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SORPTION OF ORGANIC ACID COMPOUNDS TO SEDIMENTS: INITIAL MODEL DEVELOPMENT

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(*Received* 13 *July* 1989; *Accepted* 15 *January* 1990)

Abstract—The adsorption to sediments and saturated soils of selected organic acid compounds was examined as a function of compound and sediment properties. Intrinsic compound properties examined included the dissociation constant (pK_a) and hydrophobic character. Properties of the sediment examined included ionic strength and composition, organic carbon content and aqueous phase pH. By varying these properties, adsorption of both the neutral and anionic forms of these compounds was shown to occur. Adsorption of the neutral species occurs similarly to that of other hydrophobic compounds that do not contain acidic functional groups. Adsorption of the anionic species was influenced, however, by intrinsic chemical as well as electrostatic factors. Adsorption of the anionic species to a specific sediment was modeled as a linearly dependent function of pH. Compounds used in this study included 2,4-dinitro-*o*-cresol (DNOC), 2-(2,4,5-trichlorophenoxy)propanoic acid (silvex), pentachlorophenol (PCP), 4-chloro-α-(4-chlorophenyl)benzeneacetic acid (DDA) and 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB).

Keywords—Sorption Organic acids Sediments pK_a pH

INTRODUCTION

Many environmentally relevant organic compounds contain acidic functional groups. Included are the chlorinated phenoxyalkanoic acids, such as 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T); phenols, such as 2,3,4,5-tetrachlorophenol, pentachlorophenol (PCP), nitrophenols and cresols; chlorinated aromatic acids, such as fenac and dicamba; sulfonated compounds, such as azo and anthraquinone acid dyes and linear alkylbenzenesulfonate (LAS) surfactants; organic sulfates and the degradation products of important pollutants, such as the mono-esters of phthalic acid. As with strictly nonpolar hydrophobic compounds, the adsorption of these organic acid compounds to natural soils and sediments significantly affects their movement and persistence in the environment. Because of the acid functional group, however, adsorption is highly dependent upon the degree of dissociation, with the neutral form adsorbing to a greater extent than the corresponding anion. The adsorption of these compounds to sediments has been modeled similarly to that of the nonpolar hydrophobic compounds, taking into account dissociation and assuming that no adsorption of the anionic form occurs [1]. This approximation, however, is only valid up to pH values greater than approximately 1 to 2 units above the pK_a value.

When this difference between pH and pK_a increases, a greater extent of the partitioning results from adsorption of the anion. For example, the partitioning of PCP ($pK_a = 4.75$) at near neutral pH can result from extensive adsorption of both the neutral and the anionic forms in both sediment–water and octanol–water mixtures [1,2]. Linear alkylbenzenesulfonate surfactants, which exist essentially only in the anionic form, adsorb appreciably to sediments, with adsorption being dependent upon chain length and benzenesulfonate position on the chain [3]. Also, various phenoxyacetic acids, having pK_a values from 2 to 3, adsorb significantly to sediments at near neutral pH [4–8].

The adsorption to sediments and soils of these and similar compounds (having pK_a values <6) has been reported using batch [1,3,5,9], saturated soil column [6–8,10], unsaturated column [11] and field [12] systems. The majority of these studies [1,3–5,9,11,12] allude to the influence that organic carbon content of the media may have upon the

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magnitude of partitioning of the anionic form, suggesting that hydrophobic attraction may play a major role in adsorption of these charged species. The adsorption of organic anions, however, is influenced also to some extent by electrostatic forces. For example, Miller and Faust [9] studied the adsorption of various phenols onto bentonite clay coated with dimethylbenzyl octadecylammonium, showing that sorption was clearly pH dependent, but the extent of ionization alone was not sufficient to account for the observed dependence. The investigators indicated that the nature of the organic covering on the clay surface also may have been affected by pH. Indeed, characterizing the adsorption of organic acids to soils or sediments must involve determining the importance of both hydrophobic as well as electrostatic effects. Few data exist, however, that clearly address both effects.

