United States
Environmental Protection
Agency

Research and Development

Robert S. Kerr Environmental
Research Laboratory
Ada, OK 74820

EPA/600/M-91/009 Mar. 1991

EPA ENVIRONMENTAL RESEARCH BRIEF

Solubility, Sorption and Transport of Hydrophobic Organic Chemicals in Complex Mixtures

P.S.C. Rao[1], L.S. Lee[1] and A.L. Wood[2]

Introduction

Environmental contamination problems commonly involve wastes consisting of complex mixtures of chemicals. The behavior of these mixtures has not been well understood because the primary chemodynamic properties (e.g., solubility, sorption, transport) of organic chemicals have usually been characterized in aqueous solutions which are simple in composition relative to many waste mixtures found at or near disposal/spill sites. Typically, laboratory studies have focused on chemodynamics of single solutes in water or in dilute electrolyte solutions.

The research summarized in this report focuses on the effects which organic cosolvents have on the sorption and mobility of organic contaminants. This work was initiated in an effort to improve our understanding of the environmental consequences associated with complex mixtures and to enhance our ability to deal with these consequences in a technically responsible manner.

Specific objectives of the project were to:

(1) measure solubility and sorption for selected organic chemicals in complex solvent mixtures consisting of mixtures of organic cosolvents and water; and

(2) utilize isocratic- and gradient-elution techniques to characterize the impacts of organic cosolvents on the transport of hydrophobic organic chemicals in soils and aquifer media.

The results of this work have application to the definition, prediction and remediation of soil and groundwater contamination problems. Since an increase in the concentration of organic cosolvents is reflected in decreased sorption, organic contaminants at waste disposal/spill sites are likely to be present at higher concentrations in pore water. Decreased sorption, in turn, will lead to organic contaminants being transported further than predicted from aqueous-based transport data. While this manifestation of cosolvency can exacerbate environmental problems, judicious application of the 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. The results presented here should be of direct use in selection of the appropriate solvent mixtures to extract the organic contaminants of interest.

Background

We define here *complex mixtures* as those systems having multiple solutes and multiple solvents. The solute mixtures of interest might consist of various combinations of nonpolar, hydrophobic organic chemicals (HOCs); hydrophobic, ionizable organic chemicals (HIOCs); and ionic organic chemicals (IOCs). The solvent may be a mixture of water and one or more organic cosolvents. Cosolvents that are soluble in water in all proportions will be referred to as completely-miscible organic solvents (CMOSs). Other solvents which have only a finite solubility in water will be referred to as partially-miscible organic solvents (PMOSs). Two types of solvent mixtures are of interest: (i) solvents consisting of water and cosolvents in a single, homogeneous liquid phase; and (ii) solvents containing water and cosolvents that form at least two distinct liquid phases. In this report, the first type will be referred to as *mixed solvents*, while the second type will be designated as *multiphasic solvents*.

In recent years, several researchers have recognized the need to study the chemodynamics of complex mixtures; and coordinated efforts were initiated to develop theoretical approaches and data bases. This work has been funded primarily by the U.S. Environmental Protection Agency (EPA), the U.S. Department of Energy (DOE), and the U.S. Air Force (USAF). Research funded by DOE, conducted primarily at Battelle PNL, has focused on competitive sorption by soils and clays from HIOC mixtures found in energy wastes (Felice et al., 1985; Zachara et al., 1987). With funding from EPA, researchers at the University of Florida have also studied the sorption from mixtures of HOCs and

---

[1] Soil Sci. Dept., Univ. of Florida, Gainesville, FL 32611; [2] R.S. Kerr Env. Res. Lab., U.S. EPA, Ada, OK 74820

Printed on Recycled Paper

PENGAD 800-631-6989
EXHIBIT
4
Johnson

HIOCs (selected to represent the so-called Appendix VIII compounds) that are commonly found at hazardous-waste land-treatment facilities (Rao et al., 1986). EPA has also funded much of the work completed to date on the effects of cosolvents on chemodynamics of organic contaminants (Yalkowsky, 1985, 1987; Rao et al., 1985; Rao and Lee, 1987; Nkedi-Kizza et al., 1985, 1987, 1989; Woodburn et Guissepi-Ellie, 1988; Walters et al., 1989). Sorption of jet fuel constituents from liquid and vapor phases has been examined with funding from the U.S. Air Force (McIntyre and deFur, 1985; Rao et al., 1988).

The log-linear cosolvency model and the UNIFAC model are among the theoretical approaches that have been used to examine cosolvent effects on solubility and sorption. 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 weighting coefficient is taken to be the volume fraction of each solvent component. Thus,

$$\log S_m = \Sigma f_i \log S_i \qquad (1)$$

where S is solubility (mg/L), f is volume fraction of the solvent, and the subscript m denotes mixed solvent while i denotes a specific solvent component. 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: (i) it has a more sound theoretical basis, (ii) activity coefficients in mixtures can be calculated given only pure component data, and (iii) 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.

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 (Rao et al., 1985; Nkedi-Kizza et al., 1985; 1987; Woodburn et al., 1986; Fu and Luthy, 1986a, 1986b; Rubino and Yalkowsky, 1985; 1987a, 1987b, 1987c). These experimental findings are consistent with the predictions of both the UNIFAC model and the log-linear cosolvency model. The successful extension of the log-linear model to describe solubility and sorption in binary, 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).

In contrast to the large amount of data on solubility and sorption of HOCs in mixed solvents with completely-miscible organic cosolvents (e.g., alcohols), similar data for mixed solvents involving partially-miscible organic cosolvents were essentially nonexistent prior to this study. Only limited data for solubility and sorption of HIOCs in mixed solvents are available (Fu and Luthy, 1986a; Zachara et al., 1988). Cosolvent impacts on kinetics of phase partitioning have been examined, though mostly in a qualitative manner (Freeman and Cheung, 1981; Nkedi-Kizza et al., 1989; Walters et al., 1989).

Laboratory studies were conducted during this project to collect solubility data, and these data were used to evaluate two theoretical approaches (the UNIFAC model and the log-linear model). Based on the solubility data collected, modifications to the log-linear model were proposed to improve its predictive capabilities. Batch equilibration and column displacement techniques were used to characterize equilibrium and nonequilibrium sorption of HOCs and HIOCs from mixed solvents. These data were used to compare cosolvent effects on solubility and sorption and to assess cosolvent interactions with the sorbent which impact equilibrium and kinetics of sorption. Partitioning of HOCs into water from complex mixtures of liquids was examined in order to provide data essential for estimating solubilization and release of aromatic constituents from fuels such as gasoline, diesel, and jet fuel, and from such wastes as coal tar and creosote. Retention of several HOCs from mixed solvents by synthetic sorbents (reversed-phase chromatography supports) and a surface soil was measured at several temperatures to characterize the energetics of HOC sorption and to better understand the sorptive mechanisms.

In the following sections, a brief summary of our findings in each of these areas is presented. Details can be found in several publications listed in Appendix A and Appendix B.

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*. The alterations in solubility might result from the following interactions: solute-solute, solute-cosolvent, cosolvent-cosolvent, and water-cosolvent. For nonpolar solutes and at low concentrations of polar/ionizable solutes, solute-solute interactions are likely to be negligible and are not considered further. The work presented here focuses on the other interactions listed above.

Sorption of organic solutes, especially HOCs, is inversely related to solubility. Thus, an increase in solubility resulting from the addition of a cosolvent leads to a proportional decrease in sorption. In addition to the interactions listed for solubility, sorption is influenced by solute-sorbent, and sorbent-cosolvent interactions. Both solute and cosolvent interactions with the sorbent were investigated in this project.

A convenient measure of cosolvency is the *cosolvency power*, defined here on the basis of the inherent ability of a cosolvent to produce an alteration in the solubility or sorption upon addition of a cosolvent. Behavior in a pure (neat) aqueous solution and a pure (neat) organic solvent will serve as the basis for quantifying the cosolvency power.

