Effect of Linear-Dodecylbenzenesulfonate and Humic Acid on the Adsorption of Tricresyl Phosphate Isomers onto Clay Minerals

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The adsorption of three tricresyl phosphate (TCP) isomers, o-, m-, and p-TCP, onto kaolin, alumina, and montmorillonite without coating or coated with linear-dodecylbenzene-sulfonate (DBS) or humic acid was studied. The amount of TCP isomers adsorbed per unit mass of mineral followed the order alumina < kaolin < montmorillonite, but that per unit surface area of mineral was in the order kaolin < montmorillonite < alumina. The amount of TCP adsorbed was almost constant between pH 4 and 9. Higher adsorption per unit surface area on alumina might be due to the strong interaction between Al and phosphate oxygen (P=O) of TCP. Adsorption of TCP isomers on kaolin and alumina followed the order o-TCP < m-TCP < p-TCP, depending on their steric hindrance. Adsorption of TCP isomers on kaolin and alumina was enhanced with an increase in DBS adsorbed. This might be due to the hydrophobic interaction of TCP isomers with DBS adsorbed on minerals. Similarly, the adsorption of TCP isomers was accelerated in the presence of humic acid. However, adsorptive capacity of TCP isomers on minerals coated with humic acid was smaller than that with DBS. This is possibly due to the difference in hydrophobicity between humic acid and DBS adsorbed. It was confirmed that the carbon-normalized adsorption coefficient (K_{oca}) decreased with increasing carbon mass fraction of DBS and humic acid adsorbed on minerals.

Introduction

Pollution in aquatic environment by the use and disposal of organic chemicals has been noted. These chemicals are disposed in surface water, adsorbed onto the sediments, eliminated through biological and/or chemical degradation, and exerted some influences on the aquatic ecosystem. Thus, we should elucidate the behavior of their chemicals in aquatic environment.

Carbon-normalized adsorption coefficient, K_{oc}, for the sorption of organic chemicals onto sediment with high organic carbon content can be estimated from water–octanol partition coefficient K_{ow} of the chemicals. This estimation is based on a very nonspecific sorbate–sorbent interaction, that is, free of site specific bonding which may involve pollutant sorption into organic component. However, in the range of very low organic content in soil, mineral had an important role for the sorption of chemicals (1–3).

It is presumed that the adsorption of organic chemicals are affected by (a) characteristics of organic chemicals themselves, (b) surface character of adsorbent including materials coated on the surfaces, and (c) interaction of organic chemicals with the surface or the coated materials. In sediments, the organic coating is usually composed of a family of substances known as humic substances. A lot of research has been done on the adsorption of organic chemicals on sediments and suspended solids coated with humic substances in a natural aquatic system (4–8). On the other hand, the studies which clarify the contribution of humic substances and surfaces of adsorbents to the adsorption of organic chemicals have been done using organic chemicals–humic substances–clay (for example, humic-ferric or aluminum oxides) systems (2, 3, 9–11). It has been found that K_{oc} depends on the property of humic acid coated on soil and sediment surfaces; for chlorinated aliphatic hydrocarbon, a good relationship was observed between K_{oc} and C/O ratio in humic acid (1). It was also reported that K_{oc} varied with polarity and aromaticity of humic acid (3, 6, 8, 10, 11). On the other hand, it was pointed out that in the sorption of hydrophobic fluoranthene, di- and trichlorobenzene, and indol the contribution of clay mineral to adsorption was quite significant for soil with low to medium organic fractions, although half of the sorption sites on the mineral surface were blocked by the humic material (2).

In this study, we focused on tricresyl phosphate (TCP) as a nonionic and hydrophobic organic chemical among a variety of hazardous chemicals. The molecular formula of TCP is $(CH_3C_6H_4O)_3P=O$. TCP is widely used as hydraulic fluid, lubricant additive, and plasticizer for agricultural plastic film and poly(vinyl chloride) resins. This chemical has some isomers, e.g., o-, m-, and p-TCP. The o-TCP isomer has been reported to possess delayed neurotoxicity for human and domestic animals (12, 13). These chemicals were detected in aquatic environment (14–18).

