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**SORPTION OF IONIZABLE ORGANIC COMPOUNDS  
TO SEDIMENTS AND SOILS**

by

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## FOREWORD

Environmental protection efforts are increasingly directed towards prevention of adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Chemistry Branch studies the chemical and physical processes that control the transport, transformation, and impact of pesticides and other pollutants in soil and water.

An important process affecting the ultimate fate of pollutants in our environment is their sorption to soils, sediments, or aquifer materials. Besides affecting the physical transport of these compounds in the environment, sorption may significantly impact the magnitude of biological and chemical degradation processes, including anaerobic and aerobic microbial degradation, photodegradation, hydrolysis, and chemical reduction. Therefore, an understanding of sorption processes is necessary, not only to understand transport of chemicals through the environment, but also to resolve the significance of these other processes in determining the ultimate fate of chemicals in our environment. This report examines the sorption of several organic acids and bases to sediments and soils. These compounds include a significant number of pesticides, such as 2,4-D, and silvex, as well as significant classes of environmental pollutants, such as the chlorinated phenols, nitrophenols, cresols, and anilines.

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#### ABSTRACT

The sorption of ionizable organic compounds to sediments and saturated soils is examined. The sorption of pentachlorophenol to two sediment silt-clay fractions as a function of pH is described. Sorption of both the neutral and the ionic species was shown to occur; results were quantitatively interpreted by accounting for sorption of both the neutral and ionic species, and by accounting for acid dissociation in the aqueous phase. In addition, factors influencing the sorption of several organic bases to sediments are described, as well as some of the inherent difficulties encountered in applying phenomenological data to distinguish among various physical and chemical processes. Finally, processes influencing the distribution of neutral and anionic surfactants are discussed briefly.

## SORPTION OF IONIZABLE ORGANIC COMPOUNDS TO SEDIMENTS AND SOILS

*Introduction*

The purpose of this report is to describe factors that influence the sorption of ionizable organic compounds to soils and sediments. Sorption to these natural materials significantly affects the environmental movement, persistence, and bioavailability of all toxic chemicals. As a result, measured or estimated soil or sediment sorption coefficients are increasingly being used to assist in risk assessment analysis to estimate the potential fate of hazardous chemicals in the environment. Sorption partition coefficients are necessary data requirements to run essentially all fate and transport models supported by The U.S. EPA's Center for Exposure Assessment Modeling (CEAM), including PRZM (Pesticide Root Zone Model) which simulates the vertical movement of pesticides and other organic chemicals in unsaturated soil, both within and below the plant root zone. This program has been used in a wide range of regulatory applications. Estimates of sorption coefficients also have been used in the identification and listing of hazardous wastes by the EPA Office of Solid Waste (OSW) under RCRA (1), and in development of Sediment Quality Criteria by the EPA Office of Water (OW).

In regulating the disposal of chemicals, OSW uses a land disposal decision model to determine maximum permissible contaminant concentrations in landfill leachate. Implementation of this model requires, among other things, knowledge of the equilibrium sorption constants ( $K_d$ 's) for each chemical-soil system tested. Ellington et al. (1) have used octanol-water partition coefficients ( $K_{ow}$ 's) to estimate sorption equilibrium constants normalized to sorbent organic carbon content ( $K_{oc}$ ) for 33 neutral organic compounds under

evaluation. Knowledge of the organic carbon content of a soil-water medium permits the calculation of the soil-water partition coefficient,  $K_p$ . In addition to the 33 neutral compounds evaluated, 11 ionizable compounds were evaluated; 9 of which will be regulated, and 6 of these have environmentally significant acid dissociation constants ( $pK_a$ ). These 6 include 2,4-dichlorophenoxyacetic acid (2,4-D), silvex, pentachlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, and pyridine (an organic base).

Equilibrium partition coefficients have been applied, also, in the development of Sediment Quality Criteria (SQC) for toxic organic chemicals. The approach taken involves the calculation of the interstitial water exposure concentration of a chemical from its sediment concentrations using the organic carbon normalized partition coefficient,  $K_{oc}$ . The calculated water concentration is then compared to the water quality criteria value. For the development of SQC, compounds of concern include, substituted phenols and anilines, some of which are those already evaluated by OSW.

The assumptions concerning the physical partitioning process of pesticides and other pollutants include: (1) the system is close to local sorption equilibrium, (2) sorption to sediments is dominated by hydrophobic interactions between the chemical and the organic carbon fraction of the sediment, and (3) surrogate parameters, such as  $K_{ow}$ 's can be used in regression equations to quantify  $K_{oc}$ 's. Given minor constraints, these assumptions are very appropriate for neutral hydrophobic organic compounds. For ionizable organic compounds, however, other factors must be considered when describing sorption reactions and when estimating partition coefficients.

The purpose of this report is to briefly describe the significance of these *other* factors that influence sorption of ionizable organic compounds.

and to show how these partition reactions can be quantitatively described. Quantitative descriptions are necessary for the development of suitable algorithms that can then be incorporated into fate and transport models.

Additionally, some initial results from studies of the adsorption and precipitation reactions of anionic surfactants in sediment systems will be described. These specific studies are important because of (1) the importance of surfactants as additives in commercial pesticide formulations, and the resultant effects of these additives on the mobility of pesticides and soil humic matter, (2) the possible beneficial use of surfactants as solubilizing agents for enhancing the biological remediation of contaminated sediments or soils, and (3) the importance of surfactants as pollutants themselves, and their possible effects on other pollutants.

#### *Experimental Design*

*Batch Experiments.* Concentration distribution ratios between sediment or soil solid phases (in the case of the surfactants, this includes precipitated compound) and aqueous phases were determined from batch incubation experiments. Generally, a known weight (0.1 to 5 g) of a sediment or soil sample was placed in each of a series of glass tubes and hydrated with water and/or salt solutions, and finally with test chemical(s) to give the final desired sediment mass to water volume ratio (m/v). The sediments and soils were collected from various locations around the Midwestern United States, air dried, and were dry sieved at 1 mm to remove larger gravel and debris. Tubes were incubated in a controlled temperature room at 25°C on a variable speed rotator. Tubes were rotated end-over-end at 8 to 10 times per minute for 1 out of every 5 minutes. After a designated time, the slurries were

centrifuged, and aqueous phases were analyzed either by HPLC for the organic acid or base compounds or by the wet chemical method developed by Motomiza *et al.* (2) for the anionic surfactants. The volumes used for the surfactant analysis were scaled to accommodate 50-ml centrifuge tubes.