The cosolvency power ($\sigma_{s,c}$) of a cosolvent for a solute (subscript s) may be defined as:

$$\sigma_{s,c} = \log [S_{s,c} / S_{s,w}] \qquad (2)$$

where S is the solute solubility (mg/L) in neat cosolvent (subscript c) or pure water (subscript w). Since HOC solubility in organic solvents is larger than that in water, $\sigma_{s,c} > 0$. Larger values of $\sigma_{s,c}$ indicate a greater solubilizing power of the solvent for a specific solute.

It may be expected that with decreasing polarity of the cosolvent, $\sigma_{s,c}$ will increase for hydrophobic solutes. Thus, $\sigma_{s,c}$ values should be inversely related to various indices of solvent polarity (e.g., dielectric constant, Rohrschneider polarity index, $E_T(30)$, and others). Rubino and Yalkowsky (1987a, 1987b) have investigated such relationships for solubilization of pharmaceutical drugs. The inverse relationship between $\sigma_{s,c}$ and $E_T(30)$ for solubilization of anthracene in several solvents is shown in **Figure 1**. For a given solvent, $\sigma_{s,c}$ values should increase with increasing hydrophobicity of the solute. Morris et al. (1988) have shown that σ values are indeed positively correlated with log K_{ow} values. Two examples of such a relationship are shown in **Figures 2A** and 2B. It is evident from the data in Figures 1 and 2 that the cosolvency power ($\sigma_{s,c}$) values can be estimated given specific properties of the solute and the solvent. Data presently available for several solute-solvent systems can be effectively utilized to estimate $\sigma_{s,c}$ for other systems.

The measured HOC solubility profiles in binary solvent mixtures generally deviate from the expected log-linear plot, primarily because of water-cosolvent interactions. The extent of such deviations may then be taken as an index for the magnitude of such interactions. The observed cosolvency power in a binary mixed solvent is defined here for solubility as,

$$\sigma_{s,m} = \log [S_{s,m} / S_{s,w}] \qquad (3)$$

and for sorption as,

$$\sigma_{s,m} = \log [K_{s,w} / K_{s,m}] \qquad (4)$$

where $\sigma_{s,m}$ is the experimentally-measured value of cosolvency power, S is the measured HOC solubility (mg/L), and K is the measured sorption coefficient (mL/g), with the subscripts m and w denoting a binary mixed solvent and water, respectively.

For operational convenience, in calculating σ values in eqs (3) and (4) we use solubility or sorption values measured in 50% (v/v) solvent mixture for CMOS-water systems and saturated solutions for PMOS-water systems. This choice also precludes problems associated with mutual miscibility of organic coslvents (e.g., methanol, acetone) with liquid solutes (e.g., benzene, toluene). When cosolvent-water interactions are significant, the predicted (eq 2) and measured (eqs 3 or 4) cosolvency powers are not equivalent. We may therefore

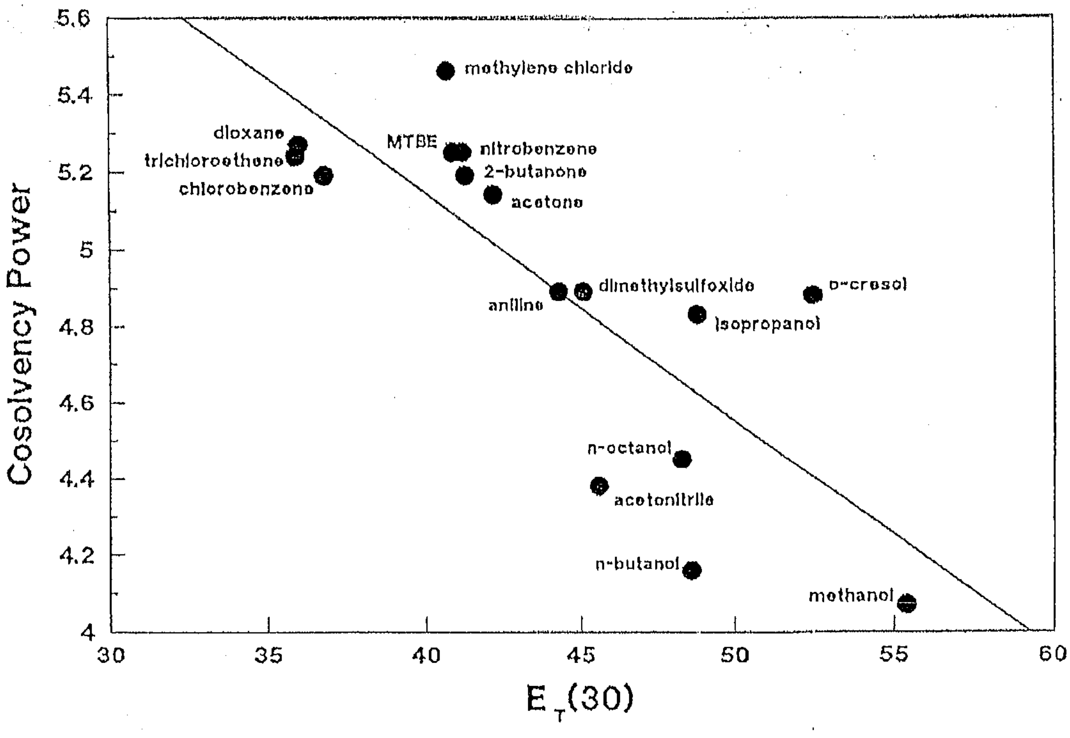

Figure 1. Inverse relationship between cosolvency power ($\sigma_{s,c}$) and solvent polarity index $E_T(30)$. Values for $E_T(30)$ were taken from Reichardt (1988).

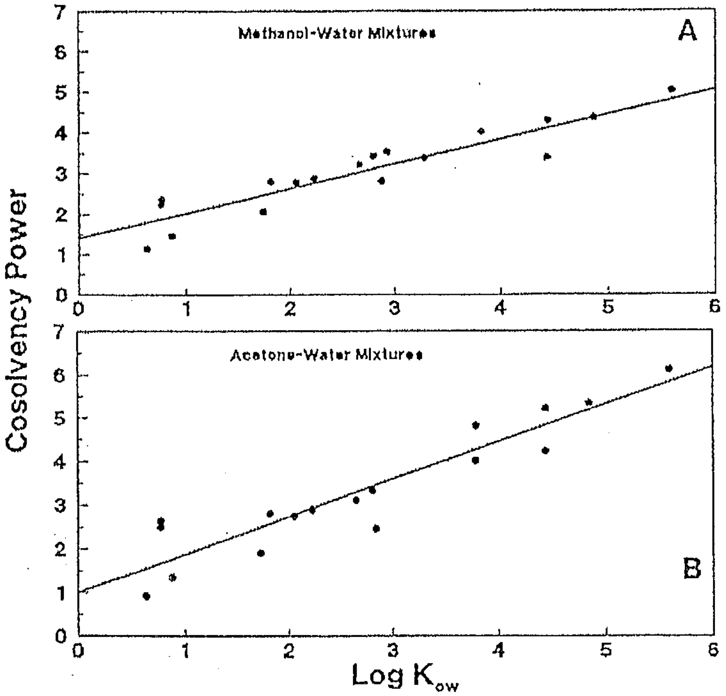

Figure 2. Direct relationship between cosolvency power ($\sigma_{s,c}$) and solute octanol-water partition coefficient (K_{ow}) for (A) methanol-water, and (B) acetone-water mixtures.

define for solubility,

$$\sigma_{s,m} = \beta \sigma_{s,c} \qquad (5)$$

and for sorption,

$$\sigma_{s,m} = \alpha \beta \sigma_{s,c} \qquad (6)$$

where the empirical constants α and β account for water-cosolvent and sorbent-cosolvent interactions, respectively, that lead to deviations from the expected log-linear behavior. Note that $\beta = 1$ implies the absence of water-cosolvent interactions, and $\alpha = 1$ suggests that the sorbent-cosolvent interactions are negligible. Work done during this project was aimed at examining the deviations from the log-linear cosolvency model, and to provide a phenomenological basis for the empirical constants α and β.

Cosolvency and Solubility

The solubilities of several HOCs were measured in binary mixtures (water-CMOS, water-PMOS) and in ternary mixtures (water-CMOS-PMOS). Several aromatic hydrocarbons (all solids) were used in these studies in order to minimize specific solute-solvent and solute-solute interactions. The cosolvents used permitted measurement of cosolvency over a broad range of solvent properties. The measured HOC solubilization profiles were compared with the predictions of the log-linear model and the UNIFAC model [*refs. 2, 12, Appendix A; ref. 7, Appendix B*].

