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SORPTION OF PHENOL AND CHLOROPHENOLS
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SORPTION OF PHENOL AND CHLOROPHENOLS ON SMECTITE-ORGANIC COMPLEXES

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ABSTRACT

SORPTION OF PHENOL AND CHLOROPHENOLS ON SMECTITE-ORGANIC COMPLEXES

By

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A number of quaternary ammonium cations were used to make smectite-organic complexes. These cations were placed on the exchange sites of clay structure, imparting various surface nature to organo-smectites. Then, the sorption of phenol and chlorophenols on these complexes was studied. The hydrophobicities of both sorbate and sorbent played an important role in the sorption process. The interaction was stronger between a sorbate and a sorbent in like nature, *i.e.*, similar hydrophobicities. For very hydrophobic organo-smectites the most hydrophobic organic compounds like pentachlorophenol were taken up in larger amounts from water, whereas phenol, the least hydrophobic one, was sorbed more by relatively hydrophilic complexes. A partitioning model was employed in accounting for hydrophobic sorption. Effects of solvent, pH, and competition on sorption were also studied. The results from this study may suggest the possibility of treating natural clays with certain organic cations to enhance their sorptive properties.

TO

My wife, Weixing Zheng, and my mother, Shengwan Liu.

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INTRODUCTION

A). Uses and Toxicity of Chlorophenols

Phenol and chlorinated phenols are important industrial chemicals, which are very corrosive and toxic. It is especially true of pentachlorophenol (PCP, C_6Cl_5OH), which is one of the most versatile biocides used throughout the world. The total world production of PCP has been estimated at about 50 million kg per annum and the use of PCP in the USA amounts to about 23 million kg per annum (Arsenault, 1976).

PCP is used because it is toxic to microorganisms, plants, and animals, but incidentally, also to the human body, causing burns and blisters on the skin, fever, hyperpnea, hypertension, hyperglycemia, cardiovascular distress, *etc.* (Crosby, 1981; Environmental Protection Agency, 1978).

It has been believed that PCP and its residues as well are very common and hazardous pollutants in the human environments, including the atmosphere, water, soil, food, *etc.*. PCP and its residues are sometimes found in μg/l amounts in domestic and industrial sewage and river water

(Crosby, 1981). PCP is very hydrophobic and poorly water soluble with a solubility in water at 20°C of 0.014 g/kg (Verschueren, 1983), that is, 14 ppm. Solubility of the phenolate ion (pKa=4.7), however, is much higher.

B). Smectite/Organic Cation Interactions

The smectites include all minerals previously classified in the montmorillonite group of expansible 2:1 layer silicates (Dixon and Weed, 1977). Smectites possess negative charges in their lattice structure, due to the isomorphous substitution of lower-valent metal cations for higher ones in the silicate layers, *e.g.* Mg^{2+} and Fe^{2+} for Al^{3+} and Fe^{3+} in octahedral sheets, and Al^{3+} for Si^{4+} in tetrahedral sheets. In natural environments, the negative charges are satisfied usually by Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, and H^{+} on the surface, which are available for exchange. The cation exchange capacities (CEC) of smectites are very high, quantitatively about 90-125 meq/100 g, mainly contributed by the interlayer exchange sites, and also by the "edge charge", that is, the broken bonds on the edges of the mineral particles. The latter may be approximately 5 meq/100 g or more depending on the fineness. Another attracting property of smectites is their large surface area (up to 800 m^2/g), resulting from the layer structure (internal surface) and the very small particle size (less than 2 μm).

Generally, smectites have been chosen for this work mainly because of:

1). their wide distribution,

2). their previous and extensive uses in the waste handling industry, and

3). their high cation exchange capacities and large surface area.

The natural smectites have a hydrophilic surface imparted by shells of water molecules of the hydrated cations that neutralize the negative charges of the structure. Thus, untreated smectites are not efficient adsorbents for hydrophobic organic pollutants in water. However, if the exchangeable cations are replaced by some organic cations, the situation is completely different.

The interactions between clays and organic cations have been studied extensively (Dixon and Weed, 1977; Mortland, 1970, 1986; Theng, 1974; Solomon and Hawthorne, 1983). Basically, the following factors that affect clay-organic-cation interactions may be involved:

1). the properties of minerals, including CEC, surface charge density, the cations on the exchange sites, the origin of charge, expandibility, *etc.*;

2). the properties of organic cations, including molecular charge, lone pair electrons, pKa, isoelectric point, polarity, molecular weight, *etc.*; and

3). the environments, including pH buffering, solution ionic strength, temperature, concentration of the organic cation, the presence of other cations, *etc.*.

It has been shown that there are many mechanisms for clay-organic interactions in general (Mortland, 1970, 1986), such as:

1). ion exchange — substitution of organic cations for hydrated metal cations on the mineral surface;

2). protonation — proton-donating and proton-accepting;

3). coordination and ion dipole — organic cations acting as ligands;

4). hydrogen bonding — relatively weak interactions between pronton and electronegative elements (*e.g.*, O, N);

5). Van der Waals forces — relatively weak physical interactions; and

6). entropy effects — increasing degrees of freedom of molecules and increasing number of particles.

When dealing with organic cations the most prominent mechanism is cation exchange, which is completed basically by Coulombic interaction, *i.e.*, static electrical attraction. The hydrated metal cations held on the natural clay surface can be replaced by the organic cations that generally have greater prefernce for the exchange sites because of high molecular weights. These organic cations include the substituted ammoniums, oxomiums, diazoniums, *etc.*. Practically, the most important are substituted ammoniums because of their great stabilities and easy availabilities. The general reaction for clay-amine complexes synthesis is:

$$R_4N^+ + M^+\text{-clay} = R_4N^+\text{-clay} + M^+.$$

Here, four R's may be different organic groups and/or proton(s). M^+ is a hydrated metal cation. Within a group of primary, secondary, and tertiary amines, the affinity of the alkylammonium cations for the clay decreases in the series:

$$R_3NH^+ > R_2NH_2{}^+ > RNH_3{}^+.$$

However, the cationic nature of these amines varies very much while pH varies, so their adsorption as cations onto the mineral surface depends upon pH to a somewhat great extent.

We have chosen quaternary amine cations of the general form like $(CH_3)_3NR^+$ or $(CH_3)_2NR_2{}^+$ to synthesize our smectite-organic complexes. Because there is no proton directly bonded to N in quaternary amines, these molecules possess a permanent positive charge that is pH independent and remain bound to the smectites regardless of pH. These smectite-organic complexes may therefore be used for sorbing organic toxicants from water over a wide pH range.

C). Organo-Smectite/Organic Compound Interactions

The uptake of a certain organic compound (a sorbate) onto a smectite-organic complex (a sorbent) is basically controlled by the sorbent-sorbate interactions, which can be grouped as:

1). hydrophobic or nonpolar interactions, and

2). other interactions.

The former is especially important to the present dicussion.

a). Hydrophobic Interactions

As we have mentioned before, the surface nature of untreated smectites is essentially hydrophilic due to hydration of exchange metal cations like Ca^{2+} and Na^+. However, when the exchange sites on the surface are occupied by the organic molecules having long-chain alkyl groups (like dioctadecyldimethyl ammonium, $DODMA^+$, and hexadecyltrimethyl ammonium, $HDTMA^+$), the surface will become very hydrophobic (Pashley *et al.*, 1985).

Many scientists have reported their work on the interactions between such a surface and some hydrophobic organic compounds, including aromatic molecules, enzymes and proteins, *etc.* (Wolfe *et al.*, 1986; McBride *et al.*, 1977; Garwood *et al.*, 1983; Boyd and Mortland, 1985a, 1985b, 1986). A theory of so-called hydrophobic bonding has been widely used. The affinity of the long-chain alkyl groups for hydrophobic, non-ionic organic molecules is probably imparted by what have been called dipole-induced-dipole (Debye force), and induced-dipole-induced-dipole (London force) interactions (Atkins, 1982). Because the mineral surface of smectite-organic complexes is almost completely shielded by hydrophobic long alkyl "tails", Coulombic attraction maybe is not a factor in the sorption described here.

Chiou *et al.* have successfully created a partition model for the sorption of nonionic, poorly water soluble organic solutes by soil humus (Chiou *et al.*, 1979, 1981, 1983, 1985a, 1985b). This mechanism is similar to the partitioning of an organic solute between water and a bulk phase solvent like hexane or octanol. It is characterized by:

1). linear isotherms,
2). lack of a competitive effect in multisolute system,
3). low heat effects, and
4). dependence of the sorption coefficient, K, on the organic matter content of the sorbent.

When a smectite-organic complex containing long-chain alkyl groups is added into a solution, two phases would be formed:

1). aqueous phase — the body of the solution, and
2). "organic phase" — the "atmosphere" of the long chains that cover the mineral surface.

The smectite-organic complex has some analogy to natural clay-organic matter complexes, and the mechanism of interaction with organic solutes may be similar. The hydrophobic sorbate (*i.e.*,the molecules of a target organic compound) may be taken up into the "organic phase" in prominently large amounts, because the sorbate-"organic-phase" interaction is much stronger than the sorbate-aqueous-phase one. If the solvent phase is also organic and hydrophobic, however, a competitive solvent effect should be expected. For such a partition model, a partition coefficient, K, may be reasonably employed, which can be calculated by dividing the amount of the sorbate sorbed (mmol/g) by the equilibrium concentration (mmol/ml).

At the concentrations typically encountered in natural water, approximately linear sorption isotherms have often been found (Chiou *et al.*, 1983; Schnellenberg *et al.*, 1984), which essentially obey the following relationship:

$$S = KC.$$

Here, S is the amount sorbed per unit weight of sorbent (mmol/g) and C is the equilibrium concentration in the aqueous phase (mmol/ml). The partition coefficient depends on:

1). the solubility of the sorbate;

2). the organic carbon content of the sorbent; and

3). the hydrophobicity of the "organic phase".

The K value is often linearly related to the octanol/water partition coefficient, Kow, for convenient comparison. In this work, it would be of interest to establish the relationship between Kow values and organic matter constants, Kom's. Here:

$$Kom = 100 \; (K \; / \; \text{organic matter} \; \% \;).$$

Such relationships have been developed and extensively used for soil organic matter (Chiou *et al.*, 1983). For example:

$$\log Kom = 0.904 \log Kow - 0.779. \qquad (r = 0.994)$$

b). Other Kinds of Interactions

The interactions between organic compounds and smectite-organic complexes containing smaller organic cations (like trimethylphenyl ammonium, $TMPA^+$, and tetramethyl ammonium, TMA^+) may be completed in different mechanisms from that we have described above.

On the surface of these smectite-organic complexes, the "organic phase" is not spread as a contінueous atmosphere, but made up of discrete small organic moieties like $-CH_3$ and $-C_6H_5$ groups. Here the mineral surface is not completely screened and some silicate oxygen and hydroxyl groups are exposed to the surroundings (McBride and Mortland, 1975). Thus, a dual function might be expected for such a surface:

1). hydrophobic interactions to the organic groups, and

2). polar interactions on the exposed mineral surface.

In many situations for these smectite-organic complexes, the hydrophilic interactions are predominating, which include Coulombic attraction, hydrogen bonding, *etc.*. Thus, these smectite-organic complexes possess mainly a hydrophilic nature and behave as conventional mineral sorbents, which could be employed for sorbing hydrophilic organic compounds.

Chapter II

ORGANIC-SMECTITES AS ADSORBENTS FOR PHENOL AND CHLOROPHENOLS

A). Abstract

Several smectite-organic complexes were synthesized by placing quaternary ammonium cations on smectite by cation exchange. They were then examined for their ability to adsorb phenol and several of its chlorinated congeners. The organic cations used were: hexadecylpyridinium ($HDPY^+$), hexadecyltrimethyl ammonium ($HDTMA^+$), trimethylphenyl ammonium ($TMPA^+$), and tetramethyl ammonium (TMA^+). The complexes containing long-chain alkyl (hexadecyl) groups were the most hydrophobic and adsorbed the phenols from water in proportion to their hydrophobicities, which increase with chlorine addition:

phenol < chlorophenol < dichlorophenol < trichlorophenol.

With n-hexane as the solvent, different adsorption was found which mainly depended on the type and degree of solvent interactions with the compound and the clay-organic complex. Thus, the amount of adsorption of these phenols on clay-organic complexes was dependent on the relative energies of adsorbent-adsorbate and adsorbent-solvent interactions.

B). Introduction

The mechanisms of clay-organic interactions have been well documented in the literature (Mortland, 1970; Theng, 1974; Solomon and Hawthorne, 1983; Mortland, 1986). By placing organic cations or metal cations with strongly bound organic ligands on the cation-exchange sites of clays, the surface properties may be significantly altered. Long-chain alkyl ammonium cations adsorbed on the clay, for example, change the nature of the surface from hydrophilic to hydrophobic. Consequently, whereas enzyme (protein) adsorption on smectite is ordinarily pH dependent (Coulombic effects), the enzyme may be strongly bound by clay-organic complexes such as $HDTMA^+$-smectite by hydrophobic binding which is completely independent of pH (Garwood *et al.*, 1983; Boyd and Mortland, 1985a, 1985b, 1986). Such interaction involves hydrophobic portions of the enzyme interacting with the hydrophobic alkyl group on the mineral surface.

McBride *et al.* (1977) showed that different kinds of clay-organic complexes have widely varying adsorption properties for benzene, phenol, and chlorobenzenes. The present work is an extension of that study in which adsorption isotherms of phenol and a series of its chlorinated analogs were obtained for several clay-organic complexes of varying hydrophobicities. The particular microenvironment provided by each organic cation on the clay surface should be reflected in different adsorption properties for the series of phenols.

C). Methods

The clay used was smectite from a Wyoming bentonite furnished by American Colloid Company. Ten grams of the Na^+-saturated clay was dispersed in 1 liter of distilled water and allowed to stand several hours to allow quartz sand and heavy minerals (5% of the whole) to settle out. The suspension was decanted and treated with the bromide or chloride salt of the appropriate organic cation in an amount just equal to the cation-exchange capacity of the clay (90 meq/100 g). A summary of the names, abbreviations, structural formulae, and carbon contents of the organic cations used appears in Table 1. Because these organic cations are strongly preferred by the exchange sites over the Na^+ cations, most of the organic cation was taken up by the exchange complex. Excess organic salt was not added because these organic salts may be adsorbed by the clay in large excess of the exchange capacity. After the treated clay was washed on filter paper with distilled water, the clay was frozen, freeze dried, and stored in bottle for use.

Adsorption isotherms were obtained by weighing duplicate 50-mg quantities of the clay-organic complex into 125-ml Erlenmeyer flasks and adding the appropriate compound in amounts equal to 0.2, 0.4, 0.6, 1.0, 1.5, 2.0 mmol/g of

Table 1. Data of ammoniums on exchange complex of smectite.

Name	Abbre.	Structure	[a]C (%)
Dioctadecyldimethyl ammonium	DODMA	$(CH_3)_2N((CH_2)_{17}CH_3)_2$	29.47
Hexadecyltrimethyl ammonium	HDTMA	$(CH_3)_3N(CH_2)_{15}CH_3$	17.32
Hexadecylpyridinium	HDPY	$C_5H_5N-(CH_2)_{15}CH_3$	[b]N.D.
Trimethylphenyl ammonium	TMPA	$(CH_3)_3N-(C_6H_5)$	6.68
Tetramethyl ammonium	TMA	$(CH_3)_4N$	4.01
4-Mercaptopyridinium	4-MP	$(HNC_5H_4)-SH$	N.D.
Ammonium	NH_4	NH_4	—

[a] Percent carbon in the clay-organic complex.
[b] N.D. is not determined.

Table 2. Data of phenol and chlorophenols.

Name	M.W.	[a]Water solubility (20° C, mg/kg)	Wavelength absorbed (nm)
phenol	94.11	7.75×10^4	269
3-chlorophenol	128.56	2.5×10^4	274
3,5-dichlorophenol	163.00	4.5×10^3	277
3,4,5-trichlorophenol	197.45	not found	292
2,4,6-trichlorophenol	197.45	8.0×10^2	293
pentachlorophenol	266.34	1.4×10	318

[a] Freier, 1976, and Verschueren, 1983.

clay. Total volume of solution was 100 ml. The flasks were shaken overnight at 20°C on a rotary shaker and then either allowed to settle or were filtered the next morning. Analysis for the appropriate compound in the solution phase were made by using a Perkin-Elmer 320 spectrophotometer utilizing an appropriate absorption band in the ultraviolet region (Table 2). X-ray powder diffraction data were obtained utilizing a Philips diffraction unit with a copper target. Samples were oriented on glass microscope slides.

D). Results

Figures 1-3 display the adsorption isotherms of phenol, 3-chlorophenol, 3,5-dichlorophenol, and 3,4,5-trichlorophenol from water onto $HDTMA^+$-, $HDPY^+$-, and $TMPA^+$-smectite. The isotherms in Figures 1 and 2 for $HDTMA^+$- and $HDPY^+$-smectite exhibit marked differences for the various phenols. As the number of chlorines on the phenol structure was increased, the greater was the adsorption on these two hydrophobic matrices. Phenol, the most hydrophilic of these molecules, was not adsorbed at all by either matrix. A good index of the hydrophilic properties of these molecules should be their solubilities in water which appear in Table 2. An inverse relationship is demonstrated between that property and the adsorption on the two hydrophobic surfaces, thus suggesting that as hydrophilic properties of molecules

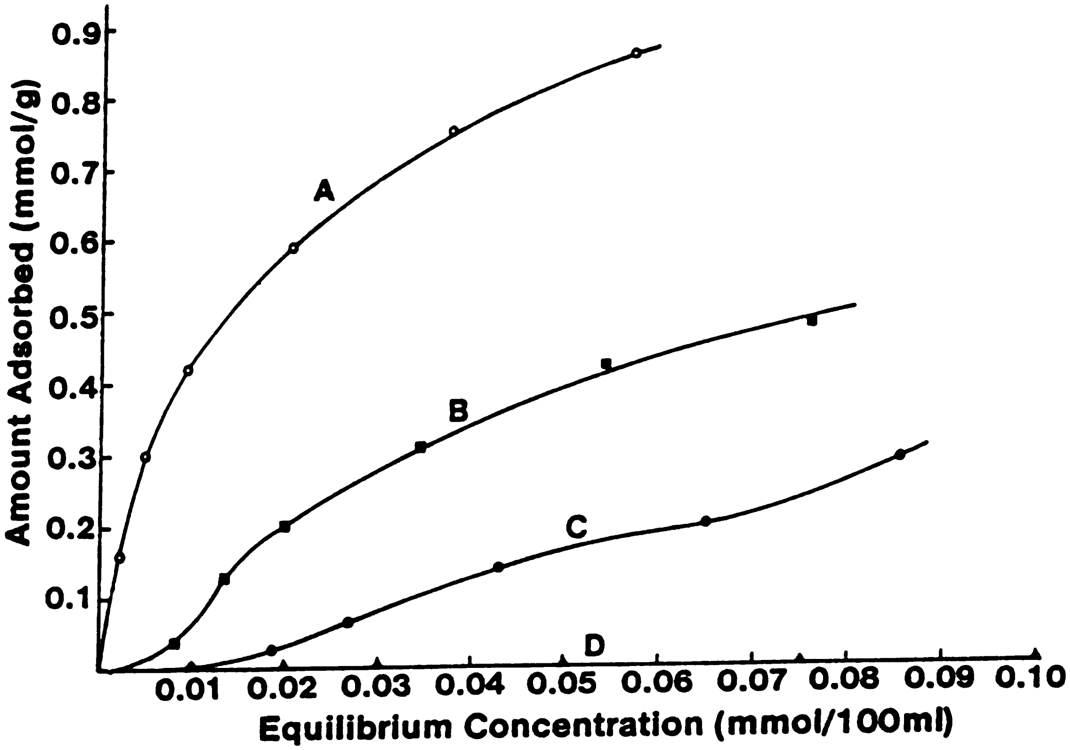

Figure 1. Adsorption isotherms (20° C) for phenols from water on HDTMA$^+$-smectite. (A): 3,4,5-trichlorophenol; (B):3,5-dichlorophenol; (C): 3-chlorophenol; (D): phenol.

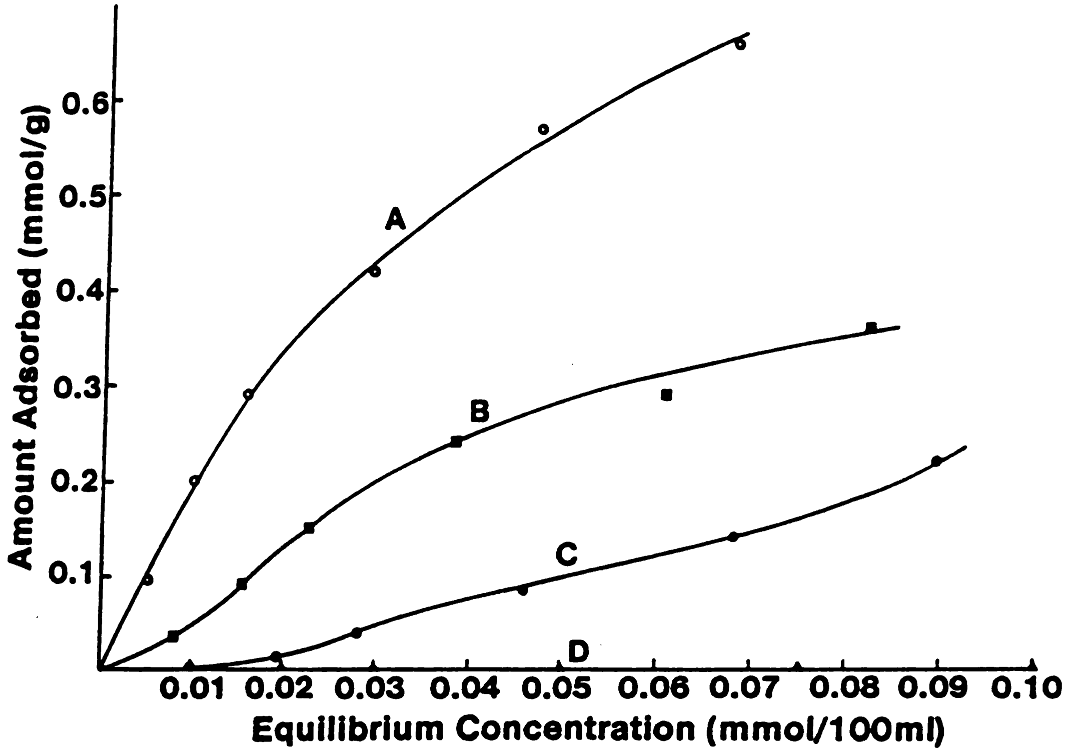

Figure 2. Adsorption isotherms (20°C) for phenols from water on HDPY$^+$-smectite. (A): 3,4,5-trichlorophenol; (B): 3,5-dichlorophenol; (C): 3-chlorophenol; (D): phenol.

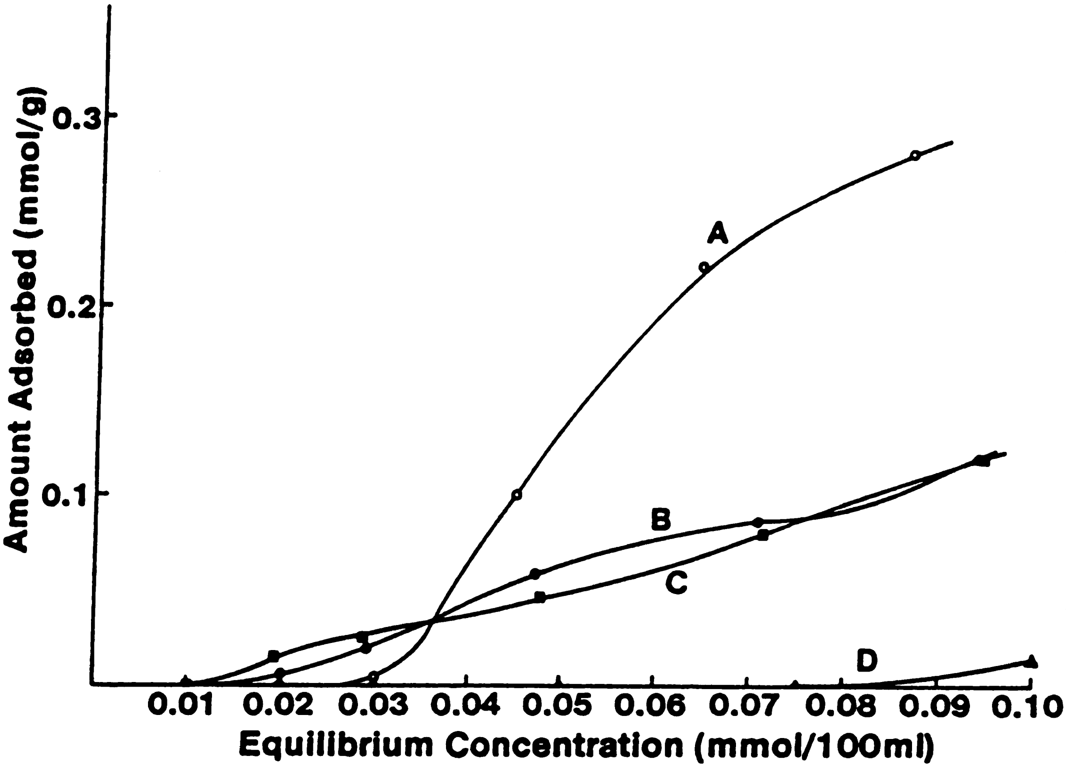

Figure 3. Adsorption isotherms (20° C) for phenols from water on TMPA$^+$-smectite. (A): phenol; (B): 3-chlorophenol; (C): 3,4,5-trichlorophenol; (D): 3,5-dichlorophenol.

decrease (or hydrophobic properties increase), adsorption increases via hydrophobic interaction. The monochlorophenol gave a type V isotherm (classification of Gregg and Sing, 1982) which was characterized by an initial convexity followed by a slight plateau and then the beginning of a final upsweep. The dichlorophenol isotherms also exhibited type V characteristics, but lacked the final upsweep. Such isotherms are characteristic of weak adsorbate-adsorbent interactions, causing adsorption at low concentrations to be small. Once a molecule is adsorbed, however, adsorbate-adsorbent forces promote the adsorption of more molecules in a cooperative fashion (Gregg and Sing, 1982). The trichlorophenol isotherms exhibited classical type I characteristics and, as such, obeyed the Langmuir equation. Here, adsorbate-adsorbent interaction was relatively strong, probably due to hydrophobic interaction. Calculation of the maximum adsorption capacity from the Langmuir plots gave 1.05 and 1.16 mmol/g for $HDTMA^+$- and $HDPY^+$-smectite, respectively. These high levels of adsorption indicate that the trichlorophenol must have penetrated into interlayer surfaces. This penetration was confirmed by X-ray powder diffraction which showed a 001 spacing at about 30 Å for $HDTMA^+$-smectite after it adsorbed large quantities of the trichlorophenol from water. The $HDTMA^+$-smectite ordinarily has a 001 spacing of 18 Å. These data indicate that as chlorines were added to the phenol structure, adsorbate-adsorbent interaction with $HDTMA^+$- and $HDPY^+$-smectite increased.

The adsorption of the phenols from water onto TMPA$^+$-smectite was quite different (Figure 3). More phenol was adsorbed than any of the chlorinated analog. The phenol isotherm, even so, was a typical type V isotherm which indicates weak adsorbate-adsorbent interaction.

The type of solvent has a profound effect on the nature of the adsorption isotherms (see Figures 4-6 in which isotherms in water and n-hexane are compared). Figure 4 shows the adsorption of 3,4,5-trichlorophenol and phenol on HDTMA$^+$-smectite from water and hexane. Whereas the former was strongly adsorbed from water, phenol was not adsorbed at all. Yet, if n-hexane was the solvent the two species were adsorbed to similar degrees. These data demonstrate the relative importance of both adsorbate-solvent and adsorbate-surface interactions on the partitioning of adsorbate molecules between solvent and surface. The adsorption of these phenols from hexane may also be affected by swelling of some of these clay-organic complexes (Theng, 1974) in hexane, thus providing interlayer surface. Figure 5 shows similar data for the adsorption of the two molecules on TMPA$^+$-smectite. These data indicate a strong preference for phenol over the chlorinated species in both solvents, adsorption being greater from hexane. Figure 6 shows adsorption isotherms of the two phenols on TMA$^+$-smectite from the two solvents. Here, neither phenol was adsorbed to any greater extent from water, but large quantities were

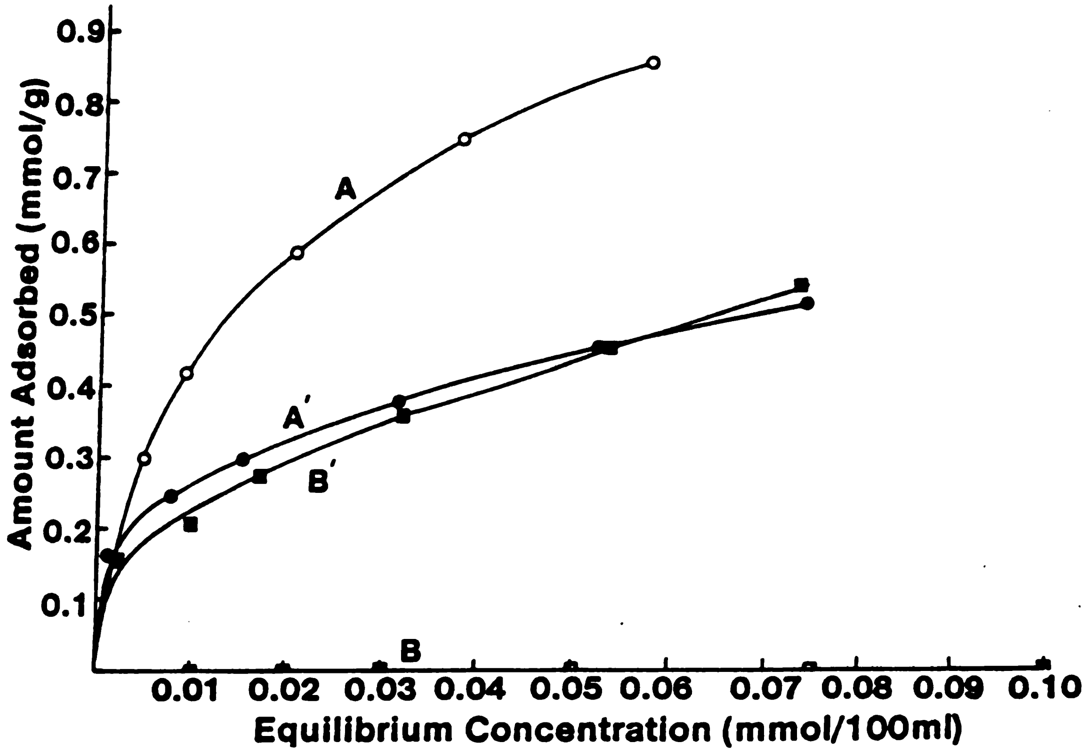

Figure 4. Adsorption isotherms (20° C) for phenol and 3,4,5-trichlorophenol from water and hexane on HDTMA$^+$-smectite. (A): 3,4,5-trchlorophenol from water; (A'): 3,4,5-trichlorophenol from hexane; (B): phenol from water; (B'): phenol from hexane.

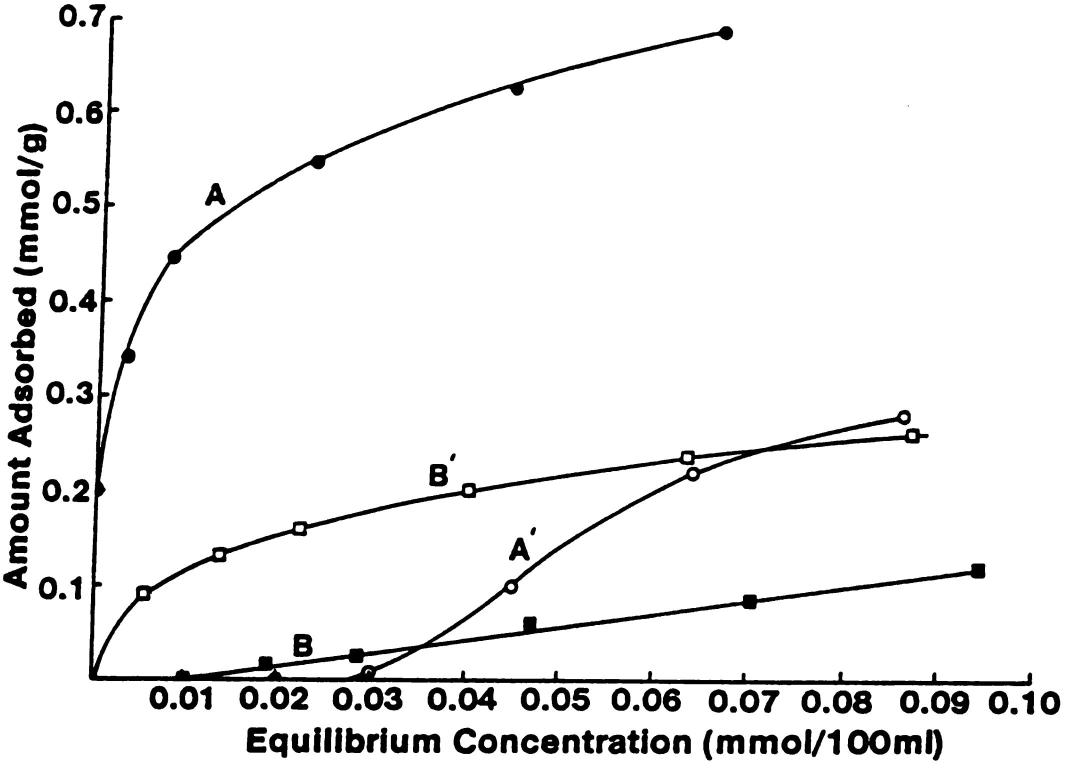

Figure 5. Adsorption isotherms (20°C) for phenol and 3,4,5-trichlorophenol from water and hexane on TMPA$^+$-smectite. (A): phenol from hexane; (A'): phenol from water; (B): 3,4,5-trichlorophenol from water; (B'): 3,4,5-trichlorophenol from hexane.

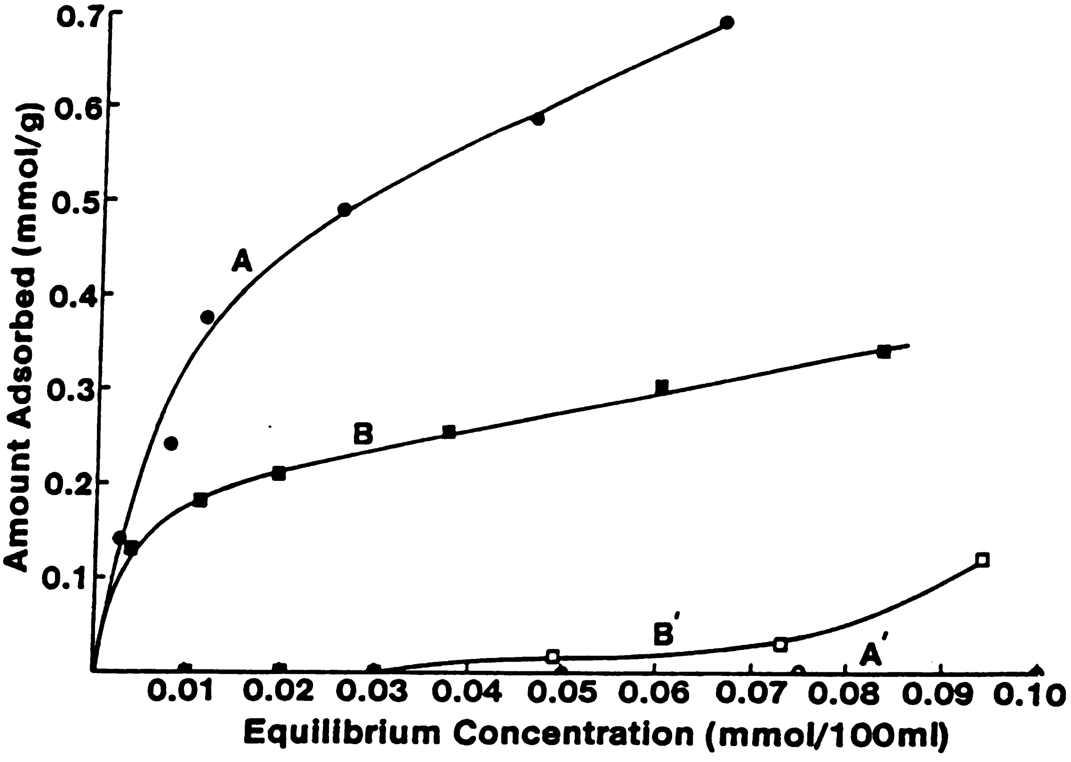

Figure 6. Adsorption isotherms (20° C) for phenol and 3,4,5-trichlorophenol from water and hexane on TMA$^+$-smectite. (A): phenol from hexane; (A'): phenol from water; (B): 3,4,5-trichlorophenol from hexane; (B'): 3,4,5-trichlorphenol from water.

adsorbed from n-hexane, the amount of phenol being about twice as much as that of the chlorinated species.

Even isomers of the same compound may show different adsorption isotherm characteristics, as demonstrated in Figure 7, which shows isotherms of 3,4,5-trichlorophenol and 2,4,6-trichlorophenol on $HDTMA^+$-smectite in water. Here, adsorption of the former compound yields a classic type I isotherm, whereas adsorption of the latter yields a type V isotherm. This comparison suggests that the 3,4,5-trichlorophenol interaction with the clay-organic complex is stronger than that of its 2,4,6-isomer. Different solvent-adsorbate adsorptions may also have produced these differences.

E). Discussion

The nature of the organic cation on the exchange complex of smectite and the nature of the solvent are of prime importance in determing the adsorption of phenol and its chloro-analogs. The different kinds of organic cations used in this study provided a variety of subtle properties which were expressed in a wide range of surface effects. These results agree with the earlier work of Garwood *et al.* (1983) and Boyd and Mortland (1985a, 1985b, 1986) wherein the activities of adsorbed enzymes were shown to vary greatly depending on the microenvironments provided by different

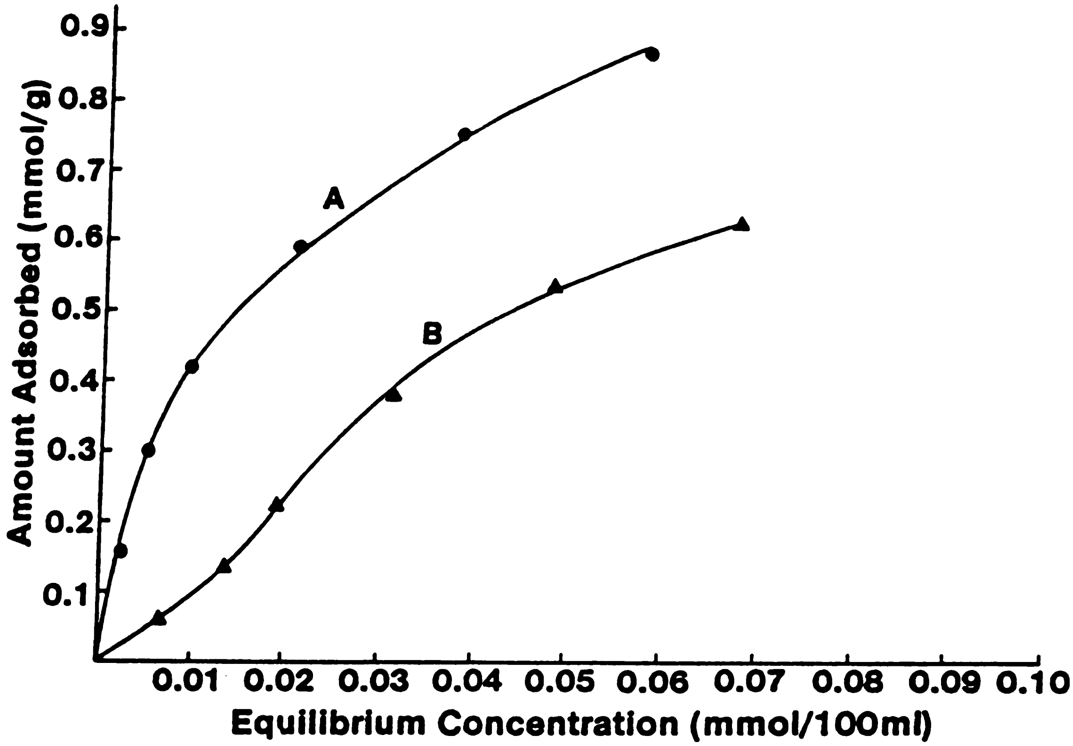

Figure 7. Adsorption isotherms (20° C) for trichlorophenol isomers from water on HDTMA$^+$-smectite. (A): 3,4,5-trichlorophenol; (B): 2,4,6-trichlorophenol.

clay-organic complexes.

In the present work the adsorption observed for a particular molecule resulted from the product of two controlling factors:

1). adsorbate-adsorbent interactions, and

2). adsorbate-solvent interactions.

Thus, in water solvent, phenol interacted strongly with water (hydrogen bonding) and was not attracted sufficiently to the hydrophobic surfaces of $HDTMA^+$- and $HDPY^+$-smectite to create a significant adsorption (Figures 1 and 2). With hexane as the solvent, phenol had a much less energetic interaction with this solvent, and the adsorbate-adsorbent interactions were strong enough to result in considerable adsorption (Figure 4). The observed adsorption was the resultant of the relative energies of the above two competing reactions. Similar arguments can be made for all the molecules used in this study. Significantly, the addition of each chlorine to the phenol structure reduced its energy of interaction with water (decreased water solubility, as in Table 2), thereby allowing a more significant hydrophobic interaction with such surfaces as $HDTMA^+$- and $HDPY^+$-smectite. The behavior of such clay-organic surfaces as $TMPA^+$- and TMA^+-smectite was less straightforward. For TMA^+- and probably $TMPA^+$-clay, some surface oxygens of the silicate structure were exposed, inasmuch as these smaller organic cations could not cover all the silicate surface. McBride and Mortland (1975) found that TMA$^+$-smectite had a surface area of 210 m^2/g (as measured by N_2 adsorption), which suggests considerable surface not covered by the TMA$^+$ cation. Consequently, such a surface may have had both hydrophobic properties bestowed on it by the organic species and more hydrophilic properties from the areas of exposed silicate oxygens.

A comparison of the adsorption behavior of TMA$^+$- and HDTMA$^+$-smectites illustrates the unique properties bestowed on the surface by the nature of the organic cation. The adsorption of 3,4,5-trichlorophenol by TMA$^+$-smectite was greater from hexane than from water (Figure 6), directly opposite to results obtained for HDTMA$^+$-smectite (Figure 4). For TMA$^+$-smectite, the absence of water on the surface apparently increased the hydrophobicity and resulted in greater adsorbate-adsorbent interaction. Thus, more adsorption was noted from hexane. For HDTMA$^+$-smectite, the hydrophobicity of this surface was not significantly altered by solvent effects, and the decrease in 3,4,5-trichlorophenol adsorption from hexane was due simply to increased adsorbate-solvent interaction. Another factor that could be important in these results is a sieving effect. Particularly where interlayer adsorption may be taking place, the size and shape of the organic cation may exclude adsorbate molecules.

The results obtained here suggest that clay minerals may be treated with specific organic cations that have specific adsorption properties for particular molecules, *e.g.*, phenols. Such adsorption specificity is applicable in the removal of a particular target molecule from a certain solvent, or in the chromatographic separation of closely related molecules. The sensitivity of these tailor-made clay-organic complexes for particular purposes is thus of interest for future development. These synthetic organo-clay complexes also appear to be useful in fundamental studies on the interactions of organic molecules with specific kinds of surfaces which can be varied with respect to hydrophobicity, aromaticity, and polarity.

Chapter III

PENTACHLOROPHENOL SORPTION BY ORGANO-CLAYS

A). Abstract

Several clay-organic complexes were prepared by placing certain organic cations on the exchange sites of smectite clays, and studied as sorbents for pentachlorophenol (PCP). The organic cations used in this study ranged from very hydrophobic in nature (*e.g.*, dioctadecyldimethyl, $DODMA^+$, and hexadecyltrimethyl, $HDTMA^+$, ammonium) to those with minimal hydrophobic properties like tetramethyl ammonium (TMA^+). In general, the more hydrophobic the cation on the smectite the greater the uptake of PCP from water. For the very hydrophobic clays ($DODMA^+$- and $HDTMA^+$-smectite) the uptake of PCP was via nonpolar interactions between the alkyl (*e.g.*, $-C_{18}$) groups on the organic cation and PCP. In a mechanistic sense, this appeared to be similar to a partitioning process between water and the organic phase of the clay-organic complex. The organic phases of $DODMA^+$-smectite were about 10X more effective than the organic matter of natural sediments for removing PCP from water. For those organo-clays containing small organic cations (*e.g.*, TMA^+), the organic phase consisted of separate small

organic moieties like the methyl group. This phase did not act as an effective partitioning medium despite significant carbon contents, and very little PCP uptake was observed. Results from this study suggest the possibility of treating soils and subsurface materials with large hydrophobic organic cations to enhance the sorptive properties of these natural materials.

B). Introduction

The nature of clay-organic interactions have been extensively reviewed in the literature (Mortland, 1970; Theng, 1974; Solomon and Hawthorne, 1983; Mortland, 1986). Mechanisms of interaction include ion exchange, protonation, coordination/ion dipole, hydrogen bonding, van der Waal's forces, and entropy effects. When a clay mineral has metal cations occupying cation exchange sites, its surface is hydrophilic because of the water molecucles in the hydration shell solvating the cations. Such a surface is not a good sorbent for removing hydrophobic, poorly water soluble organic molecucles from water. However, when certain organic cations are place on the exchange complex by cation exchange, the surface becomes hydrophobic and in turn, organophilic. Organic cations possessing long chain alkyl groups are particularly able to impart the hydrophobic quality to the mineral surface (Pashley *et al.*, 1985). Such clay-organic complexes are able to sorb molecules wich themselves are hydrophobic by what has been called hydrophobic bonding (McBride *et al.*, 1977; Garwood *et al.*, 1983; Wolfe *et al.*, and 1985; Boyd and Mortland, 1985, 1986). This process is essentially a nonpolar interaction between the organic phase of the clay-organic complex and the hydrophobic organic molecule. A partitioning process has been used to describe the sorption of nonionic organic compounds by soil organic matter (Chiou *et al.*, 1979, 1983). This mechanism appears to account for many of the fundamental characteristics of nonpolar interactions which have often been referred to as hydrophobic bonding.

Chapter II has shown that phenol and its several chlorinated congeners were sorbed by $HDTMA^+$-smectite and $HDPY^+$-smectite in proportion to the number of chlorine atoms on the phenol structure. Thus, phenol itself was not sorbed significantly by these complexes, but trichlorophenol was strongly sorbed. In other words, as hydrophobicity of the molecule increased sorption increased. The work reported here is an extension of that wherein PCP, a widespread pollutant in water, was studied with respect to its sorption on a variety of synthetic smectite-organic complexes. The hydrophobic nature of these complexes was varied by placing different organic cations on the clay. Wolfe *et al.* (1986) prepared several clay-organic complexes and obtained adsorption isotherms for several organic pollutants on these matrices. The organic cations they used were primary amines whose cationic nature and, therefore, their adsorption as cations on the clay, was very much a function of pH. For that reason we have used quaternary ammonium cations whose cationic nature is not affected by pH and thus will remain on the cation exchange sites of the mineral by Coulombic forces, regardless of pH. These clay-organic complexes may be useful sorbents for removing organic toxicants from contaminated waters over a wide range of pH.

C). Methods

The clay-organic complexes used were synthesized in the same way as described in Chapter II. A summary of the names, abbreviations, structural formulae, and total carbon contents of the organic cations used appears in Table 1. The total carbon contents were determined by Huffman Laboratories (Golden, Colorado).

Sorption isotherms were obtained by using the batch equilibration method. 50 mg of clay or carbon was weighed into 125-ml Erlenmeyer flasks. 100 ml of a saturated solution of PCP (7.5×10^{-5} mol/l) was added to the flask and shaken over night at 20° C on a rotary shaker. Other concentrations of PCP were also used in the amounts of 80, 60, 40, 20, and 10 percent of the saturated solution, all made up to 100 ml total volume with distilled water. At the end of the equilibration period, the solid and liquid phases were separated by filtration. PCP concentrations in the aqueous phase were measured immediately by UV absorption. In a competition study, 0.1, 0.2, and 0.5 3,4,5-trichlorophenol per gram of sorbent were added to the above systems, then sorption isotherms of PCP obtained as above. The isotherms of PCP on HDTMA$^+$-smectite at pH's 5.5 and 10.0 were obtained by using the ambient pH for the former and adding drops of NaOH for the latter. Analyses of the equilibrium solutions for PCP were obtained using a Perkin-Elmer 320 spectrophotometer set at 318 nm.

^{14}C PCP (10 mci/mmol), uniformly ring labelled, was purchased from Pathfinder Laboratories, St. Louis, MO and had a radiochemical purity of >98%. ^{14}C PCP was dissolved in methanol and portions of this solution (10 to 100 µl) were added to flasks containing the clay or carbon (50 mg) and water (100 ml). The equilibration was conducted as described above. PCP concentrations in the aqueous phase were determined by passing 1 ml in 10 ml scintillation cocktail using liquid scintillating counting.

D). Results

Figure 8 shows sorption isotherms (20° C) of PCP onto several modified smectite clays and carbon. Smectites with DODMA$^+$ and HDTMA$^+$ as the exchange cations show no measurable PCP in solution over the first three increments of PCP

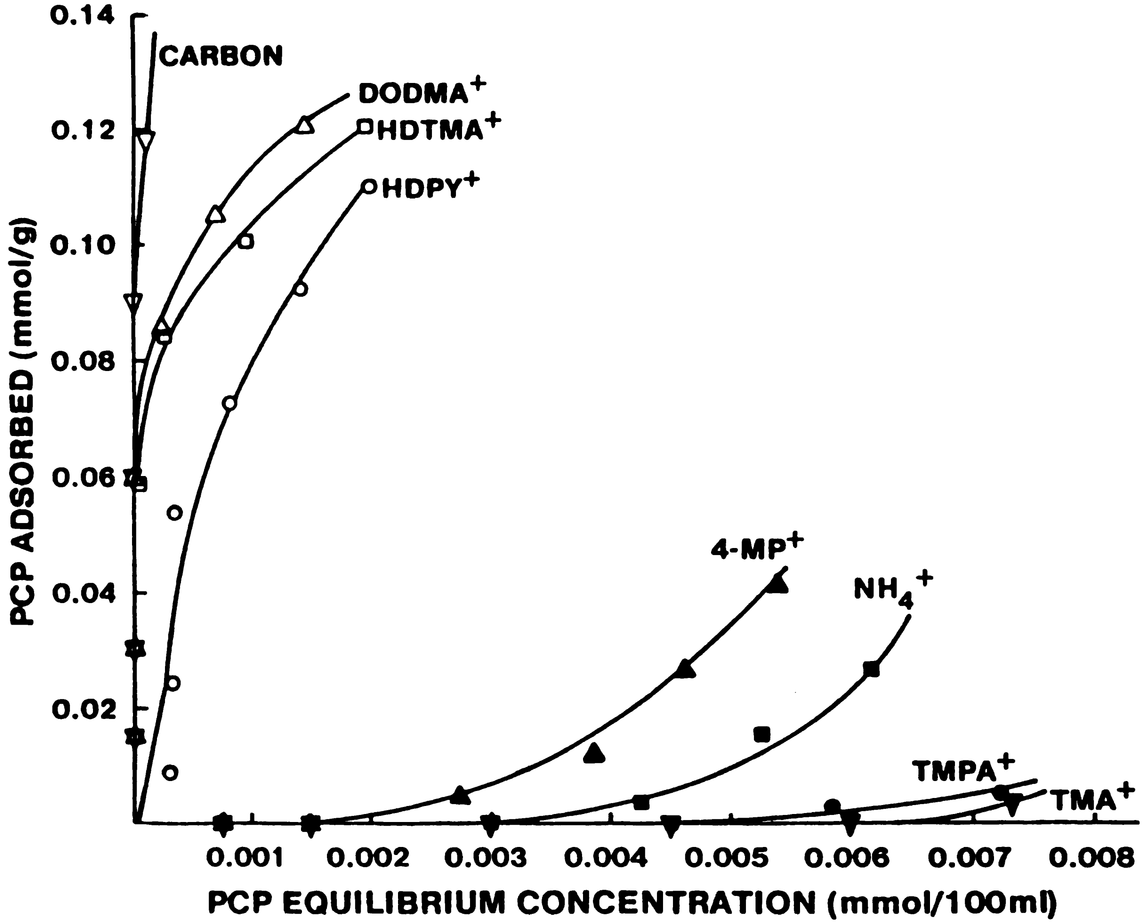

Figure 8. Sorption isotherms (20° C) PCP on organo-smectites and carbon from water.

concentration. Sorption by HDPY$^+$-smectite was nearly as effective. In contrast smectite saturated with TMA$^+$ or TMPA$^+$ cations shows very weak sorption characteristics for PCP. The 4-MP$^+$ and NH$_4^+$ clad smectites show somewhat stronger affinities for PCP but still are type V isotherms (Gregg and Sing, 1982) which are typical for weak adsorbent-adsorbate interactions. The weakness of the adsorbent-adsorbate interactions causes the adsorption at low concentration to be small, but once a molecule becomes adsorbed, it promotes the adsorption of more molecules in a cooperative fashion.

A closer examination of sorption on carbon, DODMA$^+$- and HDTMA$^+$-smectite at low PCP concentration was made utilizing ^{14}C-labelled PCP. Figure 9 presents these sorption isotherms which show carbon to be the strongest sorbent followed closely by DODMA$^+$- and then HDTMA$^+$-smectite. The adsorption of PCP by carbon reported here is nearly identical to that reported earlier (USEPA, 1980). The isotherms over this concentration range were highly linear even though different sorptive mechanisms may be operative. Clearly, uptake of PCP by carbon is via adsorption, whereas for DODMA$^+$- and HDTMA$^+$-smectite a partitioning-like process may exist (Chiou *et al.*, 1979, 1983). Partition coefficients can be calculated from the isotherms in Figure 9 to give a relative comparison of the degree of uptake. The partition coefficient K was calculated by dividing the amount of PCP sorbed (mmol/g) by the PCP equilibrium

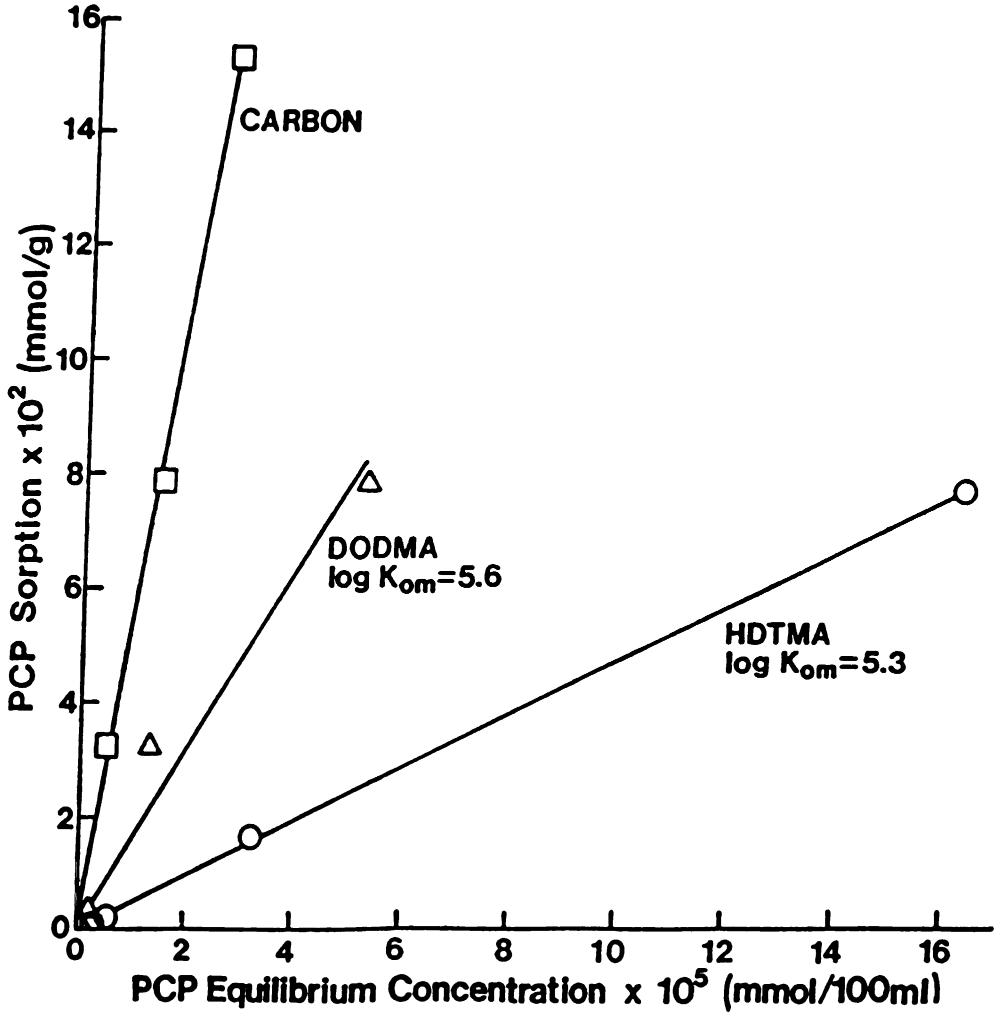

Figure 9. Sorption isotherms (20°C) PCP on organo-smectites and carbon from water utilizing ^{14}C labelled PCP.

concentration (mmol/ml). Since the isotherms are linear the values of K is constant over the concentration range used in Figure 9. The log K values for DODMA$^+$- and HDTMA$^+$-smectite were 5.2 and 4.7, respectively. When normalized on the basis of the organic matter (OM) content (Table 1) (Kom = 100K / OM%), log Kom values were 5.6 and 5.3.

Figure 10 shows the sorption isotherms of PCP on HDTMA$^+$-smectite in the presence of 0.0, 0.1, 0.2, and 0.5 mmol of 3,4,5-trichlorophenol per gram of clay. Results of these studies suggest very minimal competitive effects on PCP sorption by HDTMA$^+$-smectite. Earlier work has shown that 3,4,5-trichlorophenol was relatively strongly sorbed by HDTMA$^+$-smectite, the isotherms being type I (Langmuir) in shape. However, its presence at these concentration levels did not greatly alter the sorption of PCP.

Figure 11 compares sorption isotherms of PCP on HDTMA$^+$-smectite at pH's 5.5 and 10.0. These data show a lack of pH effect on the isotherms. Even though at pH 10.0, the phenol would be completely ionic (pKa=4.7), it was still sorbed strongly by the smectite-organic complex. This supports the view that most of the sorption is non-Coulombic and that hydrophobic or nonpolar interactions between alkyl groups on the smectite with PCP is likely the chief mode of interaction. Schellenberg *et al.* (1984) observed a significant uptake of the PCP ion by the organic matter of natural sediments.

It was of interest to find out if sorbed chlorophenol

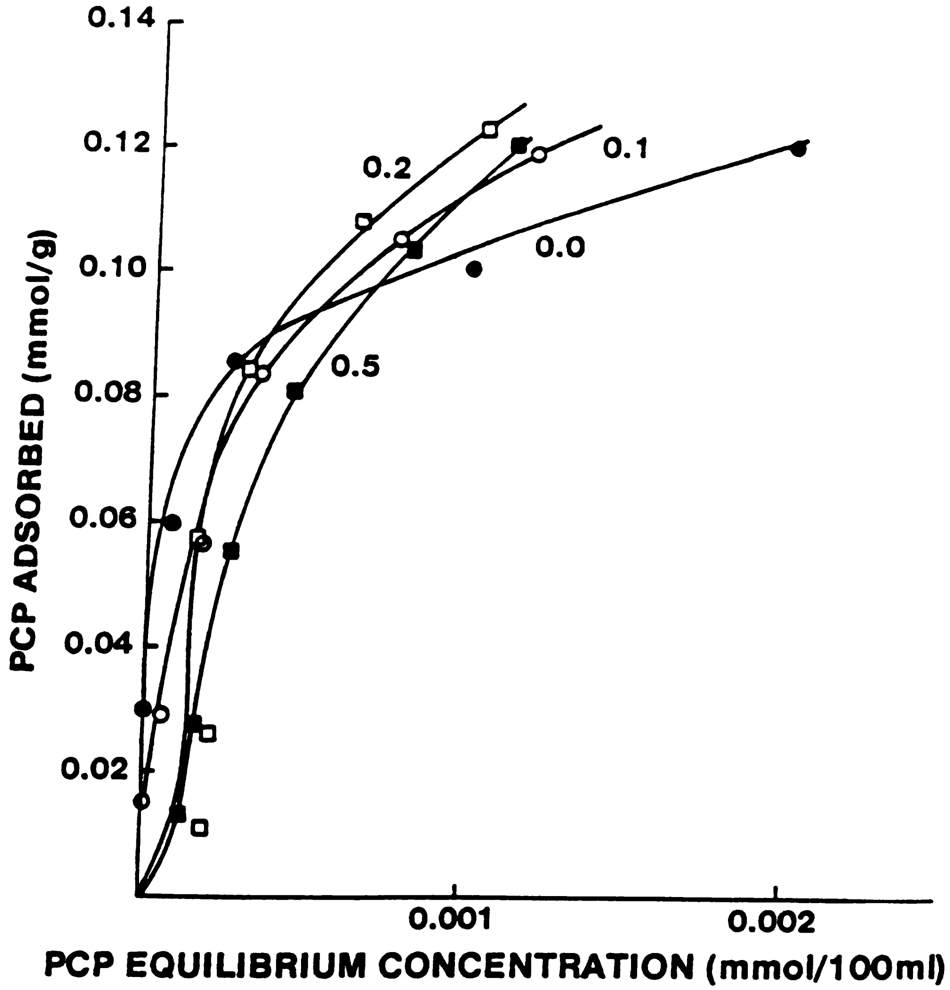

Figure 10. Sorption isotherms (20° C) for PCP on HDTMA$^+$-smectite from water in presence of 3,4,5-trichlorophenol (0.0, 0.1, 0.2, and 0.5 mmol/g of clay).

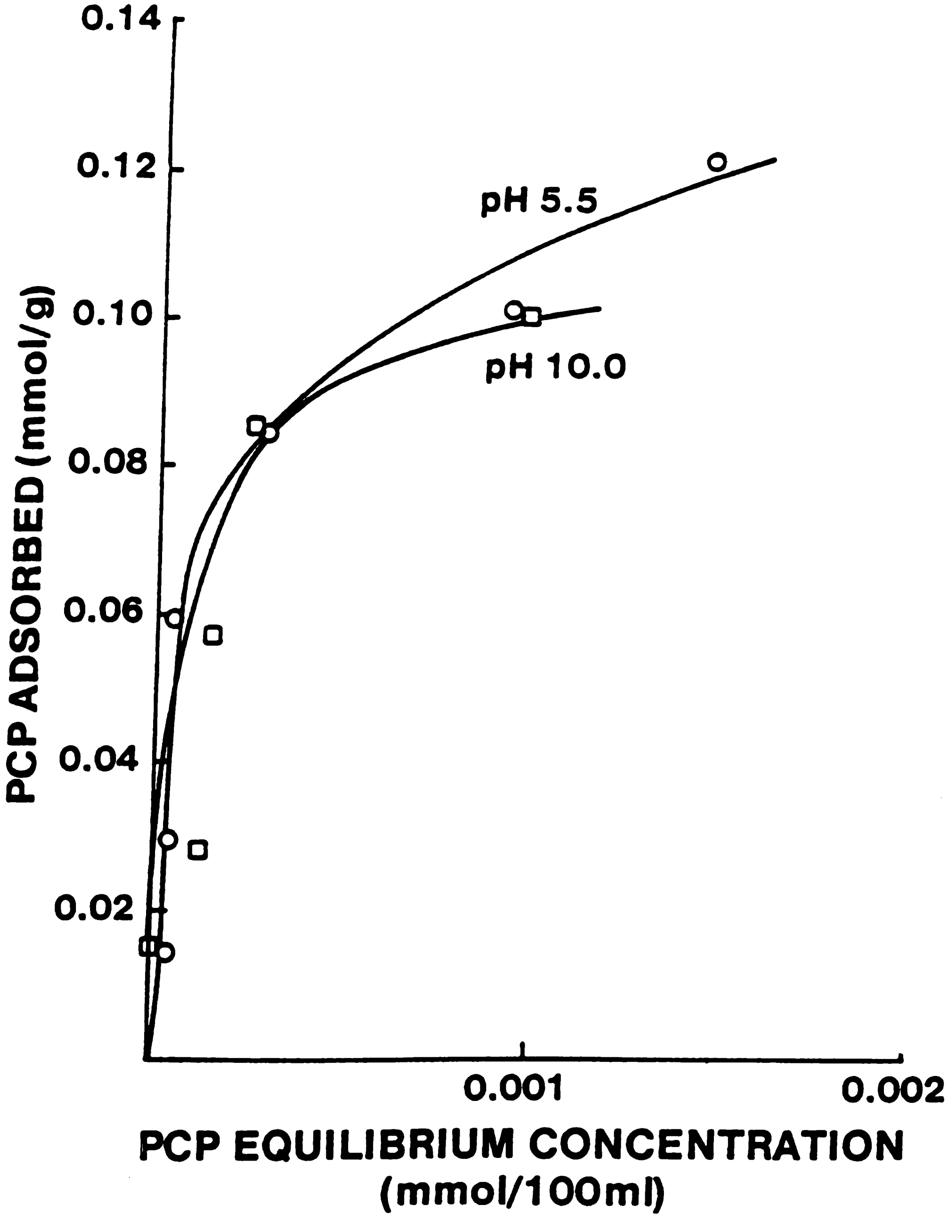

Figure 11. Sorption isotherms (20° C) for PCP on HDTMA$^+$-smectite from water at pH 5.5 and 10.0.

could be removed from the clay-organic complexes. In order to do this 3,4,5-trichlorophenol and PCP were sorbed from water onto HDTMA$^+$-smectite, DODMA$^+$-smectite and carbon. They were then extracted with three different solvents using soxhlet extractor. These data (Table 3) indicate several points. Firstly, at the levels of trichlorophenol (0.2 mmol/200 ml) and PCP (0.015 mmol/ 200 ml) used, almost all was sorbed on the three matrices from water when there was 0.5 g of sorbent present. Secondly, trichlorophenol was more easily extracted than was PCP. Thirdly, the efficiency of extraction varied with solvent, methylene chloride being most efficient, n-hexane least, and carbon tetrachloride intermediate. Finally, it seems for the most part that it is easier to extract the chlorophenols from the two clay-organic complexes used, than from the carbon.

E). Discussions

The data presented here demonstrate the wide diversity of clay-organic complexes for the sorption of PCP. Depending upon the nature of the organic cation placed on the exchange complex of the clay, there can be very little if any sorption of PCP as in the case of TMA$^+$-smectite, or extremely strong sorption as in the case of DODMA$^+$-smectite. The general observation would be that the more hydrophobic the group(s) associated with the quaternary ammonium entity,

Table 3. Data of extraction (24 hrs.) of two phenols from HDTMA$^+$- and DODMA$^+$-smectites.

Sorbent	Amt. added to water (mmol/200 ml)	Amt. sorbed by complex (mmol/0.5g)	% extracted by		
			C_6H_6	CCl_4	CH_2Cl_2
3,4,5-Trichlorophenol					
HDTMA$^+$-smectite	0.200	0.184	42.0	43.0	100
DODMA$^+$-smectite	0.200	0.199	15.2	70.0	100
Carbon	0.200	0.200	14.0	35.0	44.0
Pentachlorophenol					
HDTMA$^+$-smectite	0.015	0.015	10.7	20.5	71.0
DODMA$^+$-smectite	0.015	0.015	2.4	32.0	60.0
Carbon	0.015	0.015	3.6	10.0	6.0

the greater will be the sorption of PCP. The sorbate (in this case PCP) is also relatively hydrophobic, having a water solubility of 14 ppm (20°C).

The sorption process for the very hydrophobic ($DODMA^+$- and $HDTMA^+$-) clays can be best represented as a partitioning of PCP between water and the hydrophobic environment provided by the alkyl groups, or as a nonpolar interaction between the alkyl groups and PCP. For these complexes the mineral surface is essentially completely obscured by the large organic cations. Thus, their sorption behavior is characteristic of an organic sorbent like soil organic matter. The log Kom values calculated for $DODMA^+$- and $HDTMA^+$-smectite compared favorable with the log Kow value (5.24) for PCP and were significantly higher than the log Kom value (4.2) reported for natural sediments (Schellenberg, 1984). The similarity in Kom and Kow values is expected for a partitioning-like interaction between PCP and the highly organophilic $DODMA^+$- and $HDTMA^+$-complexes. Another indication of a partitioning-type mechanism is the lack of a competitive effect on PCP uptake when 3,4,5-trichlorophenol was present. Even at levels (0.5 mmol/g of 3,4,5-trichlorophenol) that exceed the maximum uptake of PCP (Figure 10) a significant competitive effect was not observed. For an adsorptive (surface) process, a strong competitive effect would be expected because both penta- and trichlorophenol would be competing for the same binding sites. The lack of a competitive effect may be an attractive feature for a system where it is necessary to remove a mixture of compounds from water.

The organo-smectites containing smaller organic cations (TMA^+, $TMPA^+$, and $4\text{-}MP^+$) or an inorganic cation (NH_4^+) behaved as conventional mineral sorbents. The organic "phase" of these complexes is made up of separate small organic moieties like the $-CH_3$ or $-C_6H_5$ group. This phase does not act as an effective partitioning medium despite significant carbon contents. The mineral surface in these complexes is exposed and occupied largely by water. PCP is not capable of displacing the strongly held water on the mineral surface. Thus, no mechanism exists for the significant uptake of PCP by these complexes.

When the solvent was changed from water to a more organophilic type, most of the PCP could be removed via soxhlet extraction (*i.e.*, CH_2Cl_2 extraction, Table 3). The $DODMA^+$- and $HDTMA^+$-smectite released PCP much more easily than carbon in the extraction process. When using methylene chloride as a solvent, the recovery of sorbed PCP was over 10X higher from $DODMA^+$- and $HDTMA^+$-smectite than from carbon. This property would be important in any system where it is desirable for a sorbent to be recycled.

The high partition coefficients observed for organo-clay such as $HDTMA^+$- and $DODMA^+$-smectite make these materials attractive as sorbents for removing organic toxicants from water. It is very likely that this simple ion exchange reaction, where hydrophobic organic cations like $HDTMA^+$ are exchanged for naturally occupying cations like Ca^{2+} or Na^{+}, would readily occur with natural soils or related geologic materials like glacial tills. A practical application of this simple reaction may be the *in situ* formation of an organo-clay sorptive phase for the immobilization of organic toxicants present in leachate water. Perhaps one of the most useful applications would be in the construction of clay landfill liners, which are formed using subsurface materials like glacial tills that have significant clay contents. By using a portion of the clay liner material during its installation, and exposing this material to hydrophobic organic cations, a sorptive phase could be created that would remove organic contaminants present in the landfill leachate. This would seem to be a simple, economical, and effective way for enhancing the containment of organic toxicants in waste disposal reservoirs.

Chapter IV

CONCLUSIONS

1). In natural environments, smectites usually have a hydrophilic surface and do not adsorb hydrophobic organic compounds, like chlorophenols, to a significant amount. However, smectites can be easily treated with some organic cations, which replace the hydrated metal cations and occupy the exchange sites on the mineral surface. This treatment would change the surface from hydrophilic to hydrophobic.

2). The formation of hydrophobic bonding is the main mechanism accounting for the sorption of hydrophobic chlorophenols (*e.g.* 3,4,5-trichlorophenol and PCP) on hydrophobic smectite-organic complexes (*e.g.* $DODMA^+$-, $HDTMA^+$-, and $HDPY^+$-smectites). The strength of the hydrophobic bonding increases while the hydrophobicities of organic compounds and/or complexes increase. The partition model may be appropriate for describing the sorption process for these smectite-organic complexes. It appears that with such large organic cations a continuous organic phase is formed involving the hydrophobic tails of the quaternary ammonium cations.

3). No significant pH effects are observed on the sorption of PCP on HDTMA$^+$-smectite, confirming that Coulombic force does not play an important role for the hydrophobic interactions.

4). The lack of competitive effects on PCP uptake when 3,4,5-trichlorophenol is present (which is strongly sorbed if no PCP in the system) supports a partitioning-like process and persuades us that uptake of PCP is not just a simple surface adsorption.

5). Different mechanisms, such as Coulombic attraction, hydrogen bonding, *etc.*, may exist for the adsorption of less hydrophobic organic compounds (*e.g.* phenol) on less hydrophobic or even hydrophilic smectite-organic complexes (*e.g.* TMPA$^+$-, TMA$^+$-, 4-MP$^+$-, and NH_4^+-smectites).

For these smectite-organic complexes, probably some surface oxygens of the silicate structure are exposed because the smaller organic cations without long chain alkyl groups can not cover all of the surface. For example, TMA$^+$-smectite has a surface area of 210 m^2/g (measured by N_2 adsorption), which suggests that considerable surface has not been covered by the TMA$^+$ cations (McBride and Mortland, 1975). These smectite-organic complexes behave more like conventional solid adsorbents. Their organic "phase" is made up of separate small organic moieties like $-CH_3$ group. This phase does not act as an effective partitioning medium.

Such a surface may possesses both hydrophobic properties from the organic cations and more hydrophilic properties from the exposed silicate oxygens. Thus, relatively polar sorbates like phenol could be adsorbed more and the sorbent-sorbate interaction might partially be dipole-dipole and dipole-induced-dipole interactions (Atkins, 1982). Non-polar sorbates like benzene may interact directly with the small organic exchange cations. Steric effects may also play an important role as these sorbates appear to interact with specific sites on the smectite-organic complexes.

6). Solvent effects represent that the uptake of a particular compound results from the contradiction of two controlling factors, that is, the sorbate-sorbent interactions and the sorbate-solvent interactions.

With water as the solvent, phenol interacts strongly with water molecule by hydrogen bonding, but very weakly with the hydrophobic surfaces of $HDTMA^+$- and $HDPY^+$-smectites. Thus almost all of the phenol molecules remain in the solution, just few adsorbed onto the hydrophobic smectite-organic complexes. When n-hexane, a non-polar alkane, is used as the solvent, the solvent-phenol interactions are largely reduced and the adsorbent-phenol interactions are relatively strengthened (except TMA^+-smectite as the adsorbent). For 3,4,5-trichlorophenol, the results are opposite to those for phenol, that is, more is adsorbed from water than from n-hexane (again except TMA^+-smectite as the adsorbent).

The exception for TMA^+-smectite is mainly due to the absence of water on the surface increasing the hydrophilicity and enhancing the adsorbent-adsorbate interactions.

7). Most of the PCP sorbed on a smectite-organic complex can be removed (up to 60.0% from $DODMA^+$-smectite and 71.0% from $HDTMA^+$-smectite) into a organophilic solvent (*e.g.* CH_2Cl_2,) by an extraction process.

8). Our work here may suggest two main applications.

a). Clay minerals can be treated with specific organic cations that have specific adsorption properties for particular molecules. Such adsorption specificity is applicable in the removal of a particular target molecule from a solvent or in the chromatographic seraration of closely related molecules, such as 3,4,5-trichlorophenol and 2,4,6-trichlorophenol.

b). The high partitioning abilities of some smectite-organic complexes, such as $DODMA^+$- and $HDTMA^+$-smectites, make these materials attractive as adsorbents for eliminating hydrophobic organic toxicants from water. It may be possible to form such a organo-clay complex *in situ* as for an example during the construction of clay landfill liners. Practically, this seems to be a simple, effective and economical technique to enhance the effectiveness of waste disposal reservoirs.

REFERENCES

Arsenault,R.D. 1976. *Proc. Amer. Wood Preservers Assoc* 72: 122.

Atkins,P.W. 1982. *Physical Chemistry.* W.H. Freeman and Co. San Francisco, CA: 782-788.

Boyd,S.A. and M.M.Mortland. 1985. Urease activity on a clay-oganic complex. *Soil Sci. Soc. Amer. J.* 49: 619-622.

Boyd,S.A. and M.M.Mortland. 1985. Manipulating the activity of immobilized enzymes with different organic-smectite complexes. *Experientia* 41: 1564-1566.

Boyd,S.A. and M.M.Mortland. 1986. Selective effects of smectite-organic complexes on the activity of immobilized enzymes. *J. Mol. Catalysis* 34: 1-8.

Chiou,C.T., L.J.Peters and V.H.Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. *Science* 206: 831-832.

Chiou,C.T., L.J.Peters and V.H.Freed. 1981. Soil-water equilibria for nonionic organic Compounds. *Science* 213: 684.

Chiou,C.T., P.E.Porter and D.W.Schmedding. 1983. Partition equilibria of non-ionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* 17: 227-231.

Chiou,C.T. 1985. Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ. Sci. Technol.* 19: 57-62.

Chiou,C.T. and T.D.Shoup. 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. *Environ. Sci. Technol.* 19: 1196-1200.

Crosby,D.G. 1981. Environmental chemistry of pentachlorophenol. *IUPAC Report on Pesicides* 14: 1053-1055.

Dixon,J.B. and S.B.Weed. 1977. *Minerals in Soil Environments.* Soil Sci. Soc. Amer., Inc. Madison, WI: 293-324.

Environmental Protection Agency. 1978. Report of the ad hoc study group on pentachlorophenol contaminants. *EPA/SAB/78/001.* Washington, D.C.

Freier,R.K. 1978. *Aqueous Solutions Data for Inorganic and Organic Compounds.* Vol. 1. Walter de Gruyter. Berlin-New York.

Garwood,G.A., M.M.Mortland and T.J.Pinnavaia. 1983. Immobilization of glucose oxidase on montmorillonite clay: hydrophobic and ionic modes of binding. *J. Mol. Catalysis* 22: 153-163.

Gregg,S.J. and K.S.W.Sing. 1982. *Adsorption, Surface Area, and Porosity.* Academic Press. New York.

Hamaker,J.W. and J.M.Thompson. 1972. Adsorption. *Organic Chemicals in the Soil Environment. Vol. I.* Marcel Dekker, NY: 49-143

Karickhoff,S.W., D.S. Brown and T.A.Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13: 241-248.

McBride,M.B.and M.M.Mortland. 1973. Segregation and exchange properties of alkylammonium ions in a smectite and vermiculite. *Clay and Clay Min.* 21: 323-330.

McBride,M.B. and M.M.Mortland. 1975. Surface properties of mixed Cu(II)-tetraalkylammonium montmorillonites. *Clay Min.* 10: 357-368.

McBride,M.B., T.J.Pinnavaia and M.M.Mortland. 1977. Adsorption of aromatic molecules by clays in aqueous suspension. *Fate of Pollutants in the Air and Water Environments. Vol.8, Pt.1.* Wiley. New York: 145-154.

Mortland,M.M. 1970. Clay-organic complexes and interactions. *Adv. Agron.* 22: 75-117.

Mortland,M.M. 1986. Mechanisms of adsorption of nonhumic organic species by clays. *Interaction of Soil Minerals with Natural Organics and Microbes.* Soil Sci.Soc. Amer.. Madison, WI: 59-76.

Pashley,R.M., P.M.McGuiggan and B.W.Ninham. 1985. Attractiv forces between uncharged hydrophobic surfaces: direct measurements in aqueous solution. *Science* 229: 1088-1089.

Schellenberg,K., C.Leuenberger and R.P.Schwarzenbach. 1984. Sorption of chlorinated phenols by natural sediments and aquifer materials. *Environ. Sci. Technol.* 18: 652-657.

Solomon,D.H. and D.G.Hawthorne. 1983. *Chemistry of Pigment and Fillers.* Wiley. New York.

Theng,B.K.G., D.J.Greenland and J.P.Quirk. 1967. Adsorption of alkylammonium ions by montmorillonites. *Clay Min.* 7: 1-17.

Theng,B.K.G. 1974. *The Chemistry of Clay-Organic Reactions.* Wiley. New York: 1-343.

Verschueren,K. 1983. *Handbook of Environmental Data on Organic Chemicals.* Van Nostrand Reinhold Co. Berlin-New York.

Wolfe,T.A., T.Demirel and E.R.Baumann. 1986. Adsorption of organic pollutants on montmorillonite treated with amines. *Journal WPCF.* 58. No.1: 68-76.