values is a direct reflection of the wide diversity in waste composition (both within and between waste types). Note that the aqueous-phase concentrations will reflect the changes in composition of the waste, as it "ages". Nonequilibrium conditions, arising from various mass-transfer constraints, as well as dilution and degradation processes will result in the actual concentration being smaller than those shown in Table 3-1. The possibilities of sampling artifacts (e.g., formation of emulsions during pumping) (Thomas and Delfino 1991) need to be examined when the measured aqueous-phase concentrations are found to be much larger than those estimated assuming ideal behavior (i.e., Raoult's law).

3.5.3. Remediation of Contaminated Soils

Contaminated aquifers have traditionally been remediated by pump-and-treat methods. With increasing awareness of the limitations to "pump-and-treat" methods to effectively clean up groundwater contaminated with organic pollutants, interest exists in new remediation techniques based on chemical additives that increase the efficiency of rate at which contaminants are removed (Palmer and Fish 1992). In situ soil flushing is one such remediation technique that involves the injection of a mixed solvent (water plus organic cosolvents) or a surfactant at a site

Table 3-1. Maximum C_w values (25°C) for Several PAHs Based on the Data Compiled for Thirty Gasolines, Four Diesel Fuels, and Eight Coal Tars. Liquid-liquid Partitioning Data Reported by Cline et al. (1991) and Lee et al. (1992a,b) Were Used to Calculate the C_w Values.

Compound	Aqueous Solubility S_w (mg/L)	Range of Maximum C_w (mg/L)		
		Gasolines	Diesel Fuels	Coal Tars
Benzene	1780	1 - 130	0.05 - .4	< 30
Toluene	515	20 - 200	0.3 - 6	< 10
Ethylbenzene	150	1 - 6	0.03 - .15	< 5
Xylenes	200	2 - 25	0.2 - 2	< 10
Naphthalene	32	--	0.1 - .3	1 - 26
1-Methylnaphthalene	27	--	0.1 - .2	0.2 - 2
2-Methylnaphthalene	26	--	0.2 - .35	1 - 1.4
Acenaphthylene	3.93	--	--	0.01 - 0.5
Acenaphthene	3.42	--	0.004 - 0.02	0.02 - 0.3
Fluorene	1.9	--	0.01 - 0.03	0.1 - 0.3
Phenanthrene	1.0	--	0.01 - 0.03	0.1 - 0.4
Anthracene	0.07	--	< 0.002	< S_w
Fluoranthene	0.27	--	< 0.005	< 0.01
Pyrene	0.16	--	--	0.02 - 0.1
Benzo(a)anthracene	0.0057	--	--	< S_w
Chrysene	0.006	--	--	< S_w
Benzo(a)pyrene	0.0038	--	--	< 0.001

contaminated with organic chemicals (U.S. EPA 1991). Site remediation efforts may involve any of the described regions. Soil flushing would be most logically applied for clean up of the source area, since removal of the source prevents further contamination of groundwater. Excavation of the soil from the source area is an alternative option, but the contaminated soil still requires treatment (e.g., incineration, solvent washing) before it can be safely disposed. Excavation can also be very expensive, especially when a large volume of soil is contaminated, and may not even be possible when, for example, the source is located under permanent structures. In such cases, soil flushing may be considered as a more plausible alternative.

In-situ soil flushing involves the following steps (U.S. EPA 1991): (1) the solvent mixture or surfactant is injected upstream of the contaminated zone, (2) the additives with the dissolved contaminants are extracted downstream and treated above ground to recover the solvent, and (3) the recovered additives may be reinjected. Physical barriers (e.g., sheet piling, slurry walls) or hydraulic control measures might be needed to prevent off-site transport of contaminants with the chemical additives. The cosolvency concepts discussed earlier may be used in developing criteria for the selection of solvents or solvent mixtures to achieve optimal extraction of the contaminants of interest. For example, other factors being equal, it may be preferable to choose a solvent with greater cosolvency power (larger σ) so that the contaminants can be extracted using less solvent. If economic or other constraints prevent the use of pure organic solvents and a mixture of water and cosolvents are to be used, the log-linear cosolvency model might provide reasonable estimates of the level of extraction achievable with various combinations of cosolvents.