Our results indicate that PMOSs can indeed significantly increase the solubility of HOCs, provided that the PMOS concentration is about 1% (v/v) or larger. In an aqueous or predominantly aqueous solvent, PMOSs such as o-cresol and aniline which have strong polar functional groups (e.g., -OH, -NO_2) would exhibit considerable cosolvency. Nonpolar PMOSs, such as trichloroethylene (and other haloalkenes) and toluene (and other aromatic hydrocarbons), are not expected to show appreciable cosolvency (< 20% increase). Only in the presence of a CMOS can the concentration of these PMOSs be sufficiently high to have a measurable impact on HOC solubility.

Preliminary evidence suggests that the greater cosolvency of polar-PMOSs relative to that of nonpolar-PMOS can be attributed, in large part, to water-PMOS interactions arising from the polar moieties such as -OH and -NO_2. The presence of strong polar functional groups has a dual effect: (i) aqueous solubility of the PMOS is higher, such that relatively high cosolvent concentrations can be achieved; and (ii) the likelihood of water-PMOS interactions is increased.

Modifications to the log-linear model were proposed to account for such specific interactions [*ref. 1, Appendix B*]. In **Figures 3A and 3B**, the measured solubility profiles for anthracene in CMOS-water (acetone-water) and in PMOS-water (butanone-water) mixtures are compared with those predicted by the modified log-linear model. While good agreement between the predicted and measured solubility profiles is encouraging, further work to understand the

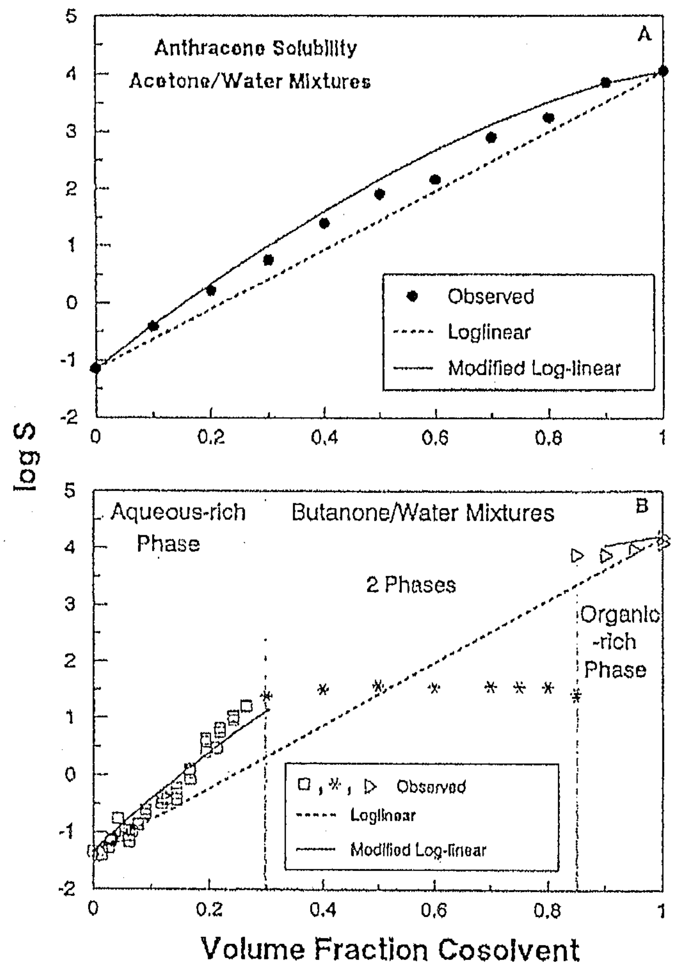

Figure 3. Predicted and measured solubility of anthracene in binary solvent mixtures: (A) acetone-water, and (B) butanone-water. Note that butanone is miscible with water only up to f_c = 0.25, while acetone is miscible with water in all proportions.

specific nature of the cosolvent-water interactions is recommended.

Results similar to those for HOCs have been observed for ionizable organic chemicals (Yalkowsky, 1985, 1986; Yalkowsky and Roseman, 1981; Fu and Luthy, 1986a). As solute polarity increased relative to the solvent, Yalkowsky and Roseman (1981) observed that cosolvency curves became increasingly more parabolic in shape until an inverse relationship was actually observed (i.e., a decrease in solubility with cosolvent additions). Such behavior was explained on the basis of the solute-solvent interactions.

HOC Partitioning from Complex Solvent Mixtures

An understanding of solubility (or partitioning) of HOCs from complex liquids is essential for predicting contaminant release from mixtures such as gasoline, coal tar, and creosote. The solubility of a given component in a mixture may be altered by other components that may act as cosolutes or cosolvents. We investigated partitioning of various aromatic compounds into water from several gasolines and from known mixtures of aromatic and aliphatic solvent mixtures [*ref. 9, Appendix A*]. The purposes of these studies were to assess: (i) the variability in gasoline-water partitioning of aromatic hydrocarbon constituents arising from variability in gasoline composition (source variations); (ii) the application of Raoult's law for the partitioning of aromatic hydrocarbons from complex solvent mixtures; and (iii) the cosolvent effects from oxygenated additives (e.g., methanol, ethanol, MTBE).

Aromatic hydrocarbon concentrations in water extracts of 31 gasoline samples varied over an order of magnitude, reflecting the diversity in gasoline composition. However, the fuel-water partition coefficients (K_{fw}) varied by less than 30%

among these samples. HOC partitioning between water and known mixtures of aromatic and aliphatic solvents was measured and used to estimate the upper and lower bounds of K_{fw} values for more complex solvent mixtures such as gasoline and diesel fuel.

Assuming that gasoline is an ideal mixture of solvents, the following relationship can be derived:

$$\log K_{fw} = A - \log S_i^w \qquad (7a)$$

$$A = \log [\, 10^3 \, (\delta / MW_o) \,] \qquad (7b)$$

where δ and MW_o are the average liquid density (g/mL) and molecular weight (g/mole), respectively, of the gasoline; and S_i^w is the aqueous solubility (μg/mL) of a specific gasoline component. The observed inverse, log-log linear dependence of K_{fw} values on aqueous solubility (**Figure 4**) could be well predicted by eq (7). These results suggest that given the gasoline composition, reliable estimates of likely concentrations in groundwater can be made.

Cosolvency and Equilibrium Sorption

Sorption of HOCs from Mixed Solvents

Sorption of several HOCs by two soils was measured from mixed solvents containing CMOSs and/or PMOSs. The utility of the log-linear cosolvency model for predicting cosolvency was evaluated. The cosolvent effects on HOC solubility and sorption were compared in order to examine cosolvent-sorbent interactions (i.e., estimation of σ and β) [*refs. 1,3, Appendix A; ref. 2, Appendix B*].

As anticipated from the solubility studies, nonpolar- PMOSs (e.g., toluene, trichloroethylene) had small or no effect on HOC sorption. Sufficiently high concentrations of these PMOSs needed to measurably decrease HOC sorption could only be achieved when CMOS concentrations were high (ca. 30% by volume or larger). In contrast, the cosolvency of polar-PMOSs was sufficiently high to cause significant reduction in sorption in predominantly aqueous solutions; however, the measured cosolvency for sorption was different (usually higher) from that predicted from solubility data. For example, sorption of anthracene by Eustis fine sand (organic carbon content of 0.39%) with increasing amounts of o-cresol was less than would be predicted based on measured solubilities (i.e, $\alpha > 1$) (**Figure 5A**). However, fluoranthene sorption measured in butanone-water mixtures (**Figure 5B**) was greater than that predicted from solubility measurements (i.e., $\alpha < 1$).