Humic substances are common in natural waters and coated over the surface of soil and sediment (4–8). Likewise, DBS (linear-dodecylbenzenesulfonate) is probably adsorbed also on the surface of suspended and bottom sediments because of wide domestic and industrial usage as an anionic surfactant. DBS is the most widely used surfactant in Japan. There are many studies on DBS or other surfactants, for example, on its accumulation on river (19) and lake sediments (20) and on its interaction with other hazardous substances (21–23).

The objective of this study is to characterize and compare the effect of humic acid and DBS on the adsorption of TCP isomers on the surface of kaolin, alumina, and montmorillonite. These clay minerals are selected as representatives of clay minerals in river sediment or aquifer soil which have low organic content and high clay content. This study was focused on (a) structural characteristics of TCP isomers in the adsorption using CAche MOPAC PM3, (b) surface character of the clay minerals and interaction of the surfaces with TCP isomers or coating materials, and (c) interaction of the coating materials with TCP isomers adsorbed.

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Experiments and Methods

Materials. *o*-, *m*-, and *p*-TCP of guaranteed reagent grade were obtained from Eastman Kodak Co. (Rochester, U.S.A.). DBS (linear-dodecylbenzenesulfonate) of guaranteed reagent grade was from Wako Pure Chemical Co. (Tokyo, Japan). Three clay minerals were used as adsorbent: kaolin (hydrated aluminum silicate) and alumina (Type A-5) were obtained from Sigma Chemical Co. (St. Louis, U.S.A.) and mont-morillonite from Fulka (Buchs, Switzerland).

Humic acid was extracted from river sediment in the Kurose River according to Saint-Fort's method (*24*). Final humic acid was obtained by freeze-drying and was stored at 4 °C. Elemental composition of this humic acid was 28.08% of C, 4.15% of H, 3.60% of N, and 64.17% of O.

Experimental Method. Surface charge was determined using electrophoresis; mobility of fine clay minerals was determined using a particle electrophoresis apparatus, model Mark II (Rank Brothers, England), and zeta (ζ) potential was calculated using its mobility. Surface area of clay minerals was determined according to the N_2 BET method. Elemental analysis of humic acid was done using a 2400II CHN analyzer (Perkin-Elmer, U.S.A.).

Batch method was used for adsorption experiment of TCP isomers on clay minerals. Pure water produced by Puric-Z (Organo Co., Tokyo, Japan) was added to clay minerals of 3 g in a 500 mL Erlenmeyer flask. The mixture was allowed to stand for 24 h after pH adjustment to 4, 7, or 9 because montmorillonite was needed to be fully swelled for 20 h. The mixture was again adjusted to pH 4, 7, or 9. TCP acetone solution of 10^{-5}–10^{-6} M was added to the solution to obtain the desired initial concentrations. Total volume of the solution was 300 mL, and the addition of TCP acetone solution was below 1% (v/v). The mixture was stirred at 20 °C for 12 h. The solid/water ratios for TCP (initial concentration = 73.6 μg L^{-1}) were about 2.0, 1.5, and 43 for kaolin, alumia, and montmorillonite, respectively. The effect of pH on the TCP adsorption was studied at pH 4, 7, and 9. Experiments for obtaining adsorption isotherms were performed at pH 7.

After attaining equilibrium, the mixture was centrifuged at 5000 rpm for 20 min. The supernatant was filtered through a glass fiber filter (Whatman GF/C) preheated at 500 °C and vacuum filtered through a Sep-pak Plus tC18 solid-phase extraction cartridge (Waters Co., Milford, U.S.A.). Water in this cartridge was removed by purging with nitrogen gas. TCP in the cartridge was eluted with 3 mL of chloroform. After drying of this eluate by N_2 purge, it was redissolved with 1 mL of 2-propanol. The concentration of the spiking solution for the sorption experiment was 0.2–4 μg L^{-1} and that for the recovery experiment was 12 μg L^{-1}. The recoveries for TCP isomers were over 90%.

The adsorption of TCP isomers on the surface of clay minerals in the presence of DBS or humic acid was conducted as follows: original aqueous solution of DBS or humic acid of various volumes to attain desired concentrations was added to the solution containing clay mineral preswelled and pH was adjusted twice as described above. The DBS or humic acid–clay mixture was stirred for 3 or 48 h at 20 °C, respectively, to attain equilibrium. Acetone solution of TCP isomers (10^{-5}–10^{-6} M) was added to the solution so as to attain the desired concentrations. The subsequent proce-dures were the same as those in single adsorption of TCP described above. Biodegradation of TCP isomers was not observed in the sorption experiment for 12 h.