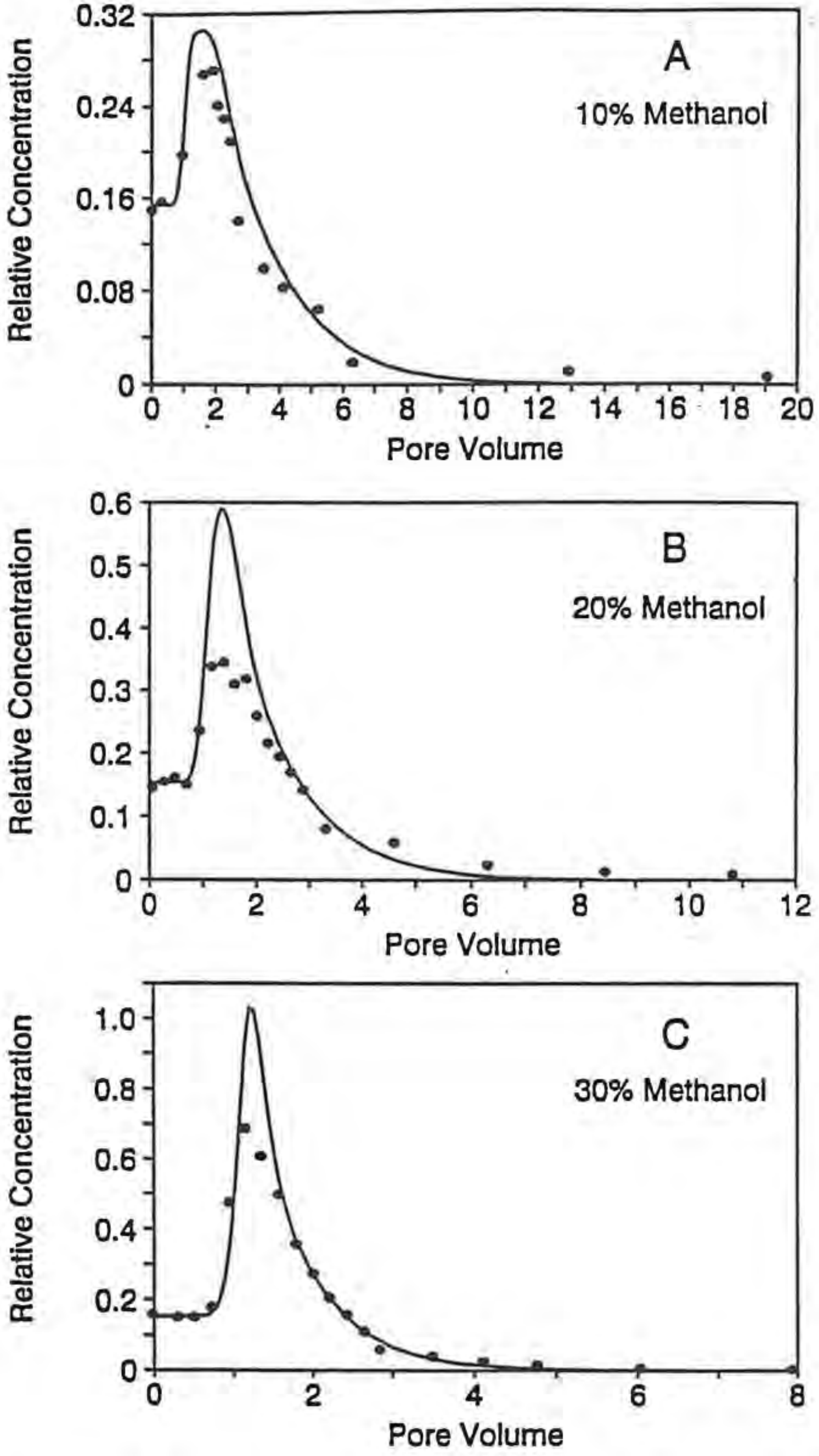
The use of surfactants for remediation of contaminated soils has been studied extensively (see review by Palmer and Fish 1992). The presence of surfactants increases the apparent solubility and decreases the sorption of HOCs. Surfactants are more efficient than mixed solvents; i.e., an equivalent increase in solubility is achieved at a much lower concentrations of a surfactant compared to a cosolvent. In addition, surfactants may facilitate emulsification of OILs (which enhances contaminant removal) to a greater extent than cosolvents. However, surfactants do not reduce nonequilibrium constraints as do cosolvents. Furthermore, when contrasted to cosolvents the delivery of surfactant solutions to the contaminated areas within a heterogenous medium might be more difficult.