A series of batch and column studies was performed to further investigate the interactions of polar- PMOS (e.g., o-cresol, aniline, butanone, MTBE) with selected soils with a broad range of organic carbon contents [*ref. 2, Appendix B*]. It was hypothesized that uptake of polar-PMOS by the sorbent organic matter decreased sorbent hydrophobicity

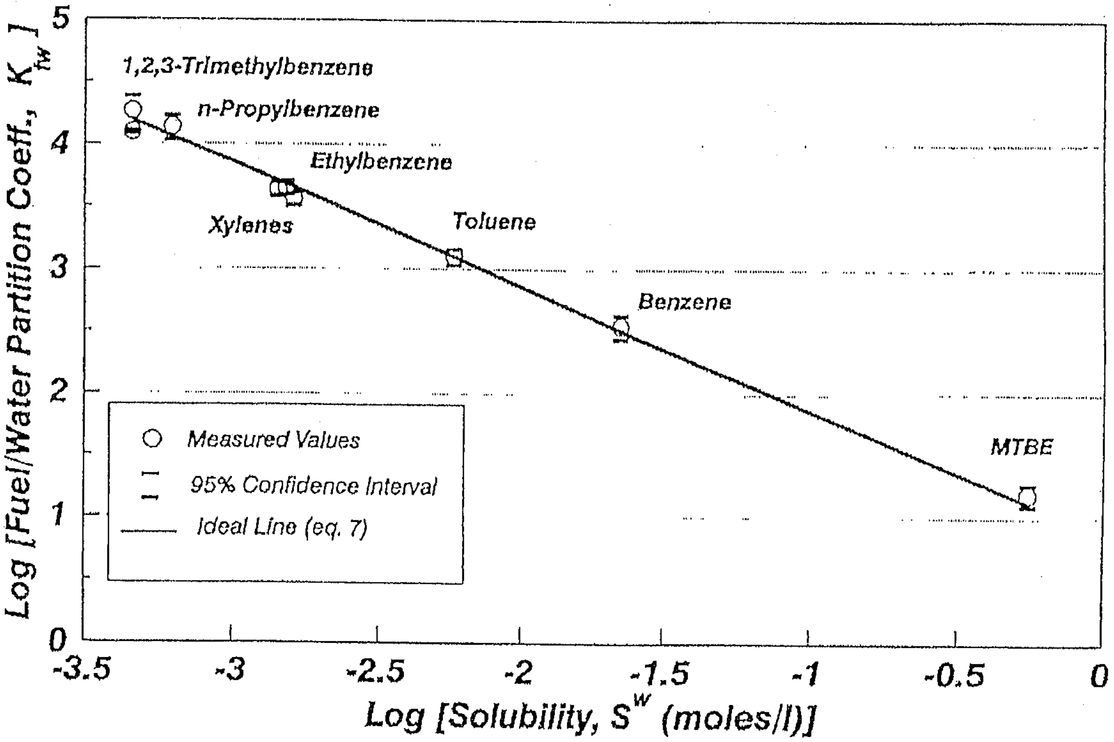

Figure 4. Relationship between fuel-water partition coefficients (K_{fw}) and aqueous solubility (S_i^w) for major gasoline constituents. The line shown is calculated assuming Raoult's law to be applicable (eq 7).

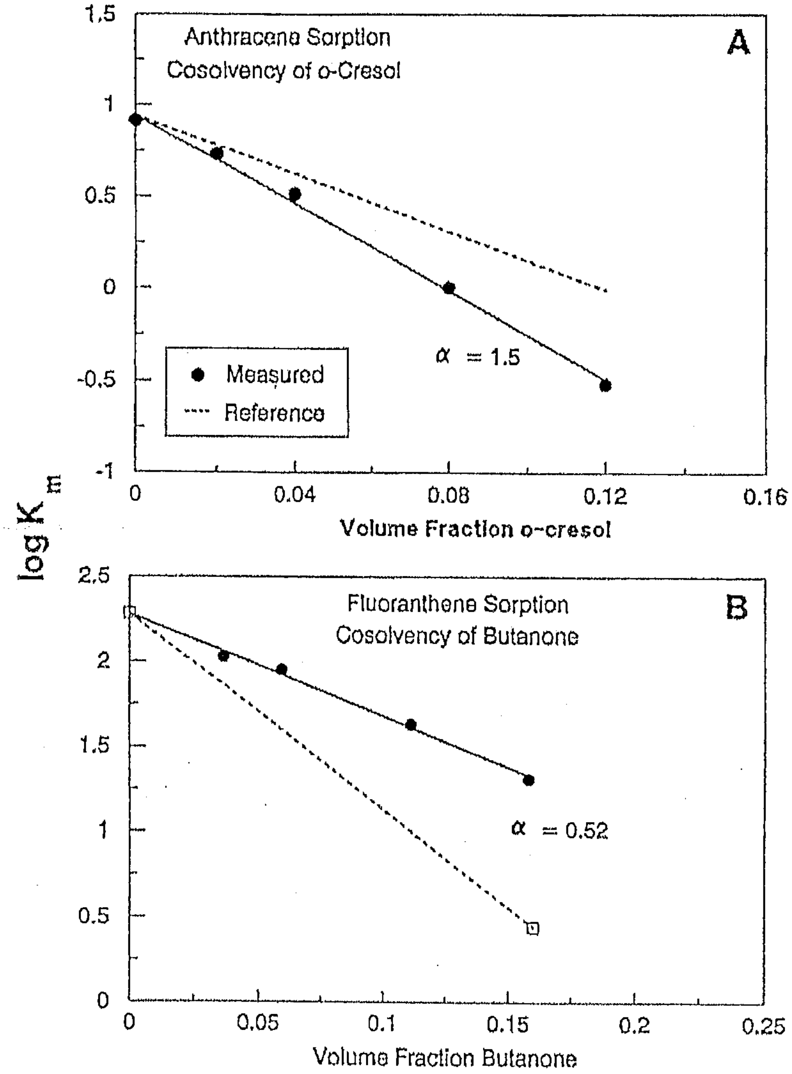

Figure 5. Cosolvency of (A) o-cresol on the solubility and sorption of ^{12}C-anthracene in 50:50 dimethylsulfoxide/water mixtures, and (B) butanone on the solubility and sorption of ^{12}C-anthracene.

resulting in reduced HOC sorption by the soil. The magnitude of such an effect would depend on the following factors: (i) the polarity and functionality of the PMOS, which determine the manner and the amount of sorption/uptake by soil; (ii) the hydrophobicity of the solute, as indicated by its K_{ow}; and (iii) the hydrophobicity of the sorbent, as indicated by its organic carbon content.

Energetics of HOC Sorption from Mixed Solvents

Reversed-phase liquid chromatography (RPLC) techniques have been used to investigate retention of hydrophobic solutes in soils and sediments (e.g., Veith et al., 1979; Swann et al., 1981; McCall et al., 1980; Szabo et al., 1990a, 1990b, 1990c). We conducted a series of RPLC studies to evaluate the suitability of RPLC supports as experimental surrogates for soils and sediments with high OC content. The retention data collected at several temperatures during isocratic, isothermal elution with binary mixtures of methanol/water and acetonitrile/water mobile phases were used to assess selected chromatographic models and to investigate the mechanisms of hydrophobic solute retention in the presence of mixed solvents [*ref. 7, Appendix A; refs. 3,4,5,6, Appendix B*].

Changes in chromatographic retention factors (k) were correlated with the following indices of solute hydrophobicity and molecular topology: octanol-water partition coefficient

(K_{ow}), hydrophobic surface area (HSA), and first-order molecular connectivity (${}^1\chi$); and with solvent indices, such as, solvent surface tension (γ) and dielectric constant index (Γ). Also, the solvophobic model (Horvath et al, 1976) and the entropy-enthalpy compensation model (Melander et al., 1978)) were successfully applied to describe the dependence of solute retention on solvent composition and temperature. Correlations obtained between solute retention factors and various solute indices, along with the thermodynamic analysis of the retention data using the entropy-enthalpy compensation model showed that alkylbenzenes behaved differently from the polycyclic aromatic hydrocarbons and the monohalobenzenes. Such distinctive thermodynamic behavior is indicative of the differences in mechanisms of retention of these compounds.