The preadsorbed amount of DBS and humic acid on the surface of clay minerals was calculated from the data measured by HPLC (High Performance Liquid Chromatog-raphy) and TOC (Total Organic Carbon), respectively. TCP isomers were determined by a gas chromatograph (Shimadzu
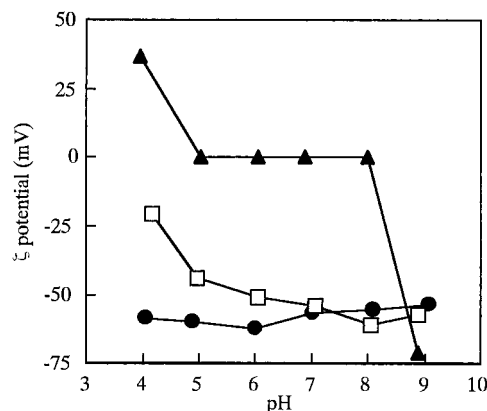

FIGURE 1. Effect of pH on ζ potential of clay mineral: □, kaolin, ▲, alumina, ●, montmorillonite.

GC-14B, Kyoto, Japan) equipped with a flame photometric detector (FPD). The column was a 20-m fused silica capillary column of inner diameter 0.25 mm (J&W, CBJ5, U.S.A.). The column temperature was increased from 100 to 300 °C at 10 °C min^{-1}. The injector and detector temperatures were 350 °C. The carrier gas was He (0.71 kg cm^{-2}) with high purity, and the injection mode was splitless (purge on 3 min). DBS was determined using an HPLC equipped with a multiwave-length detector (λ = 200 nm); MD-910, Jasco, Tokyo, Japan). The column was TSK-gel ODS-120A (Tosoh, Tokyo, Japan). The column temperature was 40 °C, and acetonitrile/0.1 M KCl (1:1) was used as eluent at a flow rate of 0.8 mL min^{-1}. The sample size was 200 μL. Quantitative analysis of humic acid as carbon was performed by a TOC analyzer (Shimadzu TOC-5000, Kyoto, Japan). Carrier gas was synthesized air with high purity (CO <0.5, CO_2 < 0.5, CH_4 < 0.5, NOx < 0.05, SO_2 < 0.05 ppm), and the pressure and flow rate were 6 kg cm^{-2} and 150 mL min^{-1}, respectively. High sensitive platinum catalyst was kept in a quartz tube at 680 °C, and the detector was a nondispersion infrared analyzer. The concentration of humic acid was determined only for the clay mineral–humic acid system.

The stable molecular structure of TCP isomers, their polarity, and electron density of each atom, etc. were calculated using CAche MOPAC (Molecular Orbital Package) PM3 (*25, 26*) at the Instrument Center for Chemical Analysis, Hiroshima University.

Results and Discussion

Surface Character of Clay Minerals. The specific surface areas of kaolin, alumina, and montmorillonite were 20.6, 0.9, and 249.7 m^2 g^{-1}, respectively. The variation in ζ potential for these clay minerals with pH is shown in Figure 1. ζ potential of kaolin was always negative and decreased with an increase in pH. On the other hand, ζ potential of alumina was +36 mV at pH 4 and −72 mV at pH 9 and was estimated to be nearly zero between pH 5 and pH 8 as indicated by the immobility of alumina particles. The marked change in ζ potential is due to the amphoteric property of alumina. The potential of montmorillonite was independent of the change in pH and was nearly constant (−54 to −59 mV).