The use of cosolvents for extraction of organic contaminants from various environmental matrices has been successfully demonstrated either at the pilot-scale or in full-scale commercial applications (U.S. EPA 1990). Currently, laboratory research is being conducted to evaluate the use of solvent-flushing (Augustijn et al. 1993; Luthy et al. 1993). Augustijn et al. (1993) presented a simulation model to predict contaminant elution curves during solvent flushing for the case of one-dimensional, steady flow through a contaminated soil. They also conducted column experiments with a Eustis fine sand that was initially equilibrated with an aqueous naphthalene solution, and then eluted with methanol-water solutions (cosolvent content 10, 20, and 30%) to remove naphthalene. The model simulations, based on parameter values estimated using literature data, agreed well with the measured elution profiles for naphthalene displacement with methanol-water solutions (see Figure 3-10). In general, the higher the cosolvent fraction and the smaller the retardation factor in water, the faster the contaminant was recovered. Model parameter sensitivity analysis suggested that the presence of nonequilibrium conditions, soil heterogeneity and type of cosolvent will influence the required time to recover the contaminant.

3.6. SUMMARY

Industrial waste disposal/spill sites are characterized by the presence of complex organic mixtures of multiple contaminants, present at high concentrations. In addition, the waste may be composed of several distinct immiscible phases of solvent mixtures. Several empirical and semi-empirical relationships have been developed to describe contaminant behavior in these complex systems were reviewed.

Three separate regions within a contaminant plume have been discussed: a near-field region, a transition zone, and a far-field region. Most data are available for the environmental fate and transport of organic contaminants in the far-field region, where the waste constituents are present in an aqueous solution.



10. Elution profiles for naphthalene displacement from a soil column with mobile phases containing different methanol contents. Measured (data points) are compared with model predictions (solid lines) for cosolvent flushing of contaminated soils. Taken from Augustijn et al. (1993).

Sorption of HOCs can be predicted from various solute properties and the OC content of the soil or aquifer material. Due to their polar nature, adsorption of HIOCs is subject to specific interactions with the soli surface. Adsorption of HIOCs has been shown to be a function of pH, OC and pK_a. In all regions nonequilibrium conditions may be present. Again, this has been best quantified for the far-field region where the sorption rate coefficient has been found to be inversely related to the equilibrium sorption coefficient.

In the transition zone, contaminants may be dissolved in a solution phase that is made up of water and varying amounts of cosolvents. Solubility increases long-linearly in the presence of cosolvents, while sorption decreases proportionately and nonequilibrium constraints are reduced. The effects of cosolvents in solubility and sorption for HOCs have been successfully described by a log-linear model. The UNIFAC model or a modified log-linear model are available to account for nonideal behavior due to solute-solvent-cosolvent interactions. Limited available data indicate that the log-linear cosolvency model may not always predict the cosolvent effects on solubility and sorption of HIOCs, especially at higher cosolvent contents. Further research is needed to explain the deviations observed from the predicted sorption of HIOCs from mixed solvents.

Phase partitioning is the primary process that determines the release of contaminants from the near-field region, which includes the source. Raoult's law has been shown to adequately describe equilibrium phase partitioning for several multi-components OIL wastes, including gasolines, diesel fuels, and tars. However, limited information is available on the rate-limiting processes controlling contaminant release in the near-field region of sites containing OIL wastes.