Sorption of four polycyclic aromatic hydrocarbons by Webster silty loam (OC = 3%) from a methanol-water mixture (30:70 v:v) at three temperatures was measured using batch equilibration methods [*ref. 7, Appendix A*]. Results from a thermodynamic analysis of the sorption data were similar to those obtained from the RPLC supports. This suggests that mechanisms for sorption/retention of polycyclic aromatic hydrocarbons from methanol-water are similar for RPLC supports and the Webster soil; however, comparable sorption data for alkylbenzenes on soils have not been measured.

Sorption of HOCs from Multiphasic Solvents

For HOC sorption in multiphasic solvents distribution between the three phases (soil, water, PMOS) can be described by the soil-water and PMOS-water partition coefficients if HOC sorption on soil is assumed to occur only through the aqueous phase (i.e., no direct solute transfer between the PMOS and soil) and if the dissolved PMOS has a negligible cosolvency effect. Sorption of the herbicide diuron (a substituted urea) by Webster silty loam and a Eustis sand was measured from aqueous electrolyte solutions (0.01 N $CaCl_2$) saturated with a PMOS, and from several biphasic solvents. The PMOSs used were n-octanol, toluene, p-xylene, and TCE, which are considered nonpolar PMOSs [*ref. 3, Appendix A*]. The sorption data are shown in **Figure 6**. These results suggest that even if present in a separate liquid phase, nonpolar PMOSs did not influence HOC sorption for these soils. As previously discussed, nonpolar PMOSs had little effect on HOC sorption due to their limited aqueous solubilities.

Cosolvency and Transport

Isocratic Elution

Miscible displacement experiments were conducted to measure the transport of three HOCs (naphthalene, phenanthrene, anthracene), a substituted urea herbicide (diuron), and an ionizable compound (pentachlorophenol) with methanol-water mixtures as the mobile phase [*refs. 4,5,6,8,10, Appendix A*]. The objectives of these studies were: (i) to utilize the column-measured retardation factors at several cosolvent contents to estimate equilibrium sorption constants (K, mL/g) for aqueous systems, and (ii) to determine sorption rate coefficients (k_2, hr^{-1}) to assess the impacts of cosolvents on sorption kinetics.

Solute retardation factors were determined from breakthrough curves measured for HOC displacement with methanol-water mixtures. The column- and batch-measured K values were generally in agreement at all cosolvent contents, indicating that cosolvency power can be estimated using either technique. Extrapolation of the mixed solvent data to $f_c = 0$ (i.e., aqueous solutions) yielded K values that were generally equal to or larger (by a factor of ≤ 2) than the batch-measured aqueous K values (**Figure 7**). It was suggested that the extrapolated values were, in fact, more

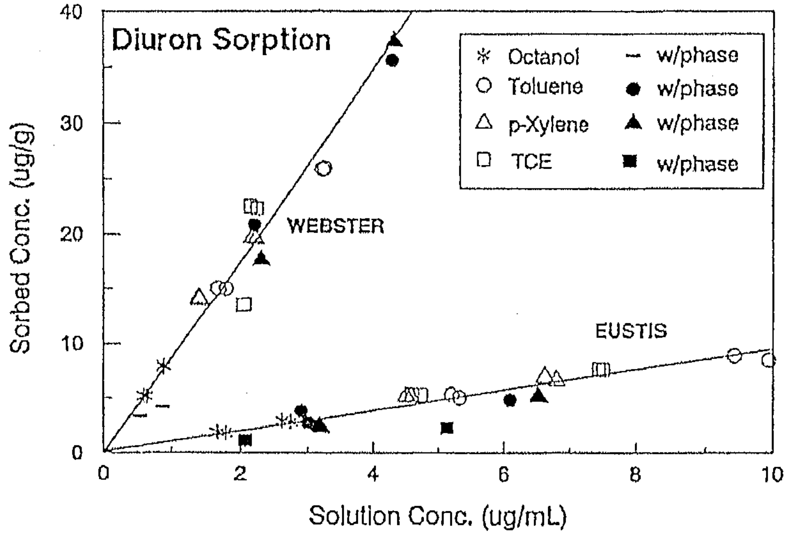

Figure 6. Equilibrium isotherms for sorption and diuron herbicide by Webster and Eustis soils from biphasic solvents and from aqueous solutions saturated with several PMOS.

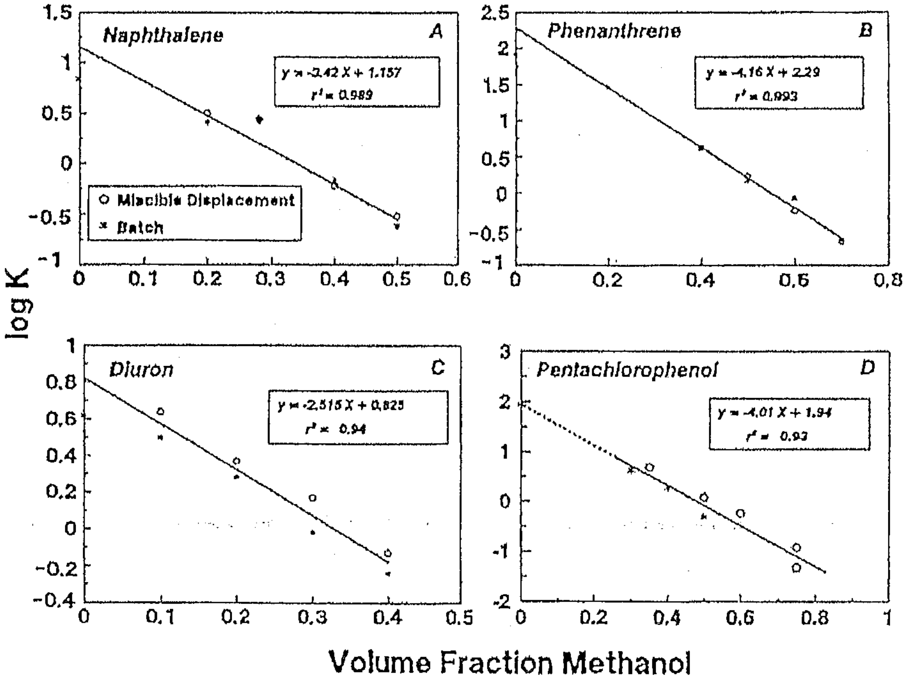

Figure 7. Comparison of batch- and column-measured K values for sorption of anthracene, phenanthrene, diuron, and pentachlorophenol as a function of volume fraction methanol.

reliable because direct measurement of sorption for strongly hydrophobic solutes was subject to several artifacts [*ref. 5, Appendix A*].

The validity of the log-linear model for describing the impact of cosolvents on the mobility of organic solutes is confirmed by the batch and the column data. For transport, this model can be written in terms of the commonly used retardation factor (R) as follows:

$$\ln (R_m-1) = \ln (R_w-1) - \alpha\sigma_{s,c}f_c \qquad (8)$$

where the subscripts m and w denote values obtained in mixed solvents and water, respectively; and other parameters are as defined previously.

The column data were also used to assess nonequilibrium sorption during HOC displacement with mixed solvents [*refs. 6,8,10, Appendix A*]. The bicontinuum sorption model was fitted to the measured breakthrough curves to estimate sorption rate constants (k_2). In this model, sorption is represented as a two-step process: initial rapid (instantaneous) sorption is followed by a slower, diffusion-controlled approach towards equilibrium; k_2 is the rate constant for the slow step (Brusseau et al., 1990). A log-linear increase in k_2 was noted with increasing volume fraction cosolvent (f_c) (**Figure 8**), implying faster sorption kinetics in mixed solvents. This relationship was expected based on the existence of a log-log, inverse relationship between K and k_2 and log-linear, inverse relationship between K and f_c. The regression coefficients for the measured log k_2 vs. f_c plots were in agreement with independent estimates based on simple empirical equations. Also, the measured k_2 values in aqueous solutions compared well with the estimates based on extrapolation of the mixed-solvents data, lending further support to the log-linear model. It was proposed that sorption kinetics are controlled by sorbate diffusion within the sorbent organic matter; the addition of a cosolvent appears to alter the conformation of the polymeric matrix of the organic matter, hence, the rate of solute diffusion [*refs. 4,5,6, Appendix A*].