Adsorption of TCP Isomers onto Clay Minerals. Figure 2 shows the variation in the adsorption of *o*-TCP as a function of pH for kaolin, alumina, and montmorillonite. The adsorption of *o*-TCP onto clay minerals was scarcely influ-enced by pH, although their surface charges significantly varied with pH except for montmorillonite. This suggests that the adsorption of TCP isomers onto these minerals is also scarcely affected by surface charge on minerals. Such a trend was also observed for *m*-TCP and *p*-TCP.
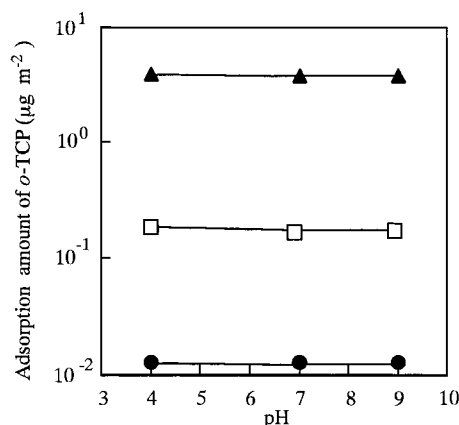
FIGURE 2. Effect of pH on the adsorption of o-TCP on clay minerals: □, montmorillonite, ▲, alumina, ●, kaolin.

TABLE 1. Adsorption Coefficients, K_{pm} and K_{pa} of TCP Isomers Adsorbed on Clay Minerals at pH 7[a]

adsorption coefficient	mineral					
	kaolin		alumina		montmorillonite	
	K_{pm}	K_{pa}	K_{pm}	K_{pa}	K_{pm}	K_{pa}
o-TCP	0.158	0.767×10^{-2}	0.118	0.132	3.870	1.550×10^{-2}
m-TCP	0.196	0.951×10^{-2}	0.144	0.160	3.399	1.361×10^{-2}
p-TCP	0.236	1.144×10^{-2}	0.177	0.197	4.614	1.848×10^{-2}

[a] K_{pm}: L g^{-1}; K_{pa}: L m^{-2}.

Table 1 shows the adsorption coefficient, K_{pm} and K_{pa} for three clay minerals. Adsorption isotherms of TCP isomers on the surface of three minerals followed to eq 1. The adsorption coefficient per unit surface area of clay minerals, K_{pa}, was calculated according to eq 2

$$Q = K_{pm}C \qquad (1)$$

$$K_{pa} \ (\text{L m}^{-2}) = K_{pm} \ (\text{L g}^{-1})/\text{surface area} \ (\text{m}^2 \ \text{g}^{-1}) \qquad (2)$$

where Q (mg g^{-1}) is the amount of TCP isomers adsorbed per g of clay minerals, C (mg L^{-1}) is the equilibrium concentration of TCP isomers, and K_{pm} (L g^{-1}) is adsorption coefficient per g of clay minerals.

The values of K_{pm} followed the order alumina < kaolin < montmorillonite for the three TCP isomers. On the other hand, the values of K_{pa} followed the order kaolin < montmorillonite < alumina, different from that of K_{pm}. With respect to each isomer of TCP, both the values of K_{pm} and K_{pa} exhibited the order o-TCP < m-TCP < p-TCP for kaolin and alumina, although the trend on montmorillonite was different (m-TCP < o-TCP < p-TCP).

The difference in adsorption of TCP isomers on kaolin and alumina, specifically their adsorptive capacities, might be explained as follows:

(1) Ligand exchange reaction (or surface complexation) (9, 11) occurs on the surfaces. Figure 3 shows the stable structure, electron densities on oxygen and phosphorus atoms, and total dipole moment of TCP isomers. CAche MOPAC (Molecular Orbital Package) PM3 (25, 26) was used in this calculation. The hydroxyl group attached to the Al atom on alumina and kaolin is exchanged by the TCP molecule; coordination bonding between the empty atomic orbital of the Al atom and the lone pair electrons of the oxygen atom in the P=O bond might be formed since electron density localized on the oxygen atom in the P=O bond is larger compared to that in the P−O− bond (see numeral in Figure

3). This ligand exchange reaction explains the significant promotion of adsorption of TCP isomers onto alumina compared to that onto kaolin because alumina has a higher content of Al atom.

(2) Steric conformation of TCP isomers influences the adsorption. When a methyl group exists at the ortho position of benzene in the TCP molecule and its molecule is adsorbed on the surface of kaolin and alumina, steric hindrance occurs due to the inhibition for the rotation around O−C and P−O axes by the methyl group. On the contrary, the steric hindrance for p-TCP is the smallest. Therefore, it might be postulated that the adsorption of TCP isomers should follow the order o-TCP < m-TCP < p-TCP.