The cosolvency concepts are useful in defining the magnitude of enhanced contaminant transport at waste disposal/spill sites. It is apparent that high cosolvent contents required to produce dramatic alterations in contaminant solubility and sorption are likely only in close proximity to the source (i.e., in the near-field region). Cosolvents may be used for remediation of contaminated soils. Commercial-scale applications of solvent extraction have been demonstrated. The use of cosolvents and surfactants for in-situ flushing of contaminated sites appears promising, as evident from laboratory-scale tests. Field-scale studies are underway to evaluate the use of surfactants for remediation of contaminated soils. Similar studies for the use of cosolvents are in the design stages.

3.7. ACKNOWLEDGEMENTS

This research was supported, in part, by funds from a Cooperative Agreement (CR-812581, CR-811144, CR-814512) between the University of Florida and the R.S. Kerr Environmental Research Laboratory, Electric Power Research Institute Contract No. RP-2879-7, and the Subsurface Science Program, Office of Health and Environmental Research, U.S. Department of Energy through a contract (no. DE-AC06-76RLO 1830) to Battelle PNL. L.S. Lee is now at Agronomy Department, Purdue University, West Lafayette, IN 47907, USA, and D.C.M. Augustijn is now at Shell Research Ltd., Sittingbourne Research Centre, Sittingbourne, Kent ME9 8AG, United Kingdom.

3.8. DISCLAIMER

Although the research presented in this article has been partially funded by the U.S. Environmental Protection Agency and the U.S. Department of Energy through cooperative agreements, it has not been subjected to technical and policy review by either Agency, and therefore this manuscript does not necessarily reflect the views of the Agencies, and no official endorsement should be inferred.

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ENVIRONMENTAL SOIL SCIENCE

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PROCEEDINGS OF A JOINT SYMPOSIUM

OF

THE CANADIAN LAND RECLAMATION ASSOCIATION
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THE CANADIAN SOCIETY OF SOIL SCIENCE

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held at
EDMONTON, ALBERTA, CANADA
1992

ENVIRONMENTAL SOIL SCIENCE

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Edited by
C.B. Powter, S.A. Abboud and W.B. McGill

Compiled by
Y.A. Kalra and W.W. Pettapiece

Proceedings of a Joint Symposium
of
The Canadian Land Reclamation Association
and
The Canadian Society of Soil Science

Held at
The University of Alberta
Edmonton, Alberta, Canada
August 10-11, 1992

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Suggested citation:

Powter, C.B., S.A. Abboud and W.B. McGill (editors) 1995. Environmental soil science: anthropogenic chemicals and soil quality criteria. Proceedings of a symposium held August 10-11, 1992. The Organizing Committee, Canadian Land Reclamation Association and Canadian Society of Soil Science, Edmonton, Canada. 278 p.

Copies of this publication may be obtained for $20.00 (includes postage) from:

Canadian Society of Soil Science
Box 21018, Westend Postal Outlet
Brandon, Manitoba
Canada R7B 3W8

ISBN: 0-9680185-0-5

PREFACE

The Environmental Soil Science conference was held August 8-13, 1992 at the University of Alberta, Edmonton, AB. It was sponsored jointly by the Canadian Land Reclamation Association (CLRA) and the Canadian Society of Soil Science (CSSS). The objective of the conference was to share theoretical and applied aspects of soil science. It also served to get participants from the sponsoring groups together to find areas of mutual interest. There were 330 participants from Austria, Bangladesh, Canada, England, France, Germany, India, Japan, New Zealand, Norway, Spain, the Netherlands, and USA.

Abstracts of the oral and poster papers were published in the Canadian Journal of Soil Science (Vol.72, No.3, August 1992. (p.299-353). Volunteer papers covered all aspects of land reclamation, soil science, and public participation in the environmental review process. Seventy six of the 164 volunteer papers were presented as posters.

The invited papers presented in the plenary sessions focused on soil quality and interaction of soils with anthropogenic chemicals, and are published in this proceedings. Publication of the proceedings has taken an unduly long time due to unavoidable circumstances and we apologize for the delay.

Grateful acknowledgement is expressed to our colleagues on the organizing committee (J.A. Robertson, Chair) for their contributions to the success of the conference.

Y.P. Kalra and W.W. Pettapiece, Compilers

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