Gradient Elution

Most studies dealing with HOC transport in mixed solvents have used time-invariant solvent composition (i.e., isocratic elution). From a practical point of view, environmental contamination problems involving solvent mixtures normally exhibit a constantly changing solvent phase. Thus, it is important to understand the behavior of contaminants under conditions of variable cosolvent composition. Therefore, we examined the utility of classical gradient-elution chromatography theory for describing HOC transport through soils under such conditions [*ref. 11, Appendix A*].

Selected HOCs were displaced through laboratory soil columns using standard isocratic- and gradient-elution chromatography techniques. The mobile phase consisted of binary mixtures of water and methanol or acetonitrile. First, isocratic elutions were used to confirm the log-linear

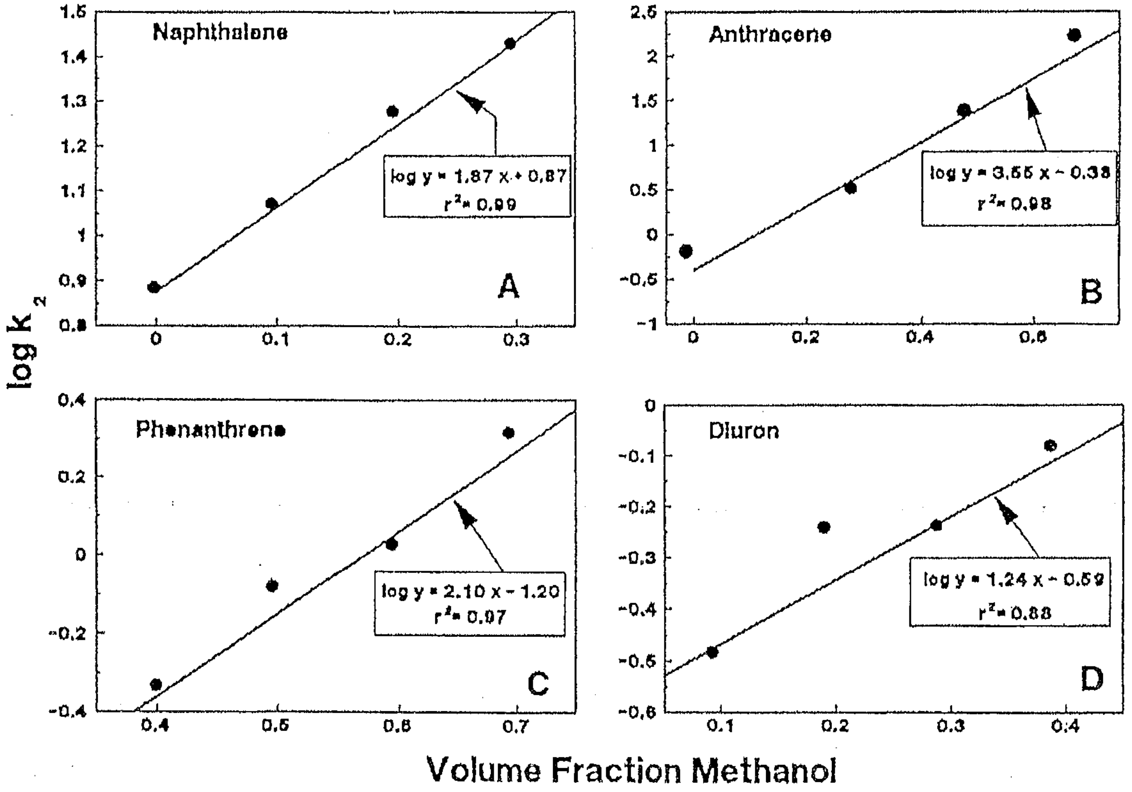

Figure 8. Relationship between sorption rate coefficient (k_2,hr^{-1}) and volume fraction cosolvent for sorption of several HOCs by Eustis soil from methanol-water mixtures.

functionality between solvent composition and the retention factor, k (equivalent to R-1). Second, retention factors were measured for elutions with several linear solvent gradients. Third, the following equation, adapted from gradient-elution theory, was used to predict observed R values:

$$(R_g - 1) = \left(\frac{v}{\sigma_{s,c} bL}\right) \ln\left[1 + \left(\frac{\sigma_{s,c} \rho bLK_I}{\theta}\right)\right] \quad (9)$$

where R_g is the retardation factor (dimensionless) measured for a specified gradient elution, v is average pore-water velocity (cm/min), $\sigma_{s,c}$ is the cosolvency power, b is the slope of the linear solvent gradient (min^{-1})(i.e., the constant rate at which the fraction cosolvent content is changed), L is the column length (cm), ρ is the soil bulk density (g/cm^3), θ is the volumetric liquid content (cm^3/cm^3), and K_I is the sorption coefficient (mL/g) value at the initial fraction cosolvent when the gradient elution is initiated. The sorption and cosolvency parameters for this model were measured independently from batch or isocratic elution data.

In general, the agreement was good between measured and predicted capacity factors (**Figure 9**). These results suggest that gradient-elution techniques and theory developed from reversed-phase chromatography are also useful for investigating cosolvent effects on HOC sorption and transport in soils and aquifer media.

Practical Applications of Project Findings

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.

This study was aimed at developing the necessary data base from laboratory studies and theoretical approaches that can be used in evaluating the likely magnitude of cosolvent

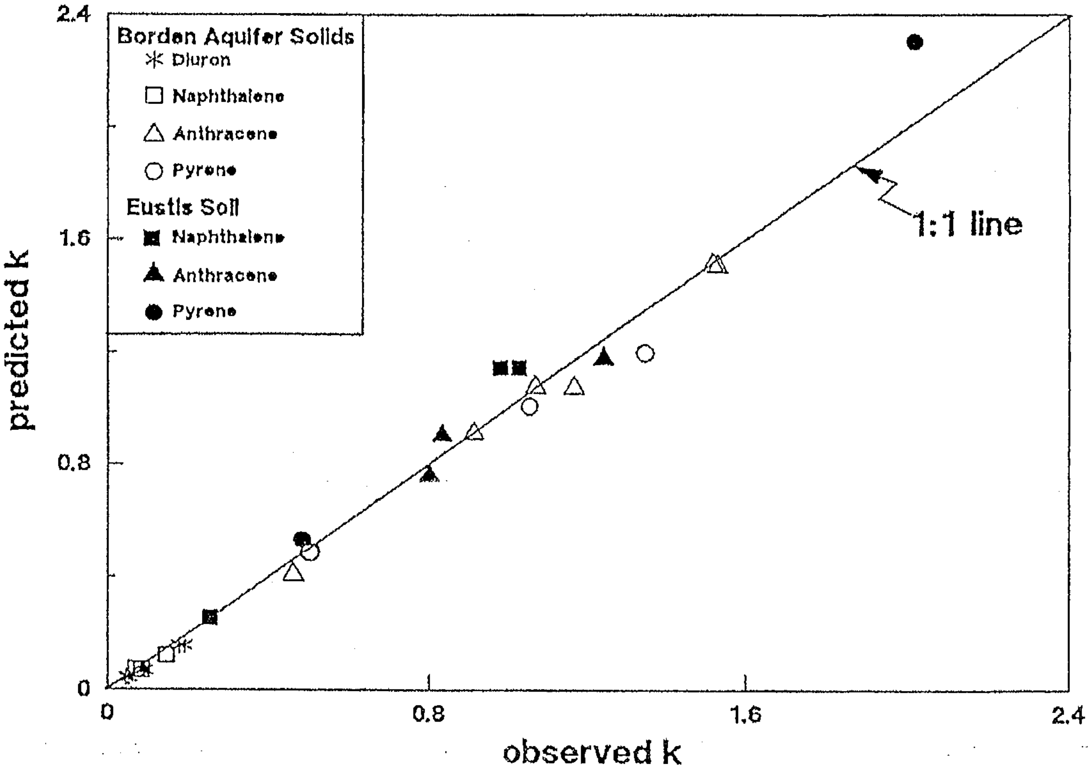

Figure 9: Comparison of measured and estimated chromatographic retention factors (k) for gradient elution of several solutes through Eustis soil column with methanol-water mixtures.

effects. 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 chemo-dynamic 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.

Partially-miscible cosolvents (e.g., MTBE, o-cresol, butanone) have greater cosolvency power compared to completely-miscible cosolvents (e.g., methanol, ethanol, acetone) and as a result they should be expected to enhance solubility or decrease retardation to the same extent at much lower concentrations. Usually equivalent decrease in retardation may be noted with a partially-miscible organic solvent at concentrations 2 to 4 times less than that of a completely-miscible organic solvent. Properties, such as high aqueous solubility, of the polar-PMOS that cause them to have greater cosolvency power than nonpolar-PMOS also lead them to be sorbed less and to have a greater mobility in soils and aquifers. Thus, significant concentrations of polar-PMOSs may be detected at considerable distances from waste disposal sites. Completely-miscible organic solvents, such as alcohols, are generally not sorbed by soils and they can readily leach with water. Hence, cosolvent effects of CMOSs and polar-PMOSs may be of concern in the "far-field" regions as well.

Dissolution of Gasoline Constituents

Our data indicate that Raoult's law can be used to provide reliable estimates of organic contaminant concentrations in groundwater in contact with multi-component nonaqueous-phase liquids (NAPLs) such as gasoline and diesel fuel. Even though these fuels are complex solvent 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 fuel constituent in groundwater, $C_{w,i}$ (mg/L), can be estimated as follows:

$$C_{w,i} = [\, C_{f,i} / K_{fw,i} \,] \qquad (10)$$

where $C_{f,i}$ is the concentration (mg/L) of the constituent in the fuel and $K_{fw,i}$ is the fuel-water partition coefficient which can be calculated using eq (7).

For fuels enriched with oxygenated additives such as methanol (a CMOS) or methyl-tertiary butyl ether (a polar-

PMOS), solubility enhancement of aromatic hydrocarbons by these cosolvents appears to be small. The concentrations of the oxygenated additives in fuels on the market now is usually less than 10% by volume. Assuming that residual NAPLs in the saturated zone do not occupy more than 20-30% of the pore spaces, the likely concentrations of the oxygenated additives in groundwater will be less than 1% by volume. Our fuel-water partitioning data are consistent with this expectation.

Alternative Fuels

Consideration is being given to wide-scale use of fuels that have much greater quantities of oxygenates, especially methanol. For example, the often mentioned "alternative fuel" M-85 is a 85:15 mixture of methanol and gasoline. This mixture will be completely miscible in water, and the aromatic constituents are likely to be transported with little or no retardation as a result of cosolvency from high methanol concentrations.

Consider a hypothetical scenario of p-xylene transport in groundwater as a result of a continuous leak of gasoline containing 10% methanol contrasted to a leak of M-85 fuel. The volume fraction of methanol in groundwater would be about 1% in the first case and about 80% in the latter case. Assuming $\alpha_c = 1$ and $\sigma_c = 2.5$, eq (8) would predict an 8-fold increase in the mobility of p-xylene as a result of the presence of methanol from the M-85 fuel. For the case of M-10 fuel, the enhancement in p-xylene mobility would be too small to be measurable and may be neglected for all pratcical purposes.

In the foregoing analysis we have assumed that the methanol content would be constant all along the flow path; this assumption would be reasonable for a large fuel spill/leak. For a smaller spill/leak, however, the methanol content in groundwater will decrease with increasing distance. For such a case, the concepts developed for gradient-elution (eq 9) could be used to provide an approximate estimate of the likely reduction in retardation.

Accidental release of alternative fuels such as M-85 into rivers or other surface water bodies with contaminated sediments might also result in the release of highly-hydrophobic organic contaminants (such as PCBs, PBBs, dioxins, etc.) into the water column. The environmental consequences of release of such contaminants and their transport further downstream ought to be carefully evaluated.

Remediation of Contaminated Soils

The remediation of contaminated soils or sediments removed from waste disposal/spill sites by extraction with organic solvents is being evaluated at present. The data collected during this project 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 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. If a CMOS-water mixture is to be used as the extracting solution, the concentration of a CMOS needed may be decreased by adding a small amount of a polar-PMOS (a better solvent). Our data suggest that for a given addition of PMOS, the reduction in the amount of CMOS is proportional to the ratios of the cosolvency powers of the two solvents. If a mixture of water and a polar-PMOS are to be used as the extractant, the addition of a small amount of a CMOS can increase the maximum concentration of PMOS and still achieve the same level of extraction efficiency.

Laboratory Protocols

Our results suggest that sorption data (for both equilibrium and kinetics) collected using mixed solvents can be reliably extrapolated to estimate HOC sorption from aqueous solutions. This is an important finding because mixed solvents can be used to facilitate the experimental measurement of sorption and transport behavior of strongly hydrophobic organic solutes (log $K_{ow} > 5$). The use of mixed solvents reduces the time needed to conduct the sorption experiments and may also reduce various artifacts, including losses via volatilization, degradation, and sorption to glassware. Our column studies with methanol as the cosolvent suggest that long-term exposure to this cosolvent had little effect on sorptive and transport properties of a surface soil. This result further lends support to our recommendation that mixed solvents, in particular methanol-water mixtures, be used for experimental facilitation.

References Cited

Abrams, D.S.; Prausnitz, J.M., *AIChE J.*, 1975, **21**, 116-128.

Brusseau, M.L.; Jessup, R.E.; Rao, P.S.C., *Env. Sci. Technol.*, 1990, **24**, 727-735.

Felice, L.J.; Zachara, J.M.; Schmidt, R.L.; Resch, R.T., pp. 39-41, IN: *Proc. 2nd Internl. Conf. on Groundwater Quality Research*, Tulsa, OK. 1985.

Fredenslund, A.; Jones, R.; Prausnitz, J.M. *AIChE J.*, 1975, **21**, 1086-1099.

Freeman, D.H.; Cheung, L.S., *Science*, 1981, **214**, 790-792.

Fu, J.K.; Luthy, R.G. *ASCE J. Environ. Eng.*, 1986a, **112**, 328-345.

Fu, J.K.; Luthy, R.G. *ASCE J. Environ. Eng.*, 1986b, **112**, 346-366.

Horvath, C; Melander, W.; Molnar, I. *J. Chromatogr.*, 1976, **125**, 129-156.

Melander, W; Campbell, D.E.; Horvath, C., *J. Chromatogr.*, 1978, **158**, 215-225.

McCall, P.J.; Swann, R.L., Laskowski, D.A.; Ungen, S.M.; Vrona, S.A.; Dishburger, H. *Bull. Environ. Contam. Toxicol.*, 1980, **24**, 190.

McIntyre, W.G.; deFur, P.O., *Chemosphere*, 1985, **14**, 103-112.

Morris, K.R; Abramowitz, R.; Pinal, R.; Davis, P.; Yalkowsky, S.H. *Chemosphere*, 1988, **17**, 285-298.

Nkedi-Kizza, P.; Rao, P.S.C.; Hornsby, A.G. *Env. Sci. Technol.*, 1985, **19**, 975-979.

Nkedi-Kizza, P.; Rao, P.S.C.; Hornsby, A.G. *Env. Sci. Technol.*,1987, **21**, 1107-1111.

Nkedi-Kizza, P.; Brusseau, M.L.; Rao, P.S.C.; Hornsby, A.G. *Env. Sci. Technol.*, 1989, **23**, 814-820.

Rao, P.S.C.; Lee, L.S. pp. 457-471, IN: *Proc. 24th Hanford Life Sci. Symp.*, DOE Symp. Series 62, Battelle PNL, Richland, WA, 1987.

Rao, P.S.C.; Nkedi-Kizza, P.; Davidson, J.M. pp. 63-72, IN: *Land Treatment: A Hazardous Waste Management Alternative*, Water Research Symp. Series 13, Austin, TX, 1986.

Rao, P.S.C.; Hornsby, A.G.; Kilcrease, D.P.; Nkedi-Kizza, P. *J. Env. Qual.*, 1985, **14**, 376-383.

Rao, P.S.C.; Rhue, R.D.; Johnston, C.T.; Ogwada, R.A. Project Completion Report, ESL-TR-88-02, ESL/AFESC, USAF, Tyndall Air Force Base, FL. 1988, 196 p.

Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, VCH Publishers, Weinheim, Germany, 1988.

Rubino, J.T.; Yalkowsky, S.H. *J. Paren. Sci. Technol.*, 1985, 39, 106-111.

Rubino, J.T; Yalkowsky, S.H. *Pharm. Res.*, 1987a, **4**, 220-230.

Rubino, J.T.; Yalkowsky, S.H. *Pharm. Res.*, 1987b, **4**, 231-236.

Rubino, J.T.; Yalkowsky, S.H. *J. Paren. Sci. Technol.*, 1987c, 41, 172-176.

Rubino, J.T.; Blanchard, J.; Yalkowsky, S.H. *J. Paren. Sci. Technol.*, 1984, 38, 215-221.

Swann, R.L.; McCall, P.J.; Laskowski, D.A.; Dishburger, H., pp. 43-48, IN: *Toxicology and Hazard Assessment : Fourth Conference*, ASTM STP 737, Philadelphia, PA, 1981.

Szabo, G.; Prosser, S L.; Bulman, R.A. *Chemosphere*, 1990a, **21**, 495-506.

Szabo, G.; Prosser, S.L.; Bulman, R.A. *Chemosphere*, 1990b, **21**, 729-740.

Szabo, G.; Prosser, S.L.; Bulman, R.A. *Chemosphere*, 1990c, **21**, 777-787.

Veith, J.T.; Austin, N.M.; Morris, R.T., *Water Res.*, 1979, **13**, 43-47.

Walters, R.; Guissepi-Ellie, A. *Env. Sci. Technol.*, 1988, 22, 819-825.

Walters, R.; Ostazeski, S.A.; Guissepi-Ellie, A. *Env. Sci. Technol.*, 1989, **23**, 480-484.

Wilson, G.M.; Deal, C.H., *Ind. Eng. Chem. Fundam.*, 1962, 1, 20-23.

Woodburn, K.W.; Rao, P.S.C.; Fukui, M.; Nkedi-Kizza, P. *J. Contam. Hydrol.*, 1986, **1**, 227-241.

Yalkowsky, S.H. Solubility of Organic Solutes in Mixed Aqueous Solvents, CR# 811852-01, U.S. Env. Prot. Agency, Ada, OK, 1985.

Yalkowsky, S.H. Solubility of Organic Solutes in Mixed Aqueous Solvents, CR# 812581-01, U.S. Env. Prot. Agency, Ada, OK, 1987.

Yalkowsky, S.H.; Roseman, T. pp. 91-134, IN: *Techniques of Solubilization of Drugs*, Yalkowsky, S.H., Ed.; Marcel Dekker, Inc., New York, 1981.

Yalkowsky, S.H.; Rubino, J.T. *J. Pharmacol. Sci.*, 74, 1984, 416-421.

Zachara, J.A.; Ainsworth, C.C.; Schmidt, R.L.; Resch,C.T. *J. Contam. Hydrol.*, 1988, **1**, 343-364.

Zachara, J.A.; Ainsworth, C.C.; Cowan, C.E.; Thomas, B.L. *Env. Sci. Technol.*, 1987, **21**, 397-402.

Appendix-A (Published Papers)

(1) Sorption and Transport of Organic Pollutants at Waste Disposal Sites. 1989. P.S.C. Rao, L.S. Lee, P. Nkedi-Kizza, and S.H. Yalkowsky. pp. 176-192, IN: *Toxic Organic Chemicals in Porous Media*, Z. Gerstl, Y. Chen, U. Mingelgrin, and B. Yaron (eds.), Springer-Verlag, Berlin, Germany.

(2) Cosolvency of Partially-Miscible Organic Solvents on the Solubility of Hydrophobic Organic Chemicals. 1990. R. Pinal, P.S.C. Rao, L.S. Lee, and P.V. Cline. *Env. Sci. Technol.*, 24:639-647.

(3) Cosolvency and Sorption of Hydrophobic Organic Chemicals. 1990. P.S.C.Rao, L.S. Lee, and R. Pinal. *Env. Sci. Technol.*, 24:647-654.

(4) Influence of Solvent and Sorbent Characteristics on Distribution of Pentachloro-phenol in Octanol-Water and Soil-Water Systems. 1990. L.S. Lee, P.S.C. Rao, P. Nkedi-Kizza, and J.J. Delfino. *Env. Sci. Technol.*, 24:654-661.

(5) Cosolvent Effects on Sorption and Mobility of Organic Contaminants in Soils. 1990. A.L. Wood, D.C. Bouchard, M.L. Brusseau, and P.S.C. Rao. *Chemosphere*, 21: 575-587.

(6) Nonequilibrium Sorption during Displacement of Hydrophobic Organic Chemicals and ^{45}Ca through Soil Columns with Aqueous and Mixed Solvents. 1989. P. Nkedi-Kizza, M.L. Brusseau, P.S.C. Rao and A.G. Hornsby. *Env. Sci. Technol.*, 23: 814-820.

(7) Comparison of Sorption Energetics for Hydrophobic Organic Chemicals by Synthetic and Natural Sorbents from Methanol/Water Solvent Mixtures. 1989. K.B. Woodburn, L.S. Lee, P.S.C. Rao, and J.J. Delfino. *Env. Sci. Technol.*, 23: 407-413.

(8) Nonequilibrium Sorption and Transport of Neutral and Ionized Chlorophenols. 1991. L.S. Lee, P.S.C. Rao, and M.L. Brusseau. *Env. Sci. Technol.* (in press).

(9) Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures. P.V. Cline, J.J. Delfino, and P.S.C. Rao. 1991. *Env. Sci. Technol.* (in press).

(10) The Influence of Organic Cosolvents on the Sorption Kinetics of Hydrophobic Organic Chemicals. M.L. Brusseau, A.L. Wood, and P.S.C. Rao. *Env. Sci. Technol.* (in press).

(11) Gradient-elution Techniques for Assessing Sorption of Hydrophobic Organic Chemicals in Solvent Mixtures. A.L. Wood and P.S.C. Rao, 1990, *Agronomy Abstracts*, p. 51.

(12) Solubility of Anthracene in Complex Solvent System. 1989. B. Gupta. Thesis, Department of Pharmaceutical Sciences, University of Arizona, Tucson, AZ.

Appendix-B (Manuscripts in Preparation)

(1) Solubility of Hydrophobic Compounds in Solvent Mixtures. R. Pinal, P.S.C. Rao, and L.S. Lee. (for *Chemosphere*).

(2) Effects of Cosolvent-Sorbent Interactions on Organic Contaminant Sorption. P.S.C. Rao, A.P. Gamerdinger, L.S. Lee, and R. Pinal. (for *Chemosphere*).

(3) Retention of Hydrophobic Solutes on Reversed-phase Liquid Chromatography Supports: Correlation with Solute Topology and Hydrophobicity Indices. K.B. Woodburn, J.J. Delfino, and P.S.C. Rao. (for *Chemosphere*).

(4) Retention of Nonpolar Solutes by Reversed-phase Liquid Chromatography Sorbents: A Study of Homologous Series of Compounds Using the Solvophobic Theory. K.B. Woodburn, P.S.C. Rao., and J.J. Delfino. (for *J. Chromatography*).

(5) Energetics of Hydrophobic Solute Retention on Reversed-phase Chromatography Supports: Effects of Solute, Solvent, and Sorbent Properties. K.B. Woodburn, P.S.C. Rao., and J.J. Delfino. (for *Env. Sci. Technol.*).

(6) Energetics of Hydrophobic Solute Retention on Reversed-phase Chromatography Supports: Evaluation of Enthalpy-entropy Compensation Model. K.B. Woodburn, J.J. Delfino, and P.S.C. Rao. (for *Env. Sci. Technol.*).

(7) Solubility of Anthracene in Complex Solvent System. 1990. B. Gupta, D. Mishra, and S.H. Yalkowsky. (for *Pharmaceutical Research*).

Disclaimer

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under cooperative agreement CR-814512 with the University of Florida. This document has been subjected to the Agency's peer and administrative review and has been approved for publication as an EPA document.

Quality Assurance Statement

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance (QA) program. This project was conducted under an approved QA project plan. Information on the plan and documentation of the QA activities are available from the Principal Investigator (P.S.C. Rao).

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

Please make all necessary changes on the above label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.

EPA/600/M-91/009