Parallel research [2; C.T. Jafvert, J.C. Westall, E. Grieder, R.E. Schwarzenbach, manuscript submitted] has described the partitioning behavior of organic anions in octanol-water. Partitioning of nonpolar organic compounds between octanol and water has been used extensively to estimate the partitioning of these compounds to sediment organic carbon and to biological lipids. For the partitioning of organic anions between octanol and water, partitioning into the octanol phase occurs by both free ions and ion-pairs. The magnitude of partitioning, therefore, is dependent upon the hydrophobicity of the organic anion, the type of counterion present (e.g., monovalent vs. divalent), and the concentration of organic and inorganic species. In these studies, ionic strength and pH-dependent octanol-water partitioning were quantitatively interpreted using equilibrium expressions: for acid dissociation; for transfer of neutral organic species between phases; for transfer of free ions, both organic and inorganic between phases, as constrained by electroneutrality of each phase and for transfer of ion-pairs between phases.

Scope of this study

Many of the same factors that influence the transfer of organic acids between octanol and water affect the transfer of these compounds in the more heterogeneous system of sediment-water. These similar factors include the degree of dissociation and the hydrophobicity and electrostatic influences of both sorbent and sorbate. The goal of this study, therefore, was to examine how these various factors quantitatively influence the partitioning of specific organic acid compounds in a variety of sediments by manipulating measurable parameters. Parameters that have been examined include the organic carbon content of the sorbent, the ionic strength and composition of the sediment-water slurry, the aqueous phase pH and factors inherent to the organic compounds, such as their dissociation constant and degree of hydrophobic character.

To this end, using 2,4-dinitro-*o*-cresol (DNOC) and 2-(2,4,5-trichlorophenoxy)propanoic acid (silvex), we measured adsorption isotherms at the natural pH for 13 different sediments or soils. In addition, isotherms were measured as a function of added NaCl and $CaCl_2$ concentration. Finally, the pH-dependent adsorption of DNOC, silvex, PCP and 4-chloro-α-(4-chlorophenyl)benzeneacetic acid (DDA) were determined using a sediment-water system in which pH was controlled to specific end points.

MATERIALS AND METHODS

All test chemicals were used as received from the Pesticide and Industrial Chemicals Repository, U.S. Environmental Protection Agency (EPA), and all had purity greater than 99% except for DDA (98.25%).

Adsorption isotherms

Distribution ratios (between sediment or soil and aqueous phases) of the organic acids used in this study were determined using well-characterized sediment and soil samples, collected at various locations across the midwestern United States (U.S.). A known weight (1 to 5 g) of air-dried sample was placed in each of a series of glass tubes and hydrated with distilled water for 1 to 3 d. During this time, the tubes were shaken periodically. Then additions to each tube were made using distilled water, and 0.1 M NaCl, or 0.1 M $CaCl_2$, followed by the final addition of test chemical. Each tube of a particular experiment was of the same final volume and solid mass. 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 min.

After a designated time (generally 24 h), the slurries were centrifuged at 12,000 rpm (Sorval RC2-B centrifuge, SS-34 rotor) for 40 min. Aqueous phases were analyzed isocratically by HPLC using a 10-μm C-18 guard column and a C-18 analytical column. The solvent system was from 25 to 40% acetonitrile in water, depending upon the hydrophobicity of the compound being analyzed and contained 50 mM phosphate (25 mM K_2HPO_4

and 25 mM KH_2PO_4). Duplicate injections were made of samples and standards. Standard curves, consisting of five or more points, were forced through the origin, and generally had correlation coefficients of greater than 0.99. Adsorption isotherms were computed by calculating the solid phase concentration by difference in total mass of compound added to total mass recovered in the aqueous phase. Several solid phases were extracted with acetonitrile, and total recovery efficiencies were generally greater than 95%.

pH-dependent experiments

To assess the effects of pH on the distribution of the organic acids in sediment-water, a pH-stat was constructed. It consisted of a Fisher Accumet 825MP pH meter, a Fisher DC load interface, a Bio-Chem Valve Corp. 12-V solenoid valve, a 5-ml burette used as the titrant reservoir, a reaction flask with ports for (a) a Ross combination rugged-glass-bulb pH probe, (b) acid or base addition and (c) a pressure release vent. Only glass and Teflon parts were exposed to sediment and water. Wetted areas of the solenoid valve (exposed to acid or base) were silicon. Reaction flask contents were mixed by a magnetic stirrer and the entire apparatus was maintained at 25°C in a constant temperature room.

For each experiment, a sediment slurry was equilibrated for 24 h without addition of acid, base or compound. Then, the slurry was spiked with a specific chemical, to give a total volume of 250 ml, and a concentration of 0.5 to 2.0 × 10^{-6} M. The slurry was equilibrated for 8 to 24 h longer, at which time a 15-ml sample was removed for centrifugation and HPLC analysis. The pH was lowered by 0.5 to 1.0 pH units by addition 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 h, another sample was taken. This process was repeated until a final pH value was reached, generally equal to 3.5 to 4.0.

To study partitioning at high pH, a new sediment slurry was titrated to high pH (9.0 to 10.0) by addition of 0.5 M NaOH by setting the lower limit on the pH meter. After 24 h, the slurry was spiked with the specific chemical to give the same total volume (250 ml) and concentration as before. The slurry was equilibrated for 8 to 24 h longer, at which time a 15-ml sample was removed for analysis. Generally, after this time period (32 to 48 h), the pH had stabilized such that addition of acid was required to lower the pH, repeating the above procedure for titration of slurries from their natural pH to lower values. For sediment 11, titration from pH 10.0 to pH 7.8 (the distilled water pH value of a 1.0 to 10 sediment-water dilution) generally resulted in a pH drift of about 0.1 units less than the set value over a 24-h period, resulting in no addition of acid after the initial addition required to reach the set point.

Octanol-water distribution ratios

Distribution ratios were determined as a function of pH between octanol and water phases following the procedures as described in another paper [C.T. Jafvert, J.C. Westall, E. Grieder, R.E. Schwarzenbach, manuscript submitted]. Aqueous phases contained 0.01 M KCl, and HCl or KOH to obtain variable pH values between 1 and 12. Aqueous phase concentrations of the organic acids were determined by HPLC. Concentrations of the organic acids in the octanol phase were determined either by difference or by UV analysis.

RESULTS

Adsorption isotherm of 2,4-DB

A first step is assessing isotherm fit and linearity. To this end, the adsorption of 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB) was measured in sediment 11 with the adsorbing chemical concentration spanning three orders of magnitude. The resulting isotherm is presented in Figure 1, and information on sediment 11 is given in Table 1 [13]. Adsorption was measured after 4 d, at which time the aqueous phase was removed and replaced with distilled water, and slurries were "re-equilibrated" for another 4 d. Below a sediment phase concentration of about 3.0 × 10^{-6} mol/kg (aqueous phase =

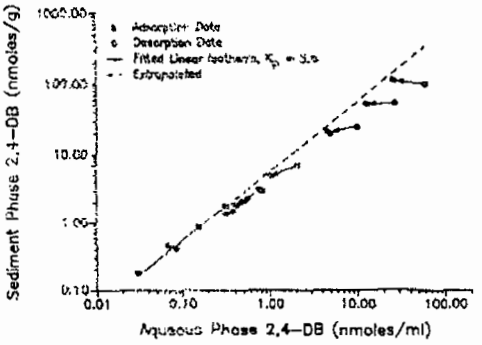

Fig. 1. Adsorption of 2,4-DB to sediment 11. Information on sediment 11 is given in Table 1. The sediment mass to water volume ratio (m/v) was 0.4 kg/L. The pK_a of 2,4-DB is 4.95 [C.T. Jafvert, J.C. Westall, E. Grieder, R.E. Schwarzenbach, manuscript submitted].

Table 1. Partitioning of DNOC and silvex to sediments and soils

	Sediment properties[a]				Aqueous phase properties					
Sediment	% Organic carbon	CEC (me/100 g)	% Clay	% Sand	pH	Conductivity (μmhos/cm)	Ca (mg/L)	K_p (Silvex)	K_p (DNOC)	K_p(Silvex)/ K_p(DNOC)
5	2.28	19.00	31.0	33.6	7.15	910	88.4	0.96 ± 0.07	4.02 ± 0.07	0.24
8	0.15	3.72	6.8	82.4	8.29	250	23.9	0.077 ± 0.048	0.38 ± 0.13	0.20
9	0.11	12.40	17.4	7.1	8.29	220	13.3	−0.03 ± 0.06	−0.16 ± 0.12	—
11	1.50	13.86	49.4	1.7	7.92	710	102.0	0.632 ± 0.02	3.57 ± 0.13	0.18
12	2.33	13.53	35.4	0.0	7.53	650	104.0	0.86 ± 0.05	5.18 ± 0.67	0.17
13	3.04	11.86	52.6	20.3	7.00	570	62.1	2.18 ± 0.18	4.75 ± 0.50	0.45
14	0.48	18.86	63.6	2.1	4.27	180	6.2	0.62 ± 0.10	2.89 ± 0.75	—
15	0.95	11.30	35.7	15.6	7.27	400	61.6	0.60 ± 0.05	2.35 ± 0.28	0.25
16	1.20	10.50	39.0	0.5	7.47	240	38.2	0.27 ± 0.03	1.19 ± 0.22	0.23
18	0.66	15.43	39.5	34.6	7.52	340	49.7	0.20 ± 0.086	1.05 ± 0.18	0.19
22	1.67	8.53	21.2	26.1	7.53	710	98.7	1.29 ± 0.15	3.62 ± 0.38	0.35
24	0.95	6.28	20.8	20.5	4.47	320	7.0	0.63 ± 0.05	5.93 ± 1.45	—
25	0.76	8.86	20.5	41.9	7.75	400	45.4	0.174 ± 0.05	0.68 ± 0.28	0.25

[a]Samples collected and characterized by J. J. Hassett et al. [13].

1.0×10^{-6} M), adsorption is linear (slope of 1.0 on a log solid phase concentration vs. log aqueous phase concentration plot); above this concentration, the adsorption curve is easily fit to a Freundlich isotherm ($K_f = 3.84$, $N = 0.8$). Similarly, at the lower concentrations, no appreciable difference exists between the adsorption and desorption data. At the higher doses, however, the adsorption and desorption data do not fall on the same line, indicating that some kinetic or nonthermodynamic limitations exist for this experimental time frame. In other experiments, these effects at higher chemical concentration were avoided by using low concentrations, within analytical constraints, to avoid the need for nonlinear data analysis. Note that extrapolation of the linear adsorption isotherm for 2,4-DB results in errors of only a factor of two or three over the entire range of measurable concentrations and requires only one fitting parameter (K_p).

Adsorption of silvex and DNOC to various sediments

To assess the variability of partitioning with sediment source or characteristics, partition coefficients (K_p) for silvex ($pK_a = 3.07$) and DNOC ($pK_a = 4.39$) were determined using sediments collected from 13 locations around the midwestern U.S. Characteristics of the sediments and of the resulting aqueous phases are given in Table 1 [13] along with the resulting K_p values. The pH of these sediments was between 7.0 and 8.3 under experimental conditions in all but two cases. In this range of pH, adsorption occurs predominantly (but not exclusively) by the anionic form of these compounds, as will be shown. Hence, the distinction is made between K_p values reported here, which may result from a combination of partitioning of the anion and the neutral species, and K_d and K_{dl} values reported later, which separate the contribution of each form into two distinct constants.

Several isotherms are shown in Figure 2 to contrast the magnitude of partitioning among the adsorbents. The influence of pH, with respect to pK_a, can be seen in Figure 2 by comparing the relative slopes of the isotherms for the two compounds, and observing the "enhanced" adsorption of DNOC in sediment 24 compared to that of silvex. The measured pH of sediment 24 was 4.47. At this pH, adsorption of silvex should occur by both the anionic and neutral forms. The adsorption of DNOC at this pH, however, occurs predominantly as the neutral species.

For the 11 adsorbents where pH was within the range 7.0 to 8.3, the adsorption coefficients of both silvex and DNOC are correlated in Figure 3 to sediment organic carbon content. The scatter in this figure supports the idea that the adsorption of compounds containing anionic or other polar functional groups is influenced by nonhydrophobic interactions on organic carbon as well as possible mineral contributions to adsorption [14]. Despite the weak adsorption observed, however, regressing the data for either silvex or DNOC gives a slope (K_{oc}) that is generally within a factor of two of all the data. Table 1 also gives the ratio K_p(silvex)/

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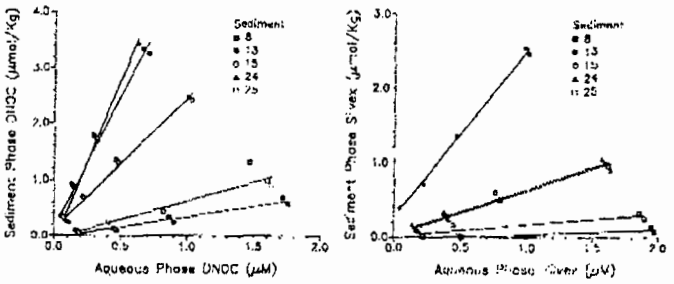

Fig. 2. Adsorption isotherms of DNOC and silvex to various sediments. Information on the sediments is given in Table 1.

K_p(DNOC) for the experiments at pH values greater than 7.0. This ratio varies only within a factor of two, also, indicating that the nonhydrophobic contributions for adsorption of polar compounds of similar structure (in this case anions) may be indexed as a constant for each sediment.

Analysis of experiments in which sediment 9 was used generally resulted in slightly greater than 100% recovery efficiency of spiked compound in the aqueous supernatant. Presumably, this "concentrating" effect was caused by negative adsorption; that is, repulsion of the organic anion from the sediment surface makes the concentration of compound in the water associated with the sediment pellet (after centrifugation) less than that in the overlying aqueous phase. Negative adsorption on clay surfaces is well-documented. The organic carbon content of this sediment is very low.

Addition of inorganic salts

Results of experiments using either NaCl or $CaCl_2$ solutions as sediment diluents are shown in Table 2 and in Figure 4. Adsorption of both compounds to the sediment was enhanced by addition of $CaCl_2$, but addition of NaCl up to 0.05 M showed little or no enhancement. Several mechanistic interpretations may be proposed for this dependence. Salting out can be ruled out [15], however, as well as any major effect caused by changes in chemical activity due to ionic strength. A more tenable explanation involves changes in the surface charge, due to increasing the calcium ion concentration at the surface, making it more conducive for anionic adsorption. This hypothesis is strengthened by the observation that adsorption or exchange coefficients for (monovalent) sodium ions onto sediments is less than that of (divalent) calcium ions, and the overall change in surface charge will be greater for the addition of the same number of calcium ions as opposed to sodium ions. In any case, appreciable addition, beyond what is found naturally, of "counter-ion" is required before significant changes are made in K_p. This analysis is complicated, however, by the simultaneous addition of chloride.

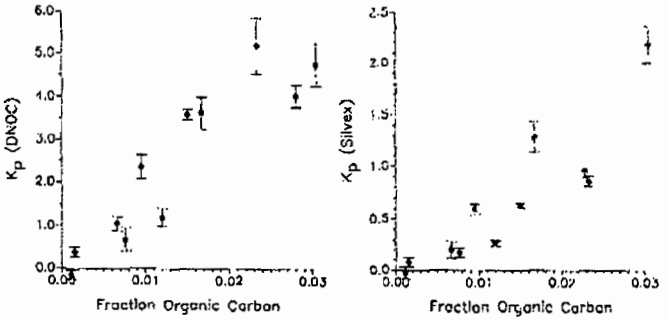

Fig. 3. Partition coefficients (K_p) of DNOC and silvex as a function of organic carbon content, where the natural pH was between 7.0 and 8.3.

Table 2. Silvex and DNOC in Sediment 11, with added $CaCl_2$ or NaCl

	pH	Conductivity (mhos/cm)	K_p(Silvex)	K_p(DNOC)
Natural	7.92	0.71	0.632 ± 0.019	3.57 ± 0.130
0.01 M $CaCl_2$	7.98	2.29	0.978 ± 0.064	4.46 ± 0.294
0.025 M $CaCl_2$	7.58	2.29	1.25 ± 0.0797	5.64 ± 0.53
0.05 M $CaCl_2$	7.43	8.72	1.45 ± 0.104	7.60 ± 0.696
0.01 M NaCl	8.03	1.77	0.732 ± 0.151	3.41 ± 0.902
0.025 M NaCl	8.10	3.32	0.618 ± 0.090	3.61 ± 0.492
0.05 M NaCl	7.90	5.90	0.741 ± 0.221	3.73 ± 0.693

Partitioning as a function of pH

Distribution ratios of four compounds were determined in sediment 11 as a function of pH. The compounds were chosen to vary in their magnitude of partitioning and in their degree of dissociation at various pH values. The main point of this exercise was to attempt to factor the partition coefficients (K_p) of these compounds into discrete coefficients for the neutral species (K_d) and the anionic species (K_{di}). These constants are defined as:

$$K_d = \frac{[HA]_{sed}}{[HA]} \quad (1)$$

$$K_{di} = \frac{[A^-]_{sed}}{[A^-]} \quad (2)$$

with

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (3)$$

where $[HA]_{sed}$ (mol/kg) and $[HA]$ (M) are the neutral species sediment and aqueous phase concentrations, respectively; and $[A^-]_{sed}$ (mol/kg) and $[A^-]$ (M) are the anionic species sediment and aqueous phase concentrations, respectively. Because only total concentration of compound in each phase can be determined analytically, mass balance equations are needed for total concentration in the aqueous phase ($[HA]_{aq}$), total concentration in the sediment phase ($[HA]_{ts}$) and total concentration in the system ($[HA]_t$, referenced to the aqueous phase volume),

$$[HA]_{aq} = [HA] + [A^-] \quad (4)$$

$$[HA]_{ts} = [HA]_{sed} + [A^-]_{sed} \quad (5)$$

$$[HA]_t = [HA]_{aq} + (m/v)[HA]_{ts} \quad (6)$$

where (m/v) is the sediment mass (kg) to aqueous volume (L) ratio.

At pH values below or near the pK_a of a compound, the distribution coefficient for the neutral species (K_d) can be calculated by combining Equations 1, 3, 4 and 6 and assuming $[HA]_{ts} = [HA]_{sed}$, giving K_d in terms of measurable parameters,

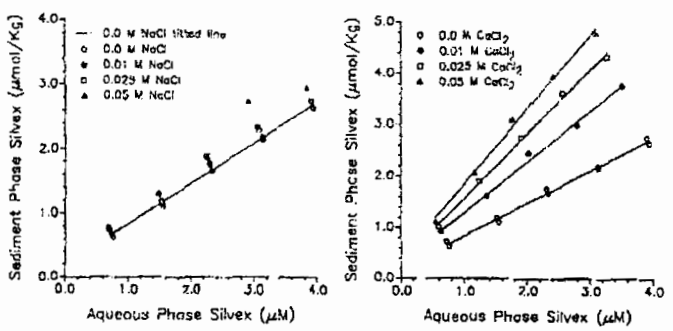

Fig. 4. Adsorption isotherms for silvex as a function of inorganic ion composition of sediment 11 slurries.

Table 3. Constants used in modeling the adsorption of organic acid compounds to sediment 11

Compound	$(m/v)^a$	pK_a[b]	$\log K_{ow}$[b]	$\log K_{owi}$[c]	$\log K_{ow}/K_{owi}$	$\log K_d$	$\log K_i$	$\log K_d/K_i$
PCP	0.05	4.75	5.24[d]	1.60	3.7	3.0	3.33	−0.33
DDA	0.08	3.66	4.48	0.70	3.8	2.45	2.31	0.14
DNOC	0.10	4.46	2.16	−0.57	2.7	1.93	2.83	−0.9
Silvex	0.10	3.07	3.80	−0.13	3.9	1.87	2.03	−0.16

[a]Sediment mass to water volume ratio (kg/L).
[b]C. T. Jafvert, J. C. Westall, E. Grieder, R. E. Schwarzenbach, manuscript submitted.
[c]K_{owi} is the octanol-water distribution ratio measured using 0.1 M KCl and 0.01 M KOH in the aqueous phase with approximately 3×10^{-4} M of the organic anion in the octanol phase.
[d]K. Schellenberg et al. [1].

$$K_d = \frac{([HA]_t - [HA]_{aq})/(m/v)}{\{H^+\}[HA]_{aq}/(\{H^+\} + K_a)} \quad (7)$$

Values of K_d, calculated from Equation 7 at low pH, for the four compounds investigated are given in Table 3.

A first approximation to adsorption of acid compounds is to assume that no adsorption of the anionic species occurs at any pH. Using this assumption (i.e., $[A^-]_{sed} = 0.0$ M), we can obtain an expression for the fraction of total compound in the aqueous phase by using the same equations as those used in determining K_d above,

$$f^{I}_{aq} = \frac{[HA] + [A^-]}{[HA]_t} = \frac{(K_a + \{H^+\})}{(K_a + \{H^+\} + K_d\{H^+\}(m/v))} \quad \text{(Model I)}$$

Results, comparing the experimentally observed adsorption of PCP in sediment 11 to calculated adsorption using Model I, are shown in Figure 5. Below pH 6 (1.25 units above the pK_a), this model fits the data reasonably well. Above this pH, appreciable adsorption of the anion occurs, as indicated by the under prediction of adsorption. Indeed, at pH = 8.0, the amount actually adsorbed is approximately 25%; however, Model I predicts this to be less than 5.0%.

If adsorption of the anion is allowed, as expressed by Equation 2, combination of Equations 1–6 results in a new expression for the fraction of total compound in the aqueous phase,

$$f^{II}_{aq} = \frac{[HA] + [A^-]}{[HA]_t} = \frac{(K_a + \{H^+\})}{(K_a + \{H^+\} + (K_d\{H^+\} + K_{di}K_a)(m/v))} \quad \text{(Model II)}$$

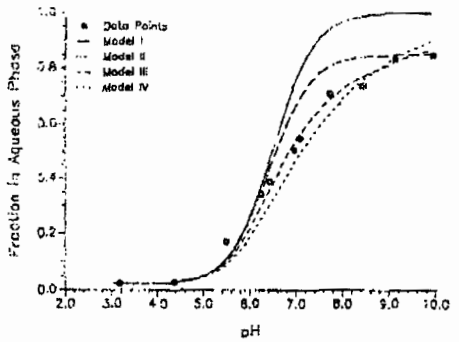

Fig. 5. The pH-dependent adsorption of PCP to sediment 11, and results using the four models presented. The sediment mass to water volume ratio (m/v) was 0.05 kg/L. Six data points result from titration down from pH 7.8 (the natural pH of the slurry), and five points result from titrating between 9.9 and 6.4 after an initial increase in pH by NaOH addition.

Results comparing this model to PCP data also are shown in Figure 5, calculating K_{di} from the distribution ratio at the highest pH value. Clearly, at intermediate pH values of environmental relevance (7.0 to 8.5), this model also underestimates adsorption of the ionic pentachlorophenate, suggesting a pH dependence on K_{di}. Values for the apparent K_{di} can be calculated for each intermediate data point on the titration curve,

$$K_{di} = \frac{[HA]_{ts}(\{H^+\} + K_a) - K_d\{H^+\}[HA]_{aq}}{K_a[HA]_{aq}} \quad (8)$$

Results of calculated K_{di} values are shown in Figure 6 as a function of pH along with the equations for the corresponding regressions for all four compounds studied. For PCP the increase in K_{di} is approximately 50% for each pH unit decrease. Using the regression equation for PCP, we can now pro-

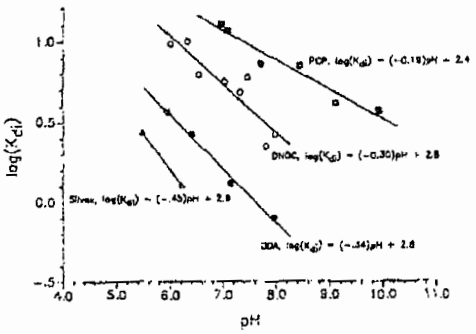

Fig. 6. Calculated values for K_{di} as a function of pH and the resulting regression equations for the four compounds.

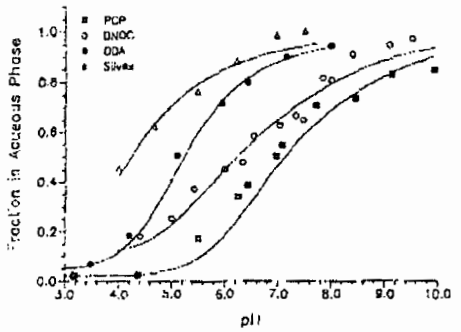

Fig. 7. The pH-dependent adsorption of the four organic acids in sediment 11, and predicted partitioning using Model IV and the values of K_d, K_i, and K_a, given in Table 3, with σ_i equal to −0.3.

pose Model III which is identical to Model II except for this pH dependence,

$$f_{aq}^{III} = f_{aq}^{II}, \text{ where } \log K_{di} = (-0.19)\text{pH} + 2.4 \qquad \text{(Model III)}$$

Results from this model also are shown in Figure 5 for PCP. Model III corresponds to the "best fit" for adsorption of an organic acid compound assuming (a) invariant adsorption from solution of the neutral species with pH, and (b) linear pH-dependent adsorption of the anionic species as described by Figure 6.

Some type of pH dependence on adsorption of the anion may seem obvious, resulting from changes in the surface charge or degree of protonation of the organic carbon matrix. Indeed, according to Stern, the total free energy of adsorption of a charged species equals the sum of the intrinsic chemical adsorption energy and the electrostatic or coulombic adsorption energy,

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{chem} + \Delta G^{\circ}_{el} \qquad (9)$$

The intrinsic chemical adsorption energy (ΔG°_{chem}) is largely a function of hydrophobic forces, whereas the electrostatic energy (ΔG°_{el}) is largely a function of the degree of ionic character expressed by the adsorbing species and of the surface potential or charge of the adsorbent. Hence, the slopes in Figure 6 correspond, in large measure, to the sediment-dependent change in the electrostatic contribution to adsorption, whereas the intercepts correspond to the relative individual compound specific electrostatic and chemical contribution. The slopes in Figure 6 may be somewhat dependent upon the specific adsorbing anion. It may be reasonable, however, to assume, both mechanistically and statistically, that these slopes result entirely from electrostatic changes in the sediment and, therefore, should be identical, or at least similar, for compounds of similar form. Using an "average" slope (σ_i) of −0.3 and the midpoints of the calculated regressions, new intercepts can be calculated for each compound, corresponding to the intrinsic chemical component of adsorption. These new intercepts (K_i) are given in Table 3. They indicate the relative magnitude of partitioning of these anions independent of pH.

Model IV is now proposed, which uses the values of K_d and K_i in Table 3, with $\sigma_i = -0.3$,

$$f_{aq}^{IV} = f_{aq}^{II}, \text{ where } \log K_{di} = \sigma_i(\text{pH}) + \log K_i \qquad \text{(Model IV)}$$

In total, this model uses five parameters. One constant, pK_a, is intrinsic to the adsorbate; two constants, K_d and K_i, describe the interactions between adsorbate and adsorbent; one constant, σ_i, is intrinsic to the adsorbent and pH (or $\{H^+\}$) is the independent variable. The experimental data for all five compounds are shown in Figure 7, along with Model IV results using the constants given in Table 3. This fit for PCP also is shown in Figure 5, to compare model sensitivities.

Because the need exists to determine a priori adsorption of these and similar compounds under a variety of natural conditions, adsorption energies

must be factored into measurable or predictable quantities, as has been attempted here. The adsorption of neutral organic compounds is the simplest case, where the adsorption energy is largely determined by hydrophobic interactions. Octanol-water distribution (K_{ow}), in turn, has been used as a measure of chemical hydrophobicity. Similarly, comparisons were made here between the distribution coefficients determined in sediment-water systems, and the distribution of the same compounds in octanol-water, at pH values where either the neutral or anionic species dominated the adsorption process. Table 3 contains the K_{ow} values for the neutral forms of these compounds, as well as the octanol-water distribution ratios (K_i) of these compounds at pH 12 in 0.1 M KCl. Because the distribution ratio of organic anions between octanol and water is a function of the organic concentration (because of ion pairing), the organic concentration in octanol, reported in Table 3, was controlled to within a factor of 2.

For PCP, DDA and silvex, organic-carbon-normalized partition coefficients are, within a factor of two, equal to the K_{ow}. A similar trend exists for distribution of the anions. The unique partitioning of DNOC can be seen more clearly by examining the difference in distribution between the neutral and anionic species in each of the systems, reported as $\log K_{ow}/K_{owi}$ for octanol and $\log K_d/K_i$ for sediment. In both cases, the difference in partitioning among PCP, DDA and silvex is approximately equal. For DNOC, however, these values are approximately an order of magnitude less. This deviation likely results from differences in polarity caused by the nitro groups on DNOC, making the relative magnitude of partitioning (of both the neutral and anionic species) to the sorbents different, while maintaining a similar "difference" in partitioning between the neutral and anionic species.

SUMMARY

This study has examined factors that influence the adsorption of various organic compounds that contain a single, relatively strong, acidic functional group. The main emphasis has been to characterize the adsorption process "mechanistically" for further quantitative structure-activity relationship development. The final model (IV) presented includes adsorption mechanisms for both the neutral and anionic species.

The adsorption of the neutral species is the simplest case, wherein the adsorption energy is largely determined by hydrophobic interactions. On the other hand, adsorption of the anionic species is influenced by intrinsic chemical as well as electrostatic factors. For the organic anions, it seems rational to assume, from the data presented, that the chemical-specific dependence stems predominantly from hydrophobic interactions, which are attenuated by the electrostatic interactions. In turn, these electrostatic interactions are most notably expressed during changes in pH of the sediment slurries. Changes in total ionic composition of the medium for natural systems may be of lesser importance compared to changes in surface properties (i.e. charge) resulting from varying pH, although the ionic composition of natural systems, also, may influence surface charge.

In this study, adsorption of the anionic species was modeled as a linearly dependent function of pH. The rationale for this dependence may result because a "distribution" of pK_a values generally exists on humic material [16, and references therein]; hence, adsorption of charged species onto this matrix should coincide with these curves. Here, only one sediment system (sediment II) was examined and clearly more evidence is needed to confirm this general pH dependence.

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