*pH-dependent Experiments.* To assess the effect of pH on the distribution of select organic acid compounds in sorbent-water slurries, experiments were

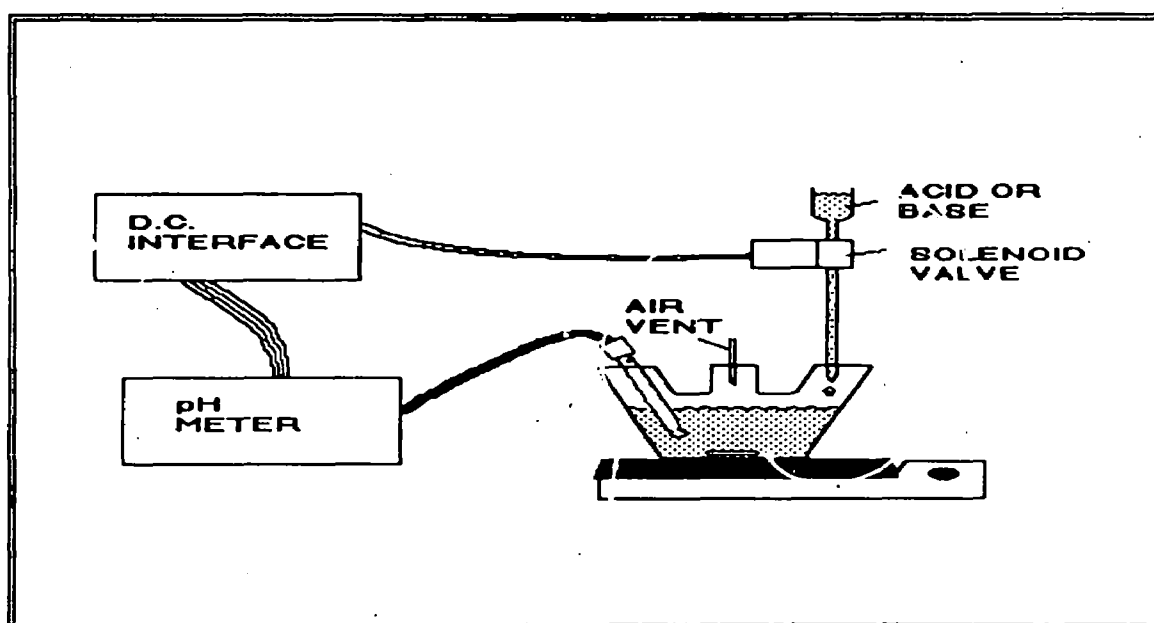


Figure 1. pH-stat schematic.

conducted in a pH-stat (Figure 1). It consists of a Fisher Accumet 825MP pH meter, a Fisher DC load interface, a Bio-Chem Valve Corporation 12-V solenoid valve, a 5-ml burette used as the titrant reservoir, a reaction flask with ports for (1) a Ross combination rugged-glass-bulb pH probe, (2) acid or base additions, and (3) a pressure release vent. Only glass or teflon parts are exposed to sediment and water. Wetted areas of the solenoid valve (exposed to acid or base) are made of silicon. Reaction flask contents are mixed by a



magnetic stirrer and the entire apparatus is maintained at 25°C in a constant temperature room.

For each experiment, a sediment slurry was equilibrated for 24 hours in the pH-stat before addition of acid, base, or compound. Then, the slurry was spiked with test chemical to give a total volume of 300 ml and a concentration of 0.5 to 2.0 x 10<sup>-6</sup> M. The slurry was equilibrated for an additional 8 to 24 hours, before a 15-ml sample was removed for centrifugation and HPLC analysis. The pH was lowered by 0.5 to 1.0 pH units by additions of 0.5 M HCl and held constant to within approximately 0.05 units by setting the upper limit on the pH meter. After 8 to 24 hours, another sample was taken and analyzed. This process was repeated until a final pH value of 3.5 to 4.0 was reached.

For kinetic experiments, the pH was first lowered to a predetermined value with the pH-stat, a compound was added 4 to 8 hours later, and samples were removed as a function of time.

Previously, whole (air-dried) rehydrated sediments had been used in the pH-stat (3); however, because the slurry is continuously mixed with the magnetic stirring bar, abrasion of the glass container and the teflon stirring-bar occurred in experiments at long time periods. As a result, whole air-dried sediments were sieved to 53 μm to remove the abrasive sand fraction. Because of the finer particles and because less sediment was required for each experiment, using the resulting silt-clay fraction in the pH-stat resulted in more uniform mixing of the slurries.

### *Results*

*Sorption of Organic Acids.* For both the octanol-water and the sediment-water systems, partitioning of organic acid compounds can be modeled as a

linear combination of independent partitioning reactions of the neutral and ionic forms of the acids. Two previous papers (3,4) and a research brief (5) describe factors that affect the octanol-water and sediment-water distribution of these compounds.

In these previous studies, the sorption of four organic acid compounds, including several pesticides, to one sediment (Sediment 11, a silty Ohio River sediment) was examined. All values of  $K_{d1}$ , the partition coefficient for the organic acid anion, were found to depend on pH (3). This dependence was hypothesized to result from changes in the surface charge or degree of protonation of the sorbent matrix with pH. For the four compounds studied,  $K_{d1}$  was expressed as,

$$\log K_{d1} = \sigma_1(\text{pH}) + \log K_1 \quad (1)$$

where,  $(\sigma_1)$  is the average pH dependence or slope, equal to approximately 0.30, and  $K_1$  is an intrinsic chemical adsorption term.

For any sediment or soil-water system, the partition constant for the neutral species,  $K_d$ , and the two for the ionic species,  $K_1$  and  $\sigma_1$ , can be calculated either in a step wise manner, or by minimizing residuals on all three constants simultaneously from sorption data obtained as a function of pH. The step wise method was chosen for its simplicity.