(3) As another possible reason, dipole interaction between the clay mineral surface and TCP isomers is considered for the amount of adsorbed o-TCP < m-TCP < p-TCP. Dipole moments of o-TCP, m-TCP, and p-TCP calculated using this MOPAC were 2.970, 4.482, and 3.540 D, respectively, taking the interaction with water molecules into consideration. The contribution of dipole interaction to sorption of TCP isomers on the minerals was markedly small as is shown in the effect of pH on the sorption of their isomers (Figure 2).

Coordination bonding of TCP isomers with surface Al atom and steric hindrance of TCP isomers have an important role in the adsorption, although physical adsorption due to dipole interaction contributes to some extent. These results suggest that the adsorption process rather than the partition process could better explain the attachment of TCP isomers onto minerals, and the adsorption was significantly affected by the surface characteristics of minerals and structure of TCP isomers.

Adsorption of TCP Isomers on Clay Minerals in the Presence of DBS. Figure 4 shows the effect of pH on the adsorption of o-TCP in the absence or presence of DBS and that of DBS in the presence of o-TCP for kaolin, alumina, and montmorillonite. The change in amount adsorbed for m-TCP and p-TCP in the presence of DBS was very similar to that for o-TCP. The amount of DBS adsorbed on kaolin increased with decreasing pH in the presence of o-TCP. Such a trend corresponds to a decrease in the surface charge of kaolin as pH decreases (Figure 1). An increase in the amount of o-TCP adsorbed was observed in the presence of DBS. On the other hand, the amounts of both o-TCP and DBS adsorbed on alumina (Figure 4B) were significantly large in comparison with those of kaolin. The adsorption of DBS in the presence of o-TCP was zero at pH 9 but increased with decreasing pH, corresponding satisfactorily to the variation in ζ potential (Figure 1). The adsorption of o-TCP did not increase in the absence of DBS. However, the adsorption of o-TCP increased with a decrease in pH in the presence of DBS.

DBS was scarcely adsorbed onto montmorillonite in the whole range of pH (Figure 4C), suggesting repulsive interaction between negatively charged SO$_3^-$ group in DBS molecule and strongly negative charged surface of montmorillonite (Figure 1). The amounts of o-TCP adsorbed on montmorillonite in the presence of DBS were markedly small in comparison with those for kaolin and alumina and hardly varied with pH. Furthermore, their amounts were nearly the same with those in the absence of DBS. These behaviors are different from those of kaolin and alumina. The adsorption of TCP isomers on montmorillonite is therefore excluded in the discussion described below.

Figure 5 shows the variations in K_{pa} of TCP isomers adsorbed on kaolin and alumina in the presence of DBS at pH 7 against organic carbon content (P_{oc}). P_{oc} was obtained from eqs 3 and 4.
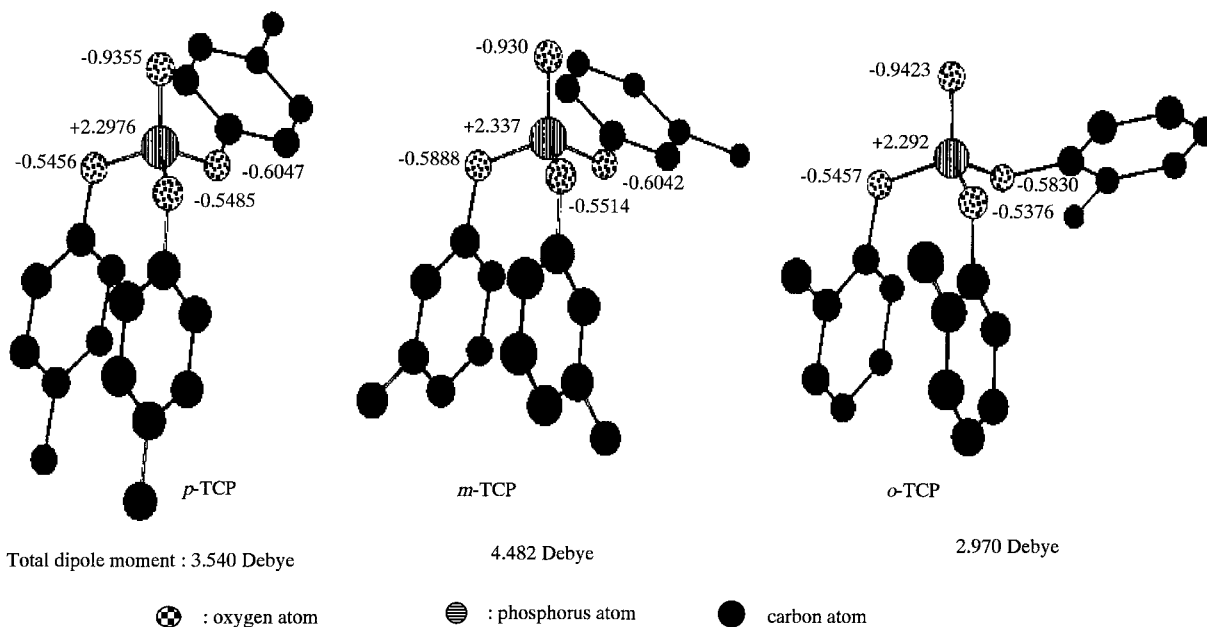
FIGURE 3. Stable structures of TCP isomers and electron densities on oxygen and phosphorus atoms. Numerals in the figure show electron and nuclear densities on oxygen and phosphorus atoms.
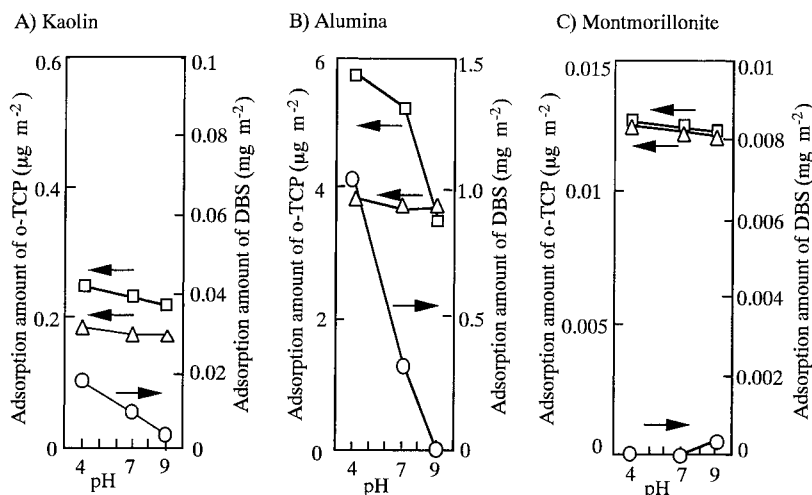

FIGURE 4. Effect of pH on the adsorption of o-TCP and DBS on kaolin, alumina, and montmorillonite; $\triangle$, adsorption of o-TCP (o-TCP = 73.7 μg L^{-1}, DBS = 0 mg L^{-1}); $\square$, adsorption of o-TCP (o-TCP = 73.7 μg L^{-1}, DBS = 10 mg L^{-1}); $\bigcirc$, adsorption of DBS (o-TCP = 73.7 μg L^{-1}, DBS = 10 mg L^{-1}).

f_{oc} = carbon mass fraction (carbon amount in DBS adsorbed on minerals) (mg C)/weight of minerals (mg)

$$(3)$$

P_{oc}, organic carbon content (%) = $f_{oc} \times 100$ $\quad(4)$

The magnitude of K_{pa} for o-TCP was 0.2 (L m^{-2}) at $P_{oc} = 0$ for alumina, and it increased with an increase in P_{oc}. On the other hand, the magnitude of K_{pa} for kaolin was small (0.01 (L m^{-2})) at $P_{oc} = 0$, and it increased slightly with an increase in P_{oc}. These might be attributable to an increasing proximity of o-TCP to DBS adsorbed on the surface of alumina because of smaller surface area and higher coverage of DBS (Figure 5B) in comparison with kaolin:hydrophobic interaction might act more strongly in TCP$-$DBS$-$alumina system than that in TCP$-$DBS$-$kaolin system.

On the other hand, the slopes of K_{pa} against P_{oc} for alumina increased in the order o-TCP $< m$-TCP $< p$-TCP and were significantly large. Such a tendency for TCP isomers was also observed for kaolin, although both the values of K_{pa} at $P_{oc} = 0$ and the slopes were small. These suggest that

relatively strong interaction between TCP and DBS, e.g. $\pi-\pi$ interaction, would also increase in the order o-TCP $< m$-TCP $< p$-TCP and get a stable configuration on the surfaces.

Adsorption of TCP Isomers on Clay Minerals in the Presence of Humic Acid. Figure 6 shows the variation in K_{pa} of TCP isomers adsorbed on kaolin and alumina in the presence of humic acid at pH 7 against P_{oc}. The slopes of K_{pa} against P_{oc} for kaolin and alumina in the presence of humic acid were lower compared to those in the presence of DBS; more so, the slopes for kaolin were significantly small.

The slopes of K_{pa} against P_{oc} in the presence of humic acid increased in the order o-TCP $< m$-TCP $< p$-TCP. Such a tendency was also found for the adsorption in the presence of DBS: $\pi-\pi$ interaction between benzene rings in TCP and humic acid would vary according to steric hindrance of the methyl group attached to the benzene ring in the TCP molecule (Figure 3). The adsorption of humic substances on the surface of alumina, kaolin, and vermiculite was proportional to their aromatic carbon content and inversely proportional to their O/C ratio of humic substances (9).
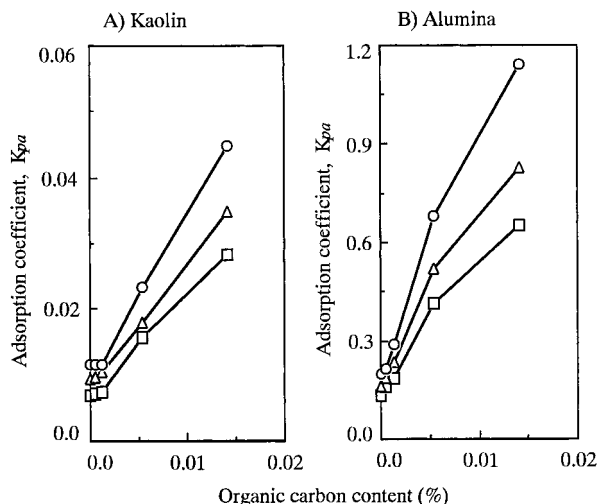
FIGURE 5. Variations in K_{pa} of TCP isomers adsorbed on kaolin and alumina in the presence of DBS at pH 7, against organic carbon content: $\square$, o-TCP; $\triangle$, m-TCP; $\bigcirc$, p-TCP.
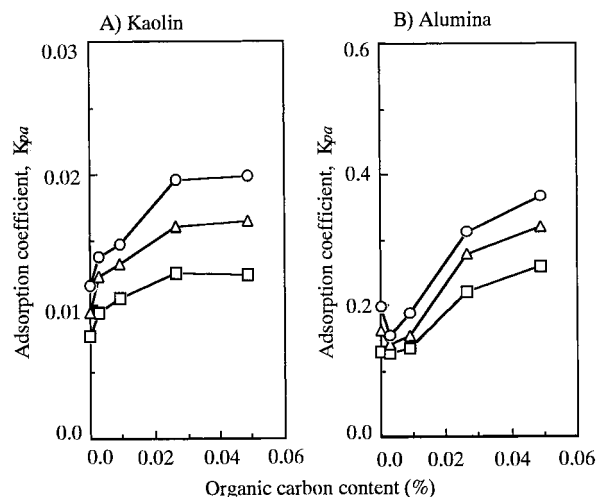

FIGURE 6. Variations in K_{pa} of TCP isomers adsorbed on kaolin and alumina in the presence of humic acid at pH 7, against organic carbon content: $\square$, o-TCP; $\triangle$, m-TCP; $\bigcirc$, p-TCP.

The values of K_{pa} for alumina in the presence of humic acid showed a minimum at 0.001% of P_{oc} and thereafter increased gradually with an increase in P_{oc}. Similarly, the values of K_{pa} for kaolin in the presence of DBS showed a slight minimum at 0.003% of P_{oc} (Figure 5). Adsorption coefficient K_{pm} has a minimum value at low content of humic acid on the surface of aquifer soil (2). This phenomenon could be explained by two opposite effects: the diminishing of adsorption site due to adsorption of humic acid onto bare mineral surface and the formation of new adsorption sites available on/in the humic part of the matrix.

Comparison between Adsorption Characteristics of TCP Isomers on Kaolin and Alumina in the Presence of DBS or Humic Acid. Figure 7 shows the comparison of K_{oca} for o-TCP adsorbed on kaolin and alumina in the presence of DBS or humic acid. K_{oca} was obtained from eq 5 and is usually used to represent an adsorption character of organic chemicals since K_{pa} increases with an increase in f_{oc}.

$$K_{oca} = K_{pa}/f_{oc} \qquad (5)$$

The values of K_{oca} for o-TCP decreased with an increase in P_{oc} in all the systems, kaolin or alumina$-$DBS or humic acid$-$o-TCP. Such a trend was also observed for m-TCP and
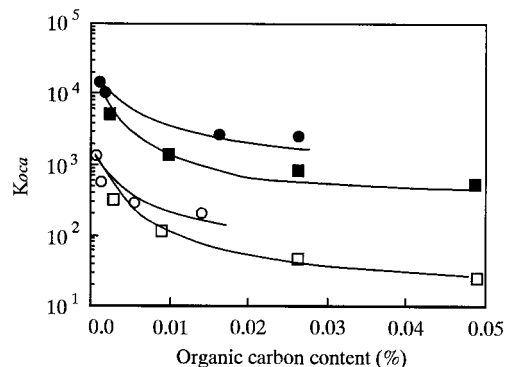

FIGURE 7. Comparison of K_{oca} for o-TCP adsorbed on kaolin and alumina in the presence of DBS or of humic acid: $\bigcirc$, DBS$-$kaolin; $\bullet$, DBS$-$alumina; $\square$, humic acid$-$kaolin; $\blacksquare$, humic acid$-$alumina.

p-TCP. The values of K_{oca} for alumina were approximately 10 times higher than those for kaolin. This might be due to high K_{pa} for alumina (Table 1) and high hydrophobic interaction of TCP isomers with DBS or humic acid adsorbed on alumina surface, suggesting the importance of surface character of clay minerals.

Comparing K_{oca} for DBS with that for humic acid, the former was slightly larger than the latter. This may be mainly responsible for the difference in hydrophobic interaction of TCP isomers with DBS or humic acid adsorbed on the mineral surfaces which is a relatively strong interaction, e.g. π-electron interaction. About 94% of humic acid was adsorbed on the surfaces of kaolin and alumina (initial humic concentration $= 5$ mg L^{-1}), while the percentages of DBS adsorbed on kaolin and alumina were approximately 26 and 43% (initial DBS concentration $= 10$ mg L^{-1}), respectively. Although the amount of adsorption for TCP increases with an increase in DBS concentration, the adsorption amount of DBS on kaolin (initial DBS concentration $= 10$ mg L^{-1}) was 0.26, 0.36, and 0.42 mg g^{-1} in the presence of TCP in which the initial concentration was $0, 5 \times 10^{-9}$, and 10^{-8} M, respectively. These suggest that complex which might be formed through the interaction of dissolved DBS with TCP in water is sorbed onto kaolin surface except for the sorption of TCP to DBS preadsorbed on the surface.

Another reason could be the lower value of K_{oca} for humic acid adsorbed on clay minerals which might be due to a low aromaticity of humic acid extracted from river sediment in the Kurose River; for Suwannee humic acid of IHSS (International Humic Substance Society), the fraction of carbon was 54.34% and the aromatic carbon was 37% (3), while for Dodder humic acid, the fraction of carbon was 48.9% and the aromatic carbon was 38% (9). Our humic acid has low aromaticity because of the low fraction of carbon (C: 28.08%, H: 4.15%, N: 3.60%, O: 64.17%) and high O/C ratio, similar to that found by Murphy (3).

It is desirable for K_{oca} to have only one value to represent the adsorption character of organic chemicals, but the values of K_{oca} decreased with increasing f_{oc}. Such a decrease in K_{oca} has been reported (3, 10). This phenomenon could be explained as follows: organic substances such as humic acid and DBS adsorbed on the mineral surface are active and fully accessible for TCP sorption at low f_{oc}, but when f_{oc} increases, their adsorbed organic substances adopt interfacial configuration which then reduces sorption (3, 10).

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