

**STUDY OF THE WATER SOLUBILITY AND SORPTION  
ON PARTICULATE MATTERS OF PHTHALATE IN THE PRESENCE  
OF HUMIC ACID USING <sup>14</sup>C LABELLED  
DI-(2-ETHYLHEXYL)PHTHALATE**

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(Received 22 August 2005; accepted 19 February 2006)

**Abstract.** Phthalate esters have become widespread contaminants in the aquatic environment, because of their extensive use as non-reactive plasticizers. There is, however, little accurate data on their solubility, transportation, and distribution in the aquatic environment. In this work, we have investigated the influence of humic acid on the water solubility of di-(2-ethylhexyl)phthalate (DEHP), one of the most frequently used phthalate esters in the laboratory studies for DEHP. We have also studied the solid–water distribution of DEHP in the presence of humic acid and particulate matter (activated carbon, ferrihydrite, and kaolinite) to simulate their distribution in a natural aquifer (ternary system). The results show that the water solubility of DEHP can be significantly increased by humic acid. The  $K_{eq}$  value, the binding constant of DEHP between water and humic acid at equilibrium, was obtained by fitting experimental data for each humic acid. The  $K_{eq}$  values in the ternary system apparently decreased in the order of ferrihydrite > kaolinite  $\approx$  octanol/water partition > activated carbon systems. This result shows that the increase in the hydrophobicity of HA remaining in the solution will lead to the apparent increase of  $K_{eq}$  in the system since more hydrophilic solid sorbs relatively more hydrophilic HA molecule. The solid–water partition coefficient ( $K_{W-P}$ ) for DEHP in the environment estimated from this study is consistent with those reported based on the experiments for natural samples. Quantitative values obtained in this study, such as  $K'_{ow}$ ,  $K_{eq}$ , and  $K_{W-P}$ , can be useful for estimating the behavior of DEHP.

**Keywords:** humic substances, di-(2-ethylhexyl)phthalate, solubility, particulate matter, sorption, hydrophobicity

## 1. Introduction

Phthalate esters have been used in the industrial production of lubricants, glues, insect repellent, dielectric fluids, and plastics (Giam *et al.*, 1984). Most phthalate esters have been used to plasticize polyvinyl chloride, which usually contains phthalate esters at about 35% by weight; in some products, however, the phthalate ester content may exceed 50%. Their large-scale production more than several million tones per annum and physical rather than chemical incorporation in the polymeric

TABLE I  
Physical, chemical, and environmental properties of DEHP

Property	Value	Reference
Molecular weight	390.6 g mol <sup>-1</sup>	
Melting point	-50 °C	
Boiling point	384 °C	
Solubility (20°C)	0.6–400 μg dm <sup>-3</sup>	Boese, 1984; Russell and McDuffie, 1986
Octanol-water partition coefficient, log $K_{ow}$	4.20–9.64	Haward <i>et al.</i> , 1985; Brooke <i>et al.</i> , 1990
Vapour pressure (23 °C)	$3.4 \times 10^{-7}$ – $6.4 \times 10^{-6}$ mmHg	Tyler <i>et al.</i> , 1998
Chemical hydrolysis half-life (25 °C, pH7)	2000 years	Giam <i>et al.</i> , 1984
Degradation half-life in natural water	2–15 days	Tyler <i>et al.</i> , 1998

matrix ensures that they are widespread contaminants (Woodfine *et al.*, 2002; Yuan *et al.*, 2002). Phthalates enter the environment in wastewater effluents during the production phase and via leaching and volatilization from plastic products during their use and after disposal (Bauer and Herrmann, 1997). Present application and emissions of phthalates are of great concern because the substances are suspected of mimicking estrogens (Staple *et al.*, 1997; Barton and Andersen, 1998). Among the phthalate esters, di-(2-ethylhexyl)phthalate (DEHP) is one of the most frequently used additives in the manufacture of flexible polyvinyl chloride. DEHP is used as a plasticizer because of its stability, fluidity, and low volatility (Tyler *et al.*, 1998). The annual global production of DEHP has been estimated to be approximately 10<sup>6</sup> tons (Nielsen and Larsen, 1996). Some physical, chemical, and environmental fate properties of DEHP are listed in Table I. Reported values for its solubility and octanol–water partition coefficient vary by several orders of magnitude, reflecting the difficulties in obtaining reliable data for phthalates. Reasons for this include the high probability of contamination from laboratory plastic ware (Leung and Giang, 1993) and other experimental artifacts. In the light of devising structure–activity relationship for organic chemicals, Staple *et al.* (1997) suggest values for the solubility and octanol–water partitioning of DEHP of about 3 μg dm<sup>-3</sup> and 10<sup>7.5</sup>, respectively, attesting to its highly hydrophobic nature.