First, the partition constant for the neutral species,  $K_d$ , is calculated from distribution data at low pH values, where sorption occurs predominantly by the neutral form. At pH values at or below the  $\text{p}K_a$  value of the compound,  $K_d$  is calculated from Equation 2,

$$K_d = \frac{([HA]^T - [HA]_{aq}^T) / (m/v)}{(H^+)[HA]_{aq}^T / ((H^+) + K_a)} \quad (2)$$

where,  $[HA]^T$  is the total concentration of compound in the system, normalized to aqueous phase volume,  $[HA]_{aq}^T$  is the total concentration of compound in the aqueous phase,  $(H^+)$  is the hydrogen ion activity,  $K_a$  is the acid dissociation constant, and  $m/v$  is the solid mass (kg) to aqueous volume (L) ratio.

Next, the pH dependent values of  $K_{d1}$  are calculated for each point along the titration curve from Equation 3,

$$K_{d1} = \frac{[HA]_{sed}^T((H^+) + K_a) - K_d(H^+)(HA)_{aq}^T}{K_a[HA]_{aq}^T} \quad (3)$$

A linear regression is then performed, correlating the values of  $\log K_{d1}$  to the corresponding values of pH according the Equation 1.

The derivations of Equations 2 and 3 result from combination of the three mass action and three mass balance equations describing the partitioning in sediment-water systems (3). The equation describing the adsorption of the neutral form is given by Equation 4,

$$K_d = \frac{[HA]_{sed}}{[HA]_{aq}} \quad (4)$$

where,  $[HA]_{sed}$  (mol/kg) and  $[HA]_{aq}$  (M) are the neutral species sediment and aqueous phase concentrations, respectively. The constant,  $K_d$ , represents the partition coefficient of the neutral species only, and as will be seen later, can be estimated from the  $K_{ow}$  (neutral form). This equation is identical to

that describing the adsorption of neutral non-ionizable organic compounds, and becomes important at pH values that are 1 to 2 units above the  $pK_a$  of the compound and below.

A similar empirical equation for adsorption of the anionic form of organic acids may be expressed,

$$K_{d1} = \frac{[A^-]_{sed}}{[A^-]_{aq}} \quad (5)$$

where,  $[A^-]_{sed}$  (mole/kg) and  $[A^-]_{aq}$  (M) are the sediment and aqueous phase concentrations, respectively, of the anionic species. As previously stated, the value of  $K_{d1}$ , is influenced by pH. The final mass action equation describes acid dissociation,

$$K_a = \frac{(H^+)[A^-]_{aq}}{[HA]_{aq}} \quad (6)$$

where,  $(H^+)$  represents hydrogen ion activity and  $K_a$  is the acid dissociation constant.

The three necessary mass balance equations describe the total concentration in the aqueous phase,

$$[HA]_{aq}^T = [HA]_{aq} + [A^-]_{aq} \quad (7)$$

the total concentration in the sediment phase, normalized to the aqueous phase volume,

$$[HA]_{sed}^T = ([HA]_{sed} + [A^-]_{sed})(m/v) \quad (8)$$

and the total concentration in the system, also normalized to aqueous phase volume,

$$[HA]^T = [HA]_{sed}^T + [HA]_{aq}^T \quad (9)$$

where,  $m/v$  is the sediment mass (kg) to aqueous phase volume (L) ratio. Equations 7 and 8, although not absolutely necessary, are useful because analytically it is considerably less difficult to measure the total concentration of compound in a phase than to measure the neutral and ionic forms separately.

The pH-dependent sorption data was used to solve for  $K_d$ ,  $K_1$ , and  $\sigma_1$ , given by Equations 1 through 3, for the sediment and soil systems examined. The intensive properties of the system;  $m/v$ ,  $(H^+)$ , and  $[HA]^T$  as well as the total concentration of HA in the aqueous phase,  $[HA]_{aq}^T$ , were measured or known. This analysis was performed for two different sediment silt-clay fractions using pentachlorophenol (PCP) as the sorbate. PCP is an ideal test compound because of its (1) hydrophobic character, (2)  $pK_a$  value of 4.8, (3) ease of analysis by HPLC methods, and (4) relatively slow biodegradability in fresh sediment slurries. Characteristics of the two silt-clay fractions and the resulting coefficients are given in Table 1. Whole sand-silt-clay fractions of these sediments have been previously used and described (3).

To determine these coefficients, experiments were performed using two different  $m/v$  ratios for each silt-clay. The values for  $K_d$  were determined from the experiments with low  $m/v$  ratios (at low pH values), while values for  $K_1$  and  $\sigma_1$  were determined from the experiments with higher  $m/v$  ratios. The

Table 1. Measured constants for the sorption of PCP in silt-clay slurries.

Silt-Clay Source (label)	Fraction Organic Carbon	$\log K_d$	$\log K_{oc}$ (neutral form)	$\log K_1$	$\sigma$
6 Missouri River, South Dakota	0.010	2.62	4.51	2.62	-.258
11 Ohio River, Ohio	0.0167	2.78	4.54	2.95	-.262

data can be represented in graphical form as the fraction of compound in the aqueous phase  $([HA]_{aq} + [A^-]_{aq})/[HA]^T$ . This fraction,  $f_{aq}$ , can be calculated with the coefficients in Table 1 as a function of pH using Equation 1 and the right side of Equation 10,

$$f_{aq} = \frac{[HA]_{aq} + [A^-]_{aq}}{[HA]^T} = \frac{(K_a + (H^+))}{(K_a + (H^+) + (K_d(H^+) + K_{d1}K_a)(m/v))} \quad (10)$$

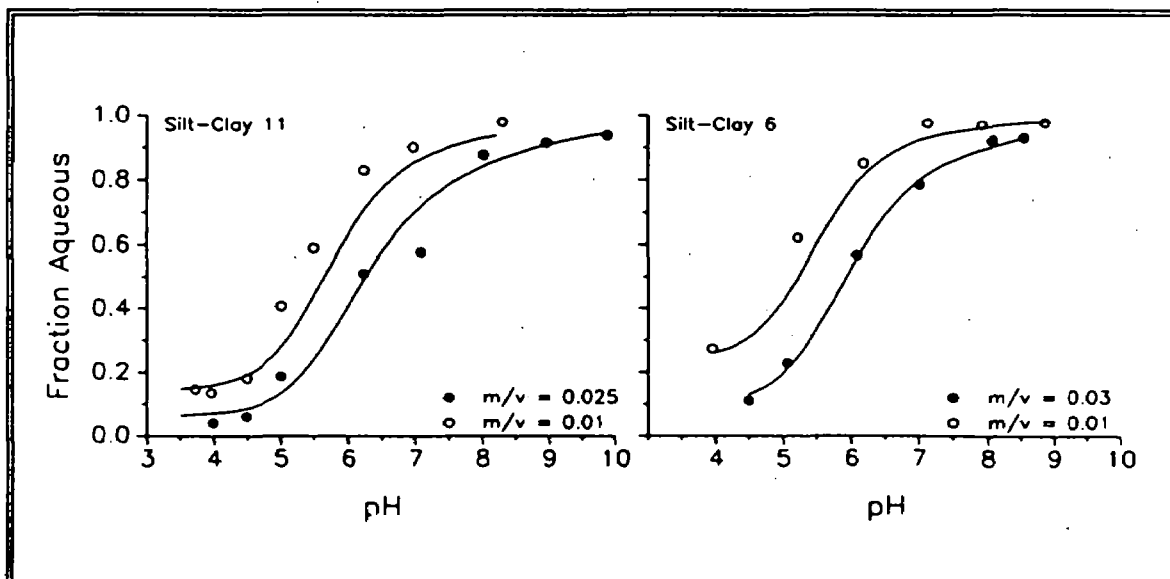


Figure 2. The pH dependent sorption of PCP in silt-clay fractions of sediments 6 and 11.

The data and calculated results (curves) are shown in Figure 2. In these silt-clay fractions, with  $m/v$  equal to 0.1 - 0.3 g / ml, sorption of PCP is dramatically influenced by pH over the pH range that encompasses most natural systems. Also, the effect of the ratio  $m/v$  is evident, as sorption is increased for the higher ratios.

Equations 1 and 10 also can be used to calculate the distribution of PCP at other  $m/v$  ratios.

Figure 3 shows calculated  $f_{aq}$ 's for PCP in Silt-clay 6 over  $s/w$  ratios of 0.001 to 1.0 g / ml. At the lowest ratio, appreciable sorption of only the neutral species occurs at low pH values. At higher  $m/v$  ratios, approaching values for soft lake sediments and groundwater systems, sorption is appreciable at all pH values, although still very pH dependent.

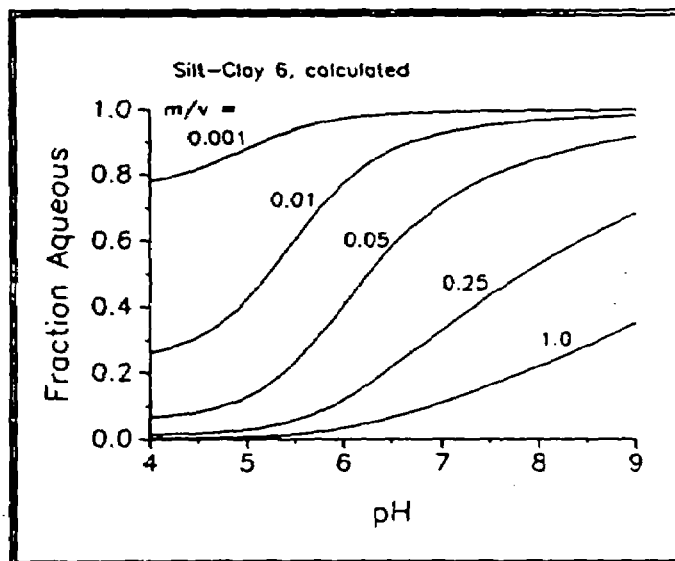


Figure 3. Calculated pH and  $s/w$  dependence of PCP sorption to Silt-Clay 6.

To show the effect of pH on the relative amount of each component in a system, the fraction of each species ( $[HA]_{aq}$ ,  $[A^-]_{aq}$ ,  $[HA]_{sed}$ , and  $[A^-]_{sed}$ ) has been calculated for PCP in Silt-Clay 6 assuming a  $m/v$  ratio of 0.03. This is shown in Figure 4. At high pH values (7.5 to 9.5), only the organic anion exists in the aqueous or sediment phases. As the pH decreases, sorption of the ionic species increases. A maximum in  $[A^-]_{sed}$  is reached at near neutral

pH. In this pH range (6.5 to 7.0), the amount of sediment-sorbed neutral species is approximately equal to the sediment-sorbed ionic species. It is this situation that prevents quantitative interpretation of partition data of similar ionizable compounds determined at only one pH value. As the pH

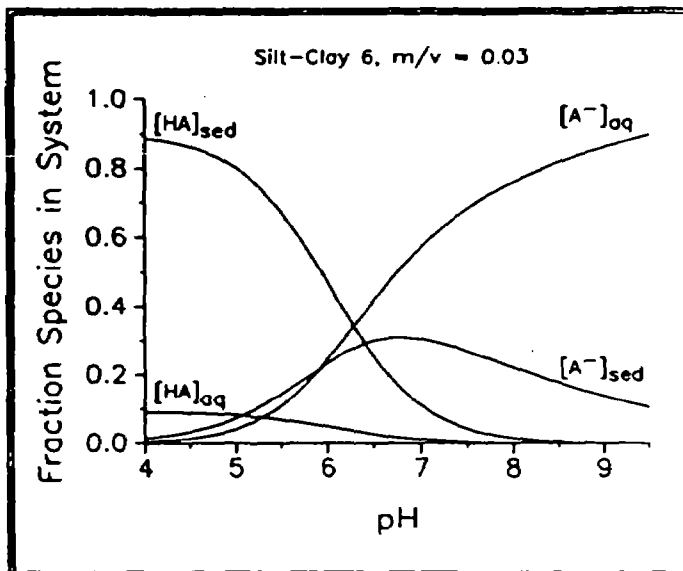


Figure 4. Calculated speciation of PCP in Silt-Clay 6,  $m/v = 0.03$ .

decreases from 7, the overall distribution is controlled to a greater extent by the equilibrium reaction of the neutral species (Equation 4).

The results given in Table 1 for the two silt-clay fractions agree with those previously determined for PCP, 4-chloro- $\alpha$ -(4-chlorophenyl)benzeneacetic acid (DDA) and silvex (3). (The other compound investigated, 2,4-dinitro-*o*-cresol (DNOC), has significantly different physical properties due to the nitro-groups). The values of  $K_d$  for the three similar compounds can be approximated to within a factor of 2 by Equation 11,

$$K_d = 1.05 f_{oc} K_{ow}^{.82} \quad (11)$$

where,  $f_{oc}$  is the fraction organic carbon. This relationship was calculated by Schellenberg et al. (6) from sorption data of chlorinated phenols onto sediment and aquifer materials.



For the three compounds previously investigated (in Sediment 11 slurries), the measured values of  $\log K_d$  correlate to the values of  $\log K_1$ , as also is the case for the two sediments of this study (one derived from Sediment 11). It should be noted, however, that although the sorption of organic anions is much weaker than that of their corresponding neutral species, because  $\log K_1$  is the intercept of Equation 1 and the slope of this equation is negative, the values of  $K_1$  and  $K_d$  approximate each other.

The correlation between  $K_1$  and  $K_d$  for both sediments may stem from the similarity of the sediments examined; however, for relatively pristine freshwater sediments, this relationship may remain valid as it is likely that the predominant factors affecting the magnitude of  $K_1$  are organic carbon content, and ionic strength and composition. Also, the value of  $\sigma_1$ , - 0.26, agrees with that reported previously, - 0.3 (3), and agrees with a value of 0.17 recently determined for the sorption of linear alkylbenzenesulfonate (LAS) surfactants on a soil sample (7). LAS surfactants exist essentially completely in their anionic form at environmentally relevant pH values. In this same study (7), the sorption of neutral alkylethoxylate surfactants was shown to depend insignificantly on pH for the same soil sample indicating that sorption of anionic organic species on natural sorbents may be pH dependent. The magnitude of  $\sigma_1$  suggests that sorption coefficients for organic anions normalized to only one parameter (such as organic carbon or cation exchange capacity) may result in errors of several orders-of-magnitude.

*Sorption of Organic Bases.* Organic bases, which include the nitrogen-heterocyclic compounds (NHCs) and the aromatic amines, comprise an important group of environmental contaminants. The NHCs are common pollutants found in waste streams generated from energy development technologies such as coal

gasification and shale oil extraction. Aromatic amines can enter the environment from the degradation of various herbicides (including the phenyl ureas, phenylcarbamates, and acylanilides), textile dyes, and munitions. All of these compounds are synthesized from the aromatic amines. In addition, loss of the aromatic amines to the environment may result from production processes or improper treatment of industrial waste streams.

Reaction processes of organic bases with soil and sediment components include partitioning reactions through hydrophobic or modified-hydrophobic mechanisms, cation or ligand exchange type reactions, and chemical reactions leading to the formation of covalent bonds through nucleophilic addition or oxidative processes. Differentiating among these processes is necessary if predictive models are to be developed. In soil and sediment systems this can be problematic, as all processes occur simultaneously and influence the magnitude of one another. For example, chemical reactions leading to the formation of covalent bonds with constituents of the sediment or soil matrix can result in essentially irreversible binding, affecting the magnitude of sorption through cation exchange or hydrophobic interactions. Furthermore, irreversible chemical binding may have important implications with regard to the persistence, bioavailability, and toxicity of the residue.

The significance of each of these various processes, of course, will depend on the chemical and physical properties of the specific organic base of interest and of the soil or sediment medium. For example, mechanisms of covalent bond formation will not be important for NHCs because of their low nucleophilicity and high oxidation potentials. Likewise, cation exchange should not be significant for weak bases ( $pK_a < 2$ ) in most natural environments at near neutral pH values.

Little quantitative information exists to describe the sorption of organic bases. Zachara and co-workers (8) have studied sorption of a series of NHCs, including pyridine ( $pK_a = 5.23$ ,  $K_{ow} = 10$ ), quinoline ( $pK_a = 4.92$ ,  $K_{ow} = 110$ ) and acridine ( $pK_a = 5.68$ ,  $K_{ow} = 2512$ ) on an acidic and a basic subsoil. They found that the sorption to each subsoil paralleled the hydrophobicity of the compounds as described by the  $K_{ow}$ 's in the order acridine > quinoline > pyridine. Also, sorption was greater in an acidic soil (solution pH = 4.18), where the cationic species and the neutral compound coexist, compared to a basic soil (solution pH = 8.15), reflecting preferential retention of the organic cation over the neutral form. Further evidence of cation exchange was the observation that competitive sorption occurred for binary mixtures of the NHCs in the acidic soil. Competitive sorption was not observed in the basic soil where the neutral compounds predominate in solution. The dominant role of cation exchange of quinoline on mineral oxides with solution pH values near or below its  $pK_a$  also has been demonstrated (9).

Because of their significance to the agrochemical industry, the study of the sorption reactions of aromatic amines have received greater attention than the NHCs. Most studies to date, however, have been compound specific. Furthermore, there has been little effort to relate substrate or system variables to experimental results, which would allow for the development of predictive models. Because of the enhanced reactivity of the amino group, formation of covalent bonds with constituents of soil and sediment systems may contribute significantly to loss of these compounds in environmental systems. In addition, other transformation pathways, such as oxidative polymerization, are likely. The challenge, therefore, is to differentiate among these collective processes in order to properly characterize factors that affect

each individually.

To gain further insight into sediment- and soil-associated reactions of

Table 2. Physical and chemical properties of substituted anilines.

Property	4-Substituent							
	CN	COCH <sub>3</sub>	CF <sub>3</sub>	Br	Cl	H	CH <sub>3</sub>	OCH <sub>3</sub>
pK <sub>a</sub>	1.74	2.19	2.54	3.86	3.98	4.60	5.10	5.34
R <sub>t</sub> <sup>a</sup>	3.75	3.21		8.24	6.73	3.88	4.96	3.29
σ <sub>B</sub> <sup>b</sup>	0.70	0.47	0.53	0.22	0.24	0.0	-0.14	
log K <sub>ow</sub> <sup>c</sup>	1.05	0.91	2.33	2.08	1.93	0.92	1.56	1.02
K <sub>d</sub> <sup>d</sup>	10.4	17.9	764	141	165	173	1330	>2300

<sup>a</sup>HPLC retention time (min) in 40:60 acetonitrile:water on Supelco pK<sub>s</sub>-100 4.0 mm x 25 cm column, flow rate = 1.5 ml / min.

<sup>b</sup>Hammett-Taft constant

<sup>c</sup>calculated by ClogP.

<sup>d</sup>Distribution coefficients (ml / g) measured at t = 288 hours in resaturated sediment (Cherokee Park, Athens, GA), m/v = 0.05

the aromatic amines, studies with 4-substituted anilines have been initiated. In addition to kinetic studies at natural pH values, experiments have been performed at different pH values using the pH-stat to enhance resolution among processes.

The substituted anilines selected for study and their chemical-physical properties are listed in Table 2. The compounds were selected in order to vary the electron-donating and -withdrawing properties of the specific 4-position substituent. Variation in this property, in turn, will affect the

reactivity of the amino moiety, which is reflected in each aniline's  $pK_a$  value, oxidation potential, and nucleophilicity.

Initially, sediment association of each aniline was measured in a resaturated pond sediment (Cherokee Park Pond, Athens, GA) at 5 % solids at pH 6.5 as a function of time. A plot of fraction of compound remaining in the aqueous phase versus time is illustrated in Figure 5.

With the exception of 4-aminobenzotrifluoride, a general trend is observed. As the  $pK_a$  of the aniline increases, there is an increase in the amount of aniline associated with the sediment phase. For example, approximately 50% of 4-cyanoaniline ( $pK_a$  -

1.74) remains in the aqueous phase after 12 days. On the other hand, 4-methoxyaniline ( $pK_a$  - 5.34) is removed from the aqueous phase within 24 hours. These results indicate that the sediment-associated reactions of these compounds are not necessarily dominated by hydrophobic interactions, as occurs in most cases for neutral compounds. The results for 4-aminobenzotrifluoride are suspect and will be investigated further.

Further analysis of the data in Figure 5 indicates that removal of the anilines is fast over the first 24-hour period of the experiment followed by a

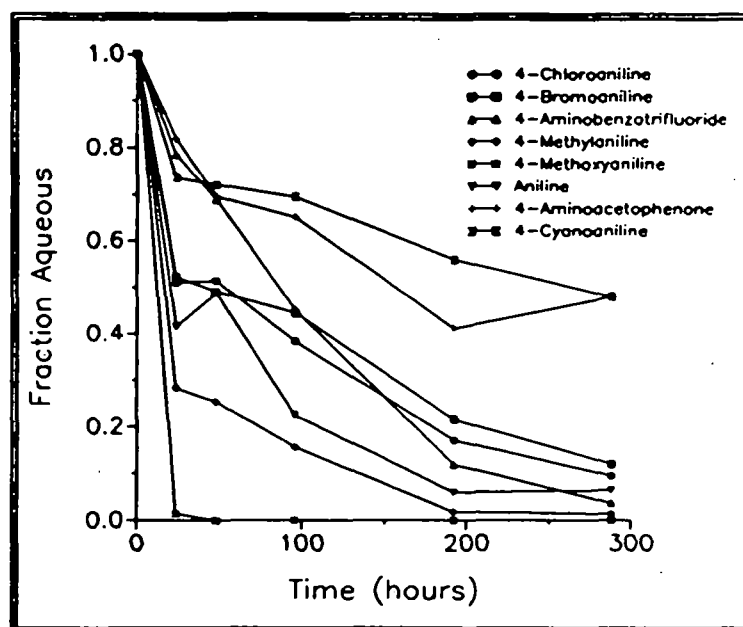


Figure 5. Time dependent loss of substituted anilines to pond sediment.

slower rate of removal. This same type of kinetic behavior has been reported by Paris (10) and by Ononye and co-workers (11) who have studied the binding of aromatic amines to humic material. They concluded that, initially, a rapid equilibrium is established, which may represent formation of imine with quinone components in the humic material, followed by a slow irreversible reaction, which may represent Michael-type addition to the quinone components followed by oxidation. The reaction of aniline with 1,4-quinone is used to illustrate these proposed reaction pathways in Figure 6.

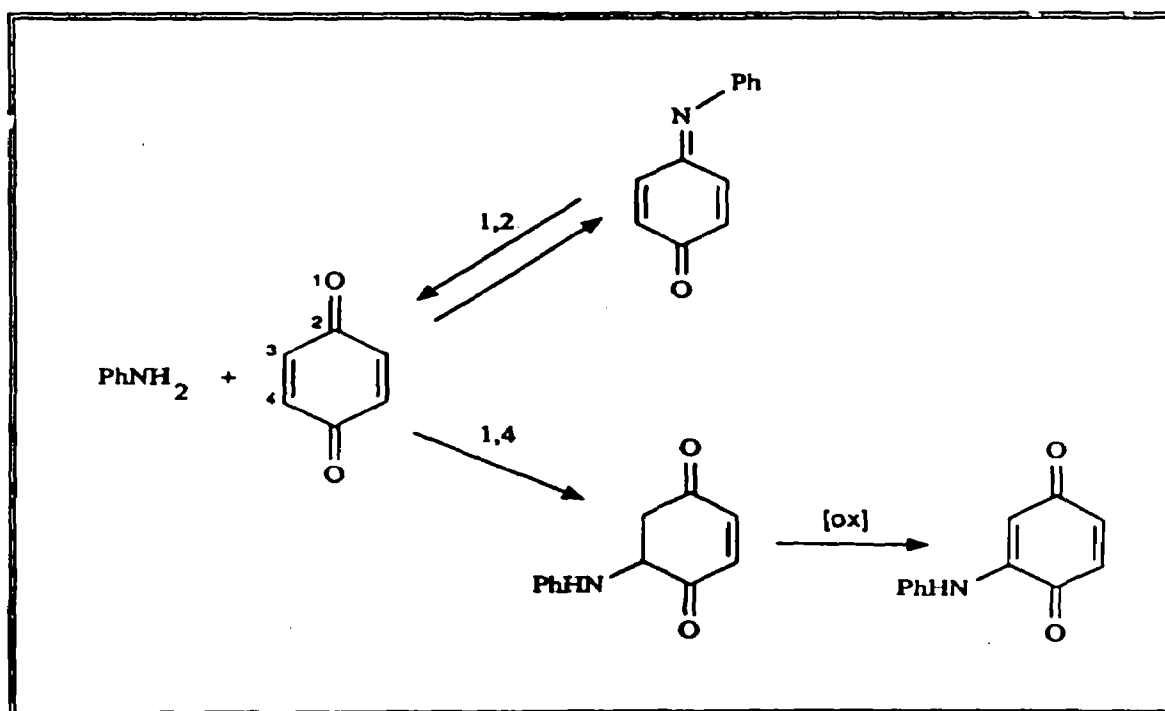


Figure 6. Nucleophilic addition of aniline to 1,4-benzoquinone.

Although the same inference can be drawn from the data in Figure 5 (that is, formation of covalent bonds with quinone-like moieties in the organic matrix), the positive correlation between sorption and  $\text{pK}_a$  suggests that cation exchange processes contribute to the sorption of the anilines. From

these data alone, it is not possible to distinguish among these mechanisms. Irreversible binding of 4-methoxyaniline, however, is strongly suggested by the inability to recover it from the sediment phase by extraction with either acetonitrile, methanol, 25 mM CaCl<sub>2</sub>, or 1 N NaOH, with and without methanol

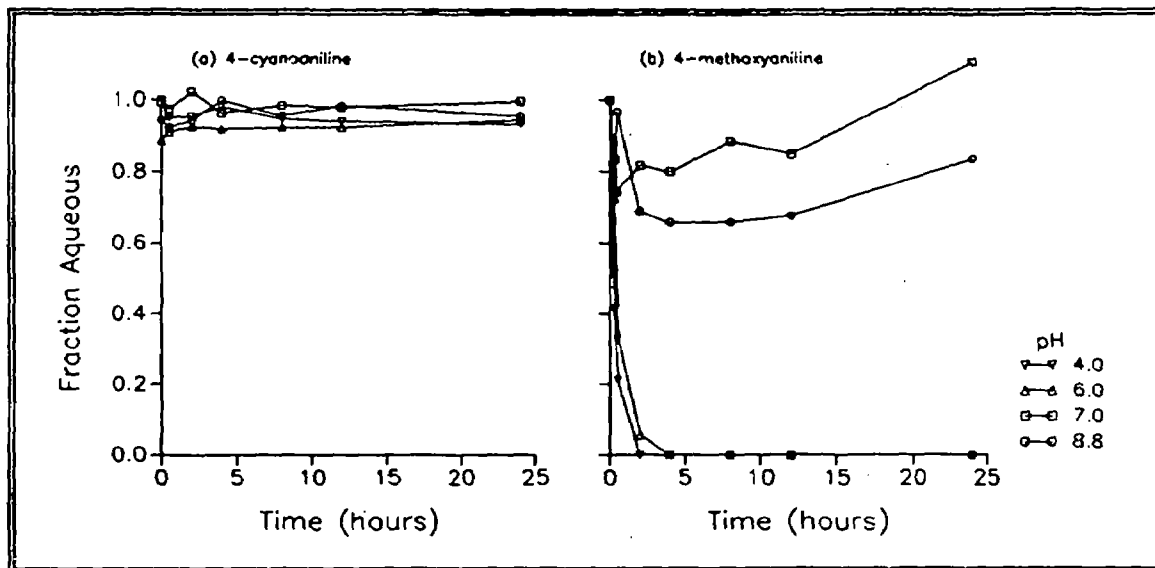


Figure 7. Loss of 4-cyano- and 4-methoxyaniline to Silt-Clay 11 slurries,  $m/v = 0.005$  g / ml.

The effect of pH on the sorption of 4-cyano- and 4-methoxyaniline in Silt-Clay 11 is illustrated in Figure 7. These data demonstrate that loss to the solid matrix of 4-cyanoaniline, the least basic compound, is independent of pH over the range 4.0 to 8.8. Over this same pH range, the sorption of 4-methoxyaniline was very sensitive to changes in pH. Lowering the pH from 7.0 to 6.0 in this system effectively removed all of the 4-methoxyaniline from the aqueous phase in approximately 4 hours. The effect of pH on loss of 4-methoxyaniline suggests that cation exchange and/or irreversible sorption through nucleophilic addition is occurring. As the pH of the silt-clay suspension is lowered (approaching the  $pK_a$  of the aniline), reactions involving the cationic species would be expected to become more significant,

whereas reactions involving the neutral species should decrease in importance. Likewise, because of changes in the rate limiting step as a function of pH for the nucleophilic addition of anilines to carbonyl groups, the optimal pH for this type of reaction for 4-methoxyaniline should occur in the range of 4 to 6 (12). Invariance in the loss of 4-cyanoaniline to the solid matrix as a function of pH ( $8.8 > \text{pH} > 4.0$ ) is explained by its low  $\text{pK}_a$  value of 1.74, and its poor nucleophilicity due to the strong electron-withdrawing effect of the cyano group.

*Sorption - Precipitation Reactions of Anionic Surfactants.* Recently, surfactants have received considerable attention because of their solubilizing effects on relatively water-insoluble compounds, such as DDT, 1,2,3-trichlorobenzene (13), chloromethanes (14, 15), and polycyclic aromatic hydrocarbons (15). This renewed interest in surfactants stems from both an appreciation for the potential of surfactants to enhance the desorption of pollutants from contaminated soils and sediments as a stage in decontamination treatment, and a concern over the environmental fate of surfactants *per se* and their effects on other chemicals, such as pesticides and other toxic organic compounds. (Anionic and/or neutral surfactants are contained in most pesticide formulations with mineral oils to form the concentrated pesticide emulsion.)

Properties of various surfactant solutions have been known for some time, including the extent to which micelles may solubilize various toxic compounds. Although various compounds are known to act differently in micellar solutions, linear free energy relationships have been established relating micelle-water partition coefficients of specific compounds to their octanol-water partition coefficients (15, 16 - 18) or their normal boiling points (19). These



relationships can be helpful in assessing the solubilizing properties of surfactant solutions, and hence their effects on the mobility of pesticides or their potential to solubilize other toxic compounds.

In assessing the possible (advantageous or disadvantageous) removal of contaminants from soils or sediments by surfactant solutions, the need arises to elucidate interactions between the surfactants and the soil or sediment matrix. Adsorption studies have been performed, however, generally at low surfactant concentrations (*7 and references therein*), similar to the majority of studies on the sorption of neutral hydrophobic compounds or other anionic compounds as reported above. These low concentrations are far below the critical micelle concentration (CMC), where minimal effects on enhanced solubilization will occur.

Studies have been initiated, therefore, to investigate the reactions of selected surfactants with soils and sediments in the range of their respective CMC values. An anionic and several neutral surfactants have been studied. Cationic surfactants have not been investigated because they are generally not used in agricultural pesticide formulations, and because they partition to sedimentary materials through cation (or ligand) exchange type reactions, making them poor solubilizing agents in these materials.

For the neutral and anionic surfactants, the interactions with sediments or soils include (1) sorption reactions of both the anionic and neutral surfactants, (2) precipitation reactions of anionic surfactants with calcium, and (3) aqueous phase micelle formation at high concentrations of both anionic and neutral surfactants (20).

Although it appears that reactions involving neutral surfactants should be the simplest to quantitatively estimate or model, this is not necessarily

the case. Most commonly used solutions of neutral surfactants are mixtures containing various hydrophobic and hydrophilic chain-length homologs, each having a unique partition coefficient and CMC. Characterization of the important reactions, therefore, is facilitated by separation of pure components from these solutions. Despite the feasibility of parameterizing these reactions, however, no model exists to predict sorption and micelle formation of these mixtures.

On the other hand, several of the important reactions of (specific homolog) anionic surfactants have been modeled recently (21). These include sorption reactions, precipitation reactions, and micelle formation. In sediment or soil systems, each of these reactions can be important depending upon system and surfactant properties. For example, all three reaction types are observed for dodecylsulfate (DS) in Sediment 11 slurries over the concentration range 0.1 to 30 mM, as shown in Figure 8. This figure shows the amount of DS recovered in the aqueous phase after addition of known amounts of DS to a 20% (m/v) slurry of Sediment 11. At low concentrations sorption to sediment occurs, as shown in Figure 8-A, and can be modeled similarly to that of other anionic organic compounds, as previously described. At intermediate concentrations (0.5 to 2 mM total), DS begins to precipitate as the calcium salt. The solubility product of calcium dodecylsulfate has been measured as  $K_{sp} = 5 \times 10^{-10} \text{ M}$  (21). When enough DS is added such that the aqueous phase monomer concentration reaches the CMC (for Sediment 11 this occurs at 20 mM, total), micelles begin to form and recovery of DS in solution is enhanced, as shown on Figure 8-B. A paper quantitatively describing these reactions is in preparation (22). It is at aqueous phase surfactant concentrations above the CMC that significant solubilization enhancement of

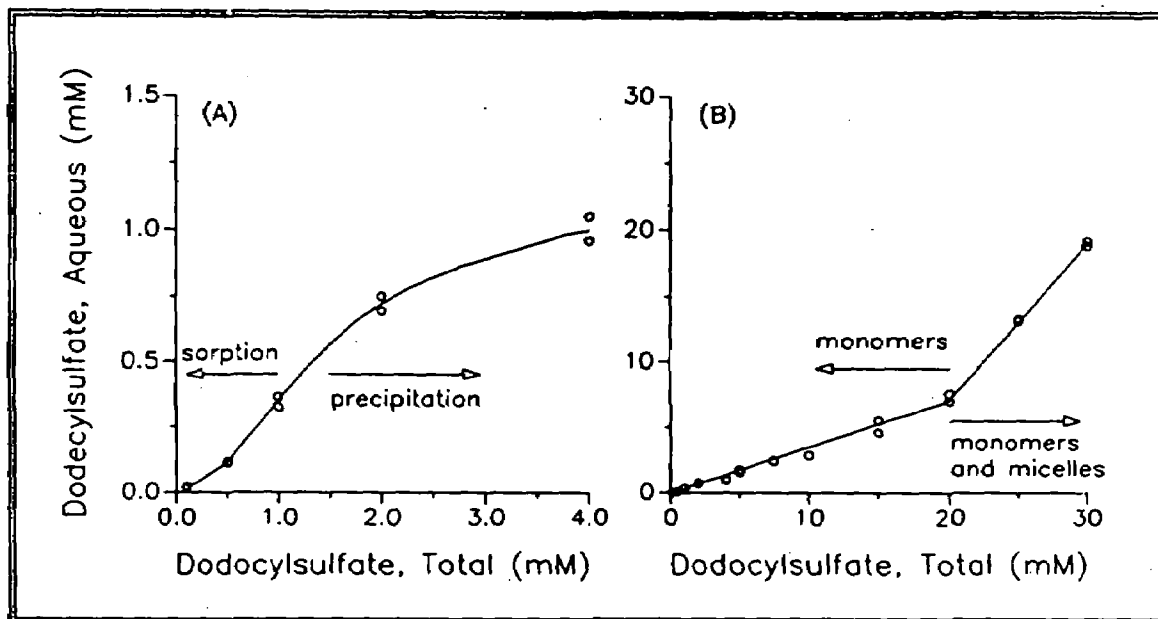


Figure 8. Recovery of aqueous phase dodecylsulfate from Sediment 11 slurries, m/v = 0.2 g / ml.

pesticides and other hydrophobic organic compounds occurs (20).

#### Summary

In the past, predicting the transport and transformation of hazardous organic compounds in the environment has generally relied on the assumption that interactions of these compounds with soil or sediment components primarily occurs through hydrophobic mechanisms. In general, the validity of this assumption has been correct due to the nature of the problem compounds of interest. These compounds or classes of compounds include such notables as the PCBs, the PAHs, DDT, chlordane, and chlorinated benzenes.

In the past, it also has been apparent that, for polar and or ionizable compounds or for systems where organic carbon normalization was not appropriate or valid, other mechanisms or factors influence measured partition coefficients (23). As a result, even for neutral organic compounds,

extrapolations of  $K_{ow}$  values or solubilities to  $K_{oc}$  values are bound by sets of constraints. For ionizable organic compounds, the system complexity necessitates an increase in the number of constraints in order to make scientifically valid estimates. Despite this, the determination of reasonable estimates on the sorption potential of various ionizable organic compounds to sediments and soils is possible, as indicated herein.

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