The fate of various non-polar organic solutes (NOS) in environment, including phthalate esters, should be interpreted from basic processes including the distribution and transportation of the pollutants between various compartments in aqueous systems. First, NOS is easily sorbed on particulate matter (PM), as depicted by the process I in Figure 1 (Brunk *et al.*, 1997). Dissolved organic carbon (DOC) such as humic acid (HA) can also interact or binds with NOS (Zhao and Vance, 1998) (process II in Figure 1). Chiou (2002) showed an enhancement of the water solubility of NOS in the presence of HA. This result shows that DOC can play an important

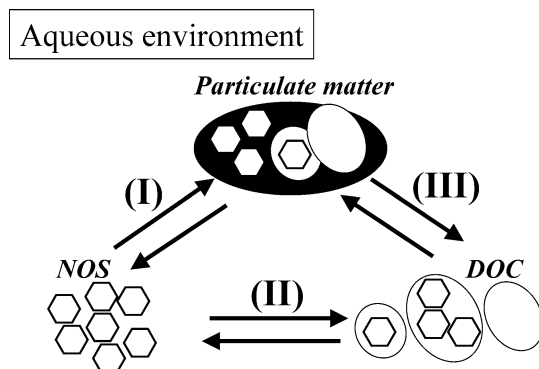


Figure 1. Schematic figure of the interactions among particulate matter (PM), DOC, and NOS in aqueous environment. See text for the details about the interactions I, II, and III.

role in the desorption of NOS from PM into an aqueous environment. On the other hand, PM can also act as a sorbent for DOC such as HA due to its surface-active characteristics (Filius *et al.*, 2000). Therefore, desorption of NOS from PM to the aqueous solution by HA might become complicated by the presence of HA–NOS complex. Although many studies concerning the enhancement of water solubility of NOS by the presence of HA have been published (Yamamoto *et al.*, 2003; Kim and Lee, 2002), there are few data about DEHP–HA interaction. Moreover, few studies have been done so far with respect to PM in aqueous systems as sorbent of both phthalate esters and HA.

In the present work, we have carried out two experiments to understand the behavior of DEHP in natural aquifers. In the first experiment, we examined the influence of HAs on the water solubility of DEHP in an octanol–water partition system. The octanol–water partition coefficient has been used as an indicator of hydrophobicity and of the potential for bioaccumulation of organic compound in the environment (Chiou, 2002). This coefficient is an important index for considering the behavior and fate of hydrophobic organic compounds in environment. We can discuss quantitatively the influence of HA on the water solubility of DEHP from the octanol–water partition experiments. Several kinds of HAs derived from various sources were employed in this work to elucidate the relationship between the characteristics of various HAs and their affinity for DEHP. We also investigated the effect of pH on the distribution between octanol–water phases, which may affect the affinity of HA for DEHP. In the second experiment, we studied the solid–water distribution of DEHP in the presence of HAs and PMs (ternary system), which is closer to the conditions in natural aquifers. Activated carbon, clay minerals (kaolinite), and metal oxide minerals (ferrihydrite) were employed as model materials as PMs in the environment. In this study, DEHP labelled with  $^{14}\text{C}$  was used in both experiments to avoid possible contamination from the surrounding environment as stated above. We could examine DEHP behaviour without considering the

TABLE II

Origin, elemental composition, and concentration of acidic sites for humic acid (HA) employed in this study

HA	Origin	%C	%H	%N	%O	C/H	Carboxylic group (mol/kg <sub>HA</sub> )	Phenolic group (mol/kg <sub>HA</sub> )
THA	Paddy soil	55.1	3.1	2.6	37.6	17.8	6.1	—
LHA	Lignite	63.81	3.70	1.23	31.27	17.2	6.62	2.06
SRHA	River	52.55	4.40	1.19	42.53	11.9	8.43	3.79

disconcertion of experimental systems by using the radioactive tracer in comparison to the determination using GC-MS analysis etc.

## 2. Methods

### 2.1. MATERIALS

Standard grade Suwannee River Humic Acid (SRHA) and Leonardite Humic Acid (LHA) were obtained from the International Humic Substances Society (IHSS) and used without further purification (IHSS numbers 1S101H and 1S104H, respectively; International Humic Substances Society, <http://www.ihss.gatech.edu>). Another HA sample (THA) was extracted by a 0.5 M NaOH solution from paddy soil in Tochigi Prefecture, Japan, separated by acidification (pH 2) and purified (Takahashi *et al.*, 1995, 1998a). Their origins, chemical compositions, and concentrations of acidic sites are summarized in Table II (IHSS Standard & Reference Collection Data Book, 2002; Takahashi *et al.*, 1998a).

[<sup>14</sup>C]DEHP (433 MBq mmol<sup>-1</sup>; purity >99%) was obtained from Sigma Chemical Co. (St. Louis, MO) and diluted by hexane to prepare a stock solution. Octanol (>99.5%; prepared for partition coefficient analysis) was obtained from Wako Pure Chemical (Tokyo). Activated carbon powder (special reagent grade, produced from coal) was obtained from Wako Pure Chemicals and used without further purification. Kaolinite recovered from a mine in Japan (Kanpaku) was obtained from the Clay Science Society of Japan and used without further purification. Ferrihydrite was synthesized as described by Schwertmann and Cornell (2000). The sample was identified as the two-line ferrihydrite using the X-ray diffractometer (MAC Science Co., M18XHF). All glasswares were heated at 200 °C prior to use. All other equipment was washed with analytical grade acetone prior to use.

### 2.2. OCTANOL–WATER PARTITIONING OF DEHP IN THE PRESENCE OF HA

Octanol–water partition system was conducted following the slow stirring method reported in Bruijn *et al.* (1989). Octanol (0.15 ml) saturated with water was added to a glass vessel containing 15 mL of an aqueous solution of HA at a certain

concentration. The concentration of HA solution ranged from 30 to 115 mgC dm<sup>-3</sup> in this experiment. The pH was adjusted using an acetate buffer (0.010 M) and [<sup>14</sup>C]DEHP dissolved in hexane was added. The hexane was removed by volatilization perfectly. After shaking the solution at 25 °C in the dark for 72 h, we measured the concentrations of <sup>14</sup>C-DEHP in both water and octanol phases with a liquid scintillation counter (Aloka, LSC-3000). The colour quenching for the scintillation counting of the water phase caused by HA was corrected using a correction curve obtained by measuring the known amount of [<sup>14</sup>C]DEHP in the presence of various concentrations of HA.

### 2.3. DESORPTION EXPERIMENTS OF DEHP FROM PM IN THE PRESENCE OF HA (TERNARY SYSTEMS)

Ternary systems were prepared as follows. This experiment was conducted based on method reported in literature (Fukushima *et al.*, 1997). The mixture of each PM (activated carbon, kaolinite, and ferrihydrite) 1.0 g and  $1.81 \times 10^{-3}$  mM DEHP in ethanol (100 mL) was stirred for 24 h. Subsequently, this mixture was filtered through a silica fiber filter (Advantec QR100), which can filtrate 99.9% of 0.3 μm particles (dioctyl phthalate). The powder of PM sorbing DEHP (PM-DEHP) was collected on the filter. After being air-dried in the dark, the PM-DEHP powder was stored in a desiccator over silica gel in the dark, prior to being employed in the ternary systems. A 0.01 g sample of the PM-DEHP was mixed with 10 mL of HA solution in a glass-tube (pH 6 by acetate buffer). The solution shaken at 25 °C in the dark for 72 h was filtered through a 0.45 μm PTFE membrane filter. The concentration of HA in the solution ranged from 0 to 300 mgC dm<sup>-3</sup> in this experiment. The concentration of DEHP in the filtrate was measured by the liquid scintillation counter. The activity of DEHP did not change by the filtration, showing that the sorption of DEHP to 0.45 μm PTFE filter did not influence the quantification of DEHP. The concentration of HA in the filtrate was measured by absorbance at 400 nm (Reid *et al.*, 1990). Since absorbance of the filtrate in the absence of HA was equal to the value of blank solution, PMs did not transfer into filtrate through the membrane filter and does not influence the determination of HA concentration in filtrate. The fraction of HA absorbed to PM was calculated by subtracting the amount of HA in the filtrate from the abundance of added HA.

## 3. Results

### 3.1. OCTANOL-WATER PARTITIONING OF DEHP IN THE PRESENCE OF HA

$K_{ow}$  is defined as:

$$K_{ow} = \frac{[\text{DEHP}]_o}{[\text{DEHP}]_{aq}} \quad (1)$$

where  $[\text{DEHP}]_{\text{O}}$  and  $[\text{DEHP}]_{\text{aq}}$  denote the concentrations of DEHP in the octanol and water phases, respectively. Examination of the dependency of  $K_{\text{ow}}$  on the shaking time showed that  $K_{\text{ow}}$  decreased with shaking time and reached equilibrium approximately after 70 h. The time was set to be the equilibrium time for the measurement of apparent  $K_{\text{ow}}$  value ( $K'_{\text{ow}}$ : apparent octanol–water coefficient in the presence of HA) in the following experiments.

The relationship between  $K'_{\text{ow}}$  and aqueous concentration of HA ( $[\text{HA}]_{\text{aq}}$ ) shows that  $K'_{\text{ow}}$  decreases with the increase in  $[\text{HA}]_{\text{aq}}$ , suggesting that DEHP has become soluble to water in the presence of HA. This observation is consistent with other studies (e.g., Schlautman and Morgan, 1993; Kim and Lee, 2002), observing a decrease in  $K'_{\text{ow}}$  of NOS with increasing concentration of HA in octanol–water partition system. DEHP concentration in water phase in the absence of HA could not be detected due to the very low activity of DEHP under the condition. Therefore, we used  $K_{\text{ow}}$  values of DEHP in the absence of HA reported by Bruijn *et al.* for comparison (Bruijn *et al.*, 1989). For each HA,  $K'_{\text{ow}}$  values when  $[\text{HA}]_{\text{aq}} > 50 \text{ mgC dm}^{-3}$  were smaller by 4–6 orders of magnitude than the  $K_{\text{ow}}$  value,  $10^{7.45}$ , in the absence of HA. This suggests that the water solubility of DEHP can be significantly increased by the presence of HA.  $K'_{\text{ow}}$  with THA was the lowest, while  $K'_{\text{ow}}$  with SRHA was the highest, which may be due to the different characteristics of the HAs used in this study.

### 3.2. DESORPTION OF DEHP FROM PM IN THE PRESENCE OF HA (TERNARY SYSTEMS)

Figure 2 shows the dependence of DEHP ( $[\text{DEHP}]_{\text{aq}}$ ) and HA ( $[\text{HA}]_{\text{aq}}$ ) concentrations in the filtrate on shaking time for the ternary system containing HA (THA) and DEHP sorbed on activated carbon. In activated carbon system, the adsorption equilibrium was achieved within 60 hrs. In ferrihydrite and kaolinite systems, the shaking time required for the adsorption equilibrium was also within 60 hrs, which was fixed as shaking time for the three systems. In the absence of THA, the fraction of DEHP in the aqueous phase ( $[\text{DEHP}]_{\text{aq}}/[\text{DEHP}]_{\text{all}}$ ) was less than 0.01% (Figure 2a). The  $[\text{DEHP}]_{\text{all}}$  was determined by the total concentration of DEHP extracted by ethanol from PMs. For all PMs, the DEHP extraction experiments were performed more than ten times, since all DEHP that sorbs on PMs could not be extracted by a single extraction. To determine DEHP abundance remaining on PMs, the extraction experiments were continued until the activity ratio of DEHP in filtrate to total extracted DEHP was less than 3%. Thus, total activity of DEHP extracted by all the extraction experiments was defined as  $[\text{DEHP}]_{\text{all}}$ . The  $[\text{DEHP}]_{\text{aq}}/[\text{DEHP}]_{\text{all}}$  ratio increased in the presence of  $50 \text{ mgC dm}^{-3}$  THA, reaching 0.05% at equilibrium. These results demonstrate that the presence of HA contributes to the enhancement of DEHP desorption from the activated carbon.

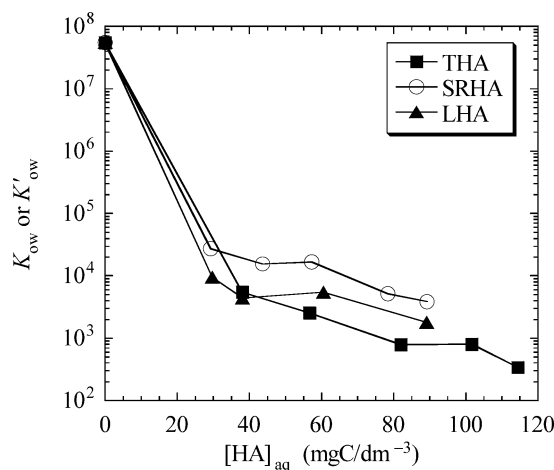


Figure 2. Relationship between  $K'_{ow}$  of DEHP and the concentration of humic acids (pH 5, 0.010 M acetate buffer) with a  $K_{ow}$  value  $10^{7.45}$  reported in Bruijn *et al.*

The  $[\text{DEHP}]_{\text{aq}}/[\text{DEHP}]_{\text{all}}$  ratio has increased right after the addition of HA, but decreased gradually afterwards. This suggests that DEHP desorbs from activated carbon at first by forming a complex with HA (HA–DEHP) in the aqueous phase. Subsequently, the DEHP re-sorbed gradually on the activated carbon as the HA–DEHP complex. The THA remaining in the aqueous phase decreased with time, reaching a plateau after 50 h for the DEHP/THA/activated carbon system (Figure 2b). Thus, the re-sorption of HA–DEHP influences the  $[\text{DEHP}]_{\text{aq}}$  at the equilibrium. It is well-known that PMs are capable of sorbing HA (Brunk *et al.*, 1997). In the presence of  $50 \text{ mgC dm}^{-3}$  THA at pH 6, approximately 40%, 10%, and 20% of the added THA was sorbed on 0.010 g of activated carbon, ferrihydrite, and kaolinite, respectively. The difference in the sorption characteristics of HA on PM can, in turn, influence the distribution of DEHP between water and PM.

### 3.3. RELATIONSHIP BETWEEN PARTITION COEFFICIENT AND HUMIC ACID CONCENTRATION

In Figure 4a–c, the values of  $K_{W-P}$ , the solid–water partition coefficient, are plotted for the ternary systems containing activated carbon, ferrihydrite, and kaolinite at various  $[\text{HA}]_{\text{aq}}$ , respectively. The value of  $K_{W-P}$  is calculated as:

$$K_{W-P} = \frac{[\text{DEHP}]_{\text{aq}}}{[\text{DEHP}]_{\text{PM}}} \quad (2)$$

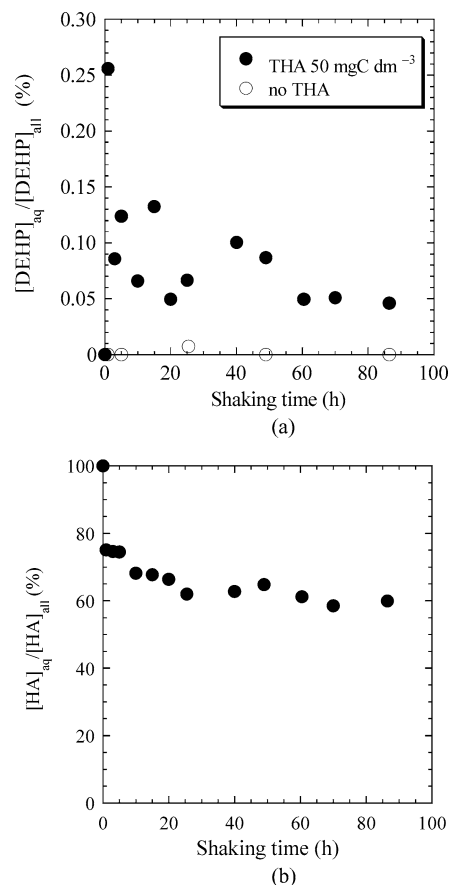


Figure 3. Effect of shaking time on  $[\text{DEHP}]_{\text{aq}}/[\text{DEHP}]_{\text{all}}$  (a) and  $[\text{HA}]_{\text{aq}}/[\text{HA}]_{\text{all}}$  (b) in the ternary system employing activated carbon as PM (THA 50 mgC dm<sup>-3</sup>, pH 6, 0.010 M acetate buffer).

where  $[\text{DEHP}]_{\text{PM}}$  is the concentration evaluated by subtraction of  $[\text{DEHP}]_{\text{aq}}$  from  $[\text{DEHP}]_{\text{all}}$ . The  $K_{\text{W-P}}$  (g dm<sup>-3</sup>) values for activated carbon, ferrihydrite, and kaolinite were approximately 10<sup>-7</sup>, 10<sup>-3</sup>, and 10<sup>-4</sup> g dm<sup>-3</sup>, respectively. Activated carbon can sorb a variety of organic matter to a great extent (Kleineidam *et al.*, 2002; Li *et al.*, 2002), so that it is natural that the  $K_{\text{W-P}}$  value in the activated carbon system is the smallest of the three. In all PM systems, the  $K_{\text{W-P}}$  value using THA was larger than those employing SRHA and LHA. This result suggests that THA has a greater ability to enhance the water solubility of DEHP, which was also shown in the octanol–water partition experiment in Figure 2. In Figure 4a–c,  $K_{\text{W-P}}$  values were all very small when  $[\text{HA}]_{\text{aq}} = 0$ . This result also indicates that PMs have a strong affinity for the hydrophobic organic matters as reported by many investigators (Filius *et al.*, 2000; Zhao and Vance *et al.*, 1998).



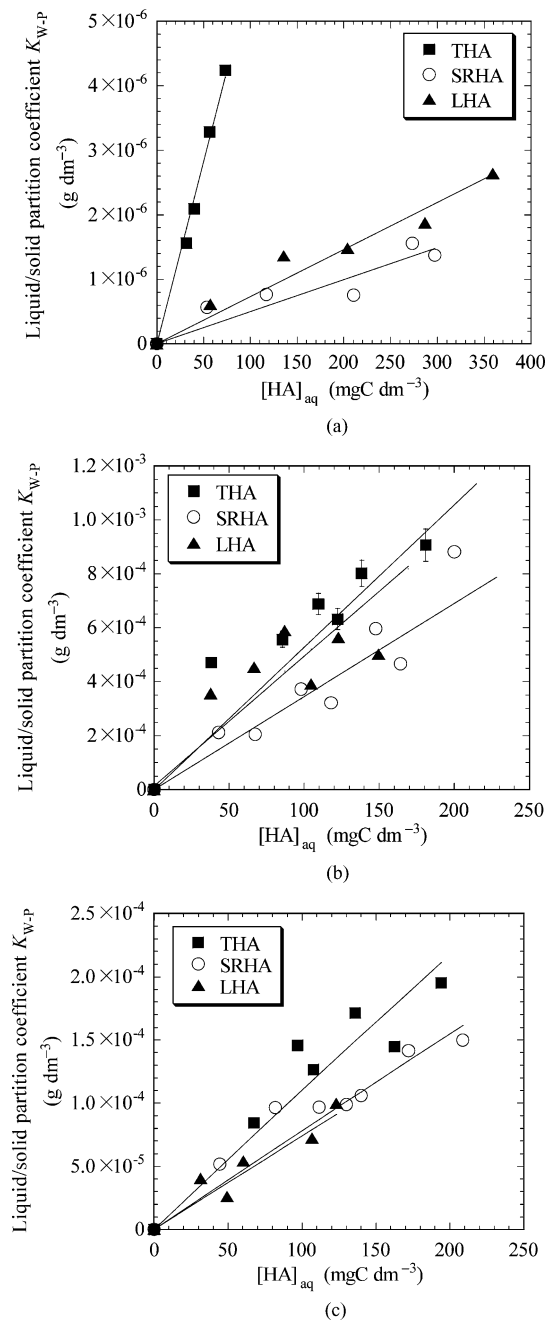


Figure 4. Relationship between  $[HA]_{aq}$  and the liquid/solid partition coefficient ( $K_{W-P}$ ) of DEHP in the presence of various concentrations of HA and 10 mg of activated carbon (a), ferrihydrite (b), or kaolinite (c). The regression curves using the model described by Equations (2), (5–10) (pH 6, 0.010 M acetate buffer) are also shown.

## 4. Discussion

### 4.1. INFLUENCE OF HA ON THE OCTANOL–WATER PARTITIONING OF DEHP

To interpret quantitatively the enhancement of water solubility of DEHP by HA, the binding constant ( $K_{\text{eq}}/\text{M}^{-1}$ ) between water and HA phase is defined as:

$$K_{\text{eq}} = \frac{[\text{DEHP} - \text{HA}]_{\text{aq}}}{[\text{DEHP}]_{\text{aq}} [\text{HA}]_{\text{aq}}} \quad (3)$$

where  $[\text{HA}]_{\text{aq}}$  and  $[\text{DEHP} - \text{HA}]_{\text{aq}}$  indicate the concentration of HA in the aqueous phase and the concentration of DEHP forming a complex with HA, respectively. Assuming that  $[\text{DEHP}]_{\text{aq}}$  in the octanol–water system when HA is absent is equal to the free  $[\text{DEHP}]$  (freely dissolved, not bound to HA) in the presence of HAs, the reciprocal  $K'_{\text{ow}}$  can be written as:

$$\frac{K_{\text{ow}}}{K'_{\text{ow}}} = 1 + K_{\text{eq}} [\text{HA}]_{\text{aq}} \quad (4)$$

where  $K'_{\text{ow}}$  is the apparent octanol–water partition coefficient of DEHP in the presence of HA. Equation (4) shows the relationship between  $1/K'_{\text{ow}}$  and  $[\text{HA}]_{\text{aq}}$ , where  $K_{\text{eq}}$  could be evaluated by a least-square regression of the experimental data set.

The linear regression lines in Figure 5 were obtained using Equation (4). Although non-linear binding of NOS to HA is often measured (e.g., Laor and Rebhun, 2002), the linear equation was employed in this study, since Equation (4) can fit to the octanol–water partition behaviour of DEHP for the SRHA and LHA systems in this  $[\text{HA}]_{\text{aq}}$  region. In Figure 5, the fitting to the THA data is not fine compared to those of LHA and SRHA. This discrepancy might result from the increase of hydrophobicity of humic acid induced by the aggregation of HA in high  $[\text{HA}]_{\text{aq}}$  range ( $[\text{HA}]_{\text{aq}} > 80 \text{ mgC dm}^{-3}$ ). It is known that the aggregation of HA facilitates solubilization of hydrophobic compounds (Terashima *et al.*, 2004). This hypothesis is supported by the results that the C/H ratio (the indicator of hydrophobicity of THA) is higher than LHA and SRHA and that the hydrophobic HA can be readily subject to aggregation. These facts can explain the discrepancy in the fitting for THA in Figure 5. An increase in hydrophobicity by the aggregation can cause the greater  $K_{\text{ow}}/K'_{\text{ow}}$  value at higher THA concentration. The evaluated  $K_{\text{eq}}$  values are summarized in Table III. Although the fitting to the THA system is not good, the  $K_{\text{eq}}$  value of THA seems to be larger than those of LHA and SRHA. From the elemental composition (Table II), the C/H ratio for THA is larger than those for LHA and SRHA. This suggests that THA contains a larger number of unsaturated carbons, since the C/H ratio is an index of the degree of unsaturation (Xing, 2001). Moreover, the number of acidic sites for THA is smaller than those for LHA and SRHA. These facts suggest that the larger  $K_{\text{eq}}$  value for THA can be ascribed to the larger degree

TABLE III

Binding constant between DEHP and humic acids (HAs) in octanol-water and ternary systems (presence of HA and particles). The  $a_{\text{HA}}$  and  $[\text{HA}]_{\text{max}}$  are evaluated by a least-squares analyses using Equation (7).

HA	Octanol-water,	Activated carbon			Ferrihydrite			Kaolinite		
	$K_{\text{eq}}$	$\log K_{\text{eq}}$	$\log a_{\text{HA}}$	$\log [\text{HA}]_{\text{max}}$	$\log K_{\text{eq}}$	$\log a_{\text{HA}}$	$\log [\text{HA}]_{\text{max}}$	$\log K_{\text{eq}}$	$\log a_{\text{HA}}$	$\log [\text{HA}]_{\text{max}}$
THA	3.1	2.4	-1.4	1.6	2.9	-1.8	1.4	2.4	-2.0	1.4
LHA	2.3	1.5	-2.3	2.3	2.9	-2.3	1.8	2.3	-2.8	2.5
SRHA	1.9	1.4	-2.0	2.1	2.9	-2.2	1.4	2.3	-2.9	2.2

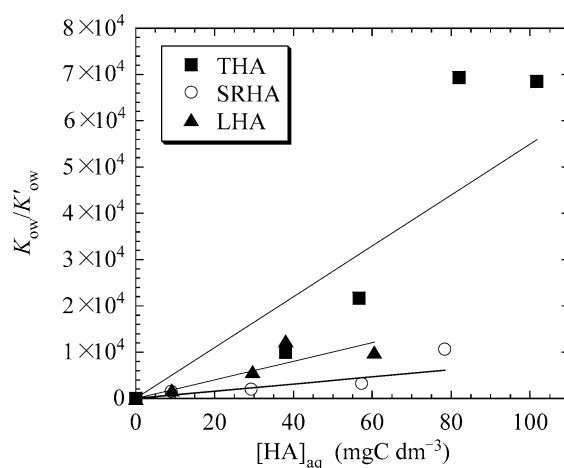


Figure 5. Relationship between  $[\text{HA}]_{\text{aq}}$  and  $1/K'_{\text{ow}}$  in the octanol-water system. The regression lines using the model described by Equations (2-5) (pH 6, 0.010 M acetate buffer) are shown.

of hydrophobicity of THA, which increases the stability of HA-DEHP complex through the hydrophobic interaction.

The importance of the hydrophobic interaction between DEHP and HA is also supported by the pH dependence. At lower pH, the degree of ionization of HA decreases, which reduces the negative charges on HA.

The present study clearly indicates that the water solubility of DEHP, or phthalate esters, is greatly affected by HA and the characteristics of the HA in the system (such as hydrophobicity etc.). Although  $[\text{HA}]_{\text{aq}}$  in our experiments ( $[\text{HA}]_{\text{aq}} > 50 \text{ mgC dm}^{-3}$ ) is relatively high compared with natural aquifer, the dependence on the characteristics of HA and pH may be valid in any environment. In addition, some natural environments have higher  $[\text{HA}]_{\text{aq}}$  such as in pore water in the sediment, where we can apply our results directly to the relation between HA and the water solubility of DEHP.

## 4.2. DESORPTION OF DEHP FROM PM IN THE PRESENCE OF HA

Similar to the octanol–water system, the partition coefficient  $K_{W-P}$  can be written using a micelle-like partition model in the following form:

$$K_{W-P} = \frac{[\text{DEHP}]_{\text{aq}} (1 + K_{\text{eq}} [\text{HA}]_{\text{aq}})}{[\text{DEHP}]_{\text{PMs}}} \quad (5)$$

If the sorption reaches equilibrium, it is considered that a part of DEHP on the PM is present as DEHP–HA complex ( $[\text{HA–DEHP}]_{\text{ads}}$ ) and as DEHP ( $[\text{DEHP}]_{\text{ads}}$ ) free from HA:

$$K_{W-P} = \frac{[\text{DEHP}]_{\text{aq}} (1 + K_{\text{eq}} [\text{HA}]_{\text{aq}})}{[\text{DEHP}]_{\text{ads}} + [\text{HA–DEHP}]_{\text{ads}}} \quad (6)$$

The sorption of HA on PM has usually been interpreted by Langmuir isotherm (Murphy *et al.*, 1992; Takahashi *et al.*, 1998b), which can be represented by

$$[\text{HA}]_{\text{ads}} = \frac{a_{\text{HA}} [\text{HA}]_{\text{max}} [\text{HA}]_{\text{aq}}}{1 + a_{\text{HA}} [\text{HA}]_{\text{aq}}} \quad (7)$$

where  $a_{\text{HA}}$  ( $\text{mgC dm}^{-3}$ ),  $[\text{HA}]_{\text{ads}}$  ( $\text{mgC g}^{-1}$ ), and  $[\text{HA}]_{\text{max}}$  ( $\text{mgC g}^{-1}$ ) are the sorption coefficient of HA on PM, the concentration of HA sorbed on PM, and the amount of maximum sorption of HA on PM, respectively. The Langmuir isotherm in Equation (7) can be rearranged as follows:

$$\frac{1}{[\text{HA}]_{\text{ads}}} = \frac{1}{[\text{HA}]_{\text{max}}} + \frac{1}{a_{\text{HA}} [\text{HA}]_{\text{max}} [\text{HA}]_{\text{aq}}} \quad (8)$$

The  $a_{\text{HA}}$  and  $[\text{HA}]_{\text{max}}$  obtained by least-squares analyses using Equation (7) are summarized in Table III.

On the other hand, both HA and HA–DEHP species are sorbed on activated carbon. However, since the DEHP molecule is much smaller than the HA macromolecule, we can assume on the first approximation that the sorption behaviour of HA–DEHP on PM is similar to that of HA (Fukushima *et al.*, 1997):

$$[\text{HA–DEHP}]_{\text{ads}} = \frac{[\text{HA}]_{\text{ads}}}{[\text{HA}]_{\text{aq}}} \text{HA} - [\text{DEHP}]_{\text{aq}} \quad (9)$$

where  $[\text{HA–DEHP}]_{\text{aq}}$  is the concentration of DEHP–HA complex in the aqueous solution. Using Equations (5–7) and (9), the partition coefficient of DEHP ( $K_{W-P}$ )

between PM and aqueous solution can be expressed as

$$K_{W-P} = \frac{1 + K_{eq} [HA]_{aq}}{\frac{1}{K_{W-P}^0} + \frac{a_{HA} K_{eq} [HA]_{max} [HA]_{aq}}{1 + a_{HA} [HA]_{aq}}} \quad (10)$$

where  $K_{W-P}^0$  is equal to  $[DEHP]_{aq}/[DEHP]_{ads}$ , an equilibrium of free DEHP between aqueous and sorbed species. Equation (10) shows the relationship between  $K_{W-P}$  and  $[HA]_{aq}$ , where  $K_{eq}$  could be determined by a nonlinear least-square regression analysis of the experimental data set. Actually, since the second term in the denominator of Equation (10) is much smaller ( $< 10^3$ ) than the first term ( $= 1/K_{W-P}^0$ ), the calculated curves based on Equation (10) become approximately linear in the  $[HA]_{aq}$  region as shown in Figures 4a–c.

The evaluated  $K_{eq}$  values are summarized in Table III. For the LHA and SRHA systems,  $K_{eq}$  values decreased in the order of ternary (ferrihydrite) > ternary (kaolinite)  $\approx$  octanol/water partition > ternary (activated carbon). The E4/E6 ratio of the spectra at pH4.5, an indicator of aromaticity of HA in solution (Stevenson, 1994), showed that THA in the solution after adsorbing to activated carbon (E4/E6 = 3.3) was less aromatic and hydrophobic than original THA (E4/E6 = 2.9). This trend indicated that the more hydrophobic fraction of the HA may be sorbed selectively on the surface of activated carbon and the more hydrophilic fraction remains in the aqueous phase, since activated carbon has neutral nature in the electronic property of the surface (Li *et al.*, 2002). Contrary to that, under the pH value (pH 6) in this study, the surface of ferrihydrite has positive charges (Langmuir, 1997). Thus, it is suggested that the more hydrophilic fraction of the original HA is selectively sorbed on the surface of ferrihydrite, and the more hydrophobic remains in the aqueous phase. Thus, in the ternary system, the fractionation of HA should occur during sorption experiments, which may alter the affinity of HA remaining in the aqueous phase for DEHP from the original HA without any fractionation. In all PM systems, since  $[HA-DEHP]_{ads}$  is much smaller than  $[DEHP]_{ads}$ , we can ignore the presence of  $[HA-DEHP]_{ads}$  in Equation (10). Thus, we can treat the partition of DEHP between solid and liquid phase as the competition of  $[DEHP-HA]_{aq}$  with  $[DEHP]_{ads}$ . Therefore, the  $K_{eq}$  obtained based on Equation (10) reflects the affinity for DEHP of the HA fraction remaining in the aqueous phase. The  $K_{eq}$  values for ferrihydrite were larger than that in the octanol–water system probably due to the increase of hydrophobicity in the HA fraction remaining in the aqueous phase, while that for activated carbon became smaller than that in the octanol–water system, which represents the  $K_{eq}$  in the absence of the PMs. These results lead to the conclusion that the fractionation of HA induced by sorption on PM influences the retention of DEHP in the aqueous phase by HA.

Among three HAs,  $K_{eq}$  values for THA are relatively similar among four systems (octanol–water system and three ternary systems). In addition, the  $K_{eq}$  values for the THA systems are again larger than those of SRHA and LHA as

observed in the octanol–water partition system (Table III). These results may be due to the small  $\log[\text{HA}]_{\text{max}}$  values for THA in the ternary systems, which suggests that the fraction remaining in the aqueous phase is largest for THA among the three HAs. This situation causes that the  $K_{\text{W-P}}$  value was not influenced greatly by the re-sorption of THA–DEHP on the PM compared to other HAs. As a result, the range of  $K_{\text{eq}}$  values in the three ternary systems and octanol–water system was smaller for THA compared with those observed for SRHA and LHA.

Figure 6 shows the comparison between the sediment–water partition coefficient  $K_{\text{W-P}}$  ( $\text{g dm}^{-3}$ ) for DEHP in natural samples and the solid–water partition coefficients estimated from the present results in the ternary system employing SRHA as DOC. Partition coefficient  $K_{\text{W-P}}$  in our study was calculated by assuming that (1) the organic concentration in the solid is 1–10 wt% ( $\text{g g}^{-1}$ , dry weight) (Kyuma *et al.*, 1984) at pH 6, (2) the three PMs studied here are the main active components for sorption of DEHP in the sediments, and (3) the concentration of each PM in sediments is 10 wt% ( $\text{g g}^{-1}$ ). The  $K_{\text{W-P}}$  values in natural samples ranges from  $10^{-4}$  to  $10^{-3}$   $\text{g dm}^{-3}$ . The  $K_{\text{W-P}}$  value ranges calculated for the kaolinite and ferrihydrite system overlap with those of natural samples. The  $K_{\text{W-P}}$  values of Turano River and Ventina Lake are lower than the ferrihydrite and kaolinite systems. This suggests that the sediments in the two natural systems contain some phases having lower  $K_{\text{W-P}}$  values, such as activated carbon. This hypothesis is supported by Bucheli and Gustafsson (2003), where it is reported that 2–20% of the organic materials in sediment may consist of elemental carbon/soot. The elemental carbon/soot is a very

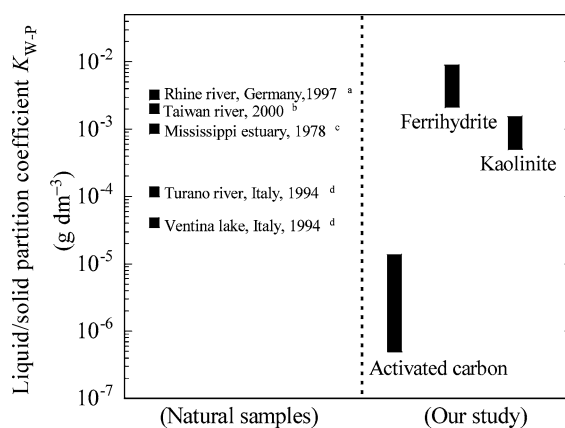


Figure 6. Comparison of liquid/solid partition coefficient ( $K_{\text{W-P}}$ ) of DEHP in natural aquifers and the values estimated based on our study assuming activated carbon, ferrihydrite, or kaolinite as the active particles in the sediment. The  $K_{\text{W-P}}$  estimated from our study was calculated by assuming that the concentration of humic acid (using the data for SRHA) in solid is 1–10 wt.%, which produces the range in the plot of the calculated  $K_{\text{W-P}}$  values. The  $K_{\text{W-P}}$  values for natural aquifers were calculated based on <sup>a</sup>Fromme *et al.*, 2003; <sup>b</sup>Yuan *et al.*, 2002; <sup>c</sup>Giam *et al.*, 1984; <sup>d</sup>Vitali *et al.*, 1997.

strong sorbent for DEHP, which may show sorption properties similar to activated carbon.

## 5. Conclusions

The present study shows that water solubility of DEHP can be significantly increased by HA in the octanol-water system and DEHP/HA/particulate matter (ternary) system. It was indicated that the degree of hydrophobic nature of HA is a key parameter controlling the distribution of DEHP into water. In the ternary system, it was suggested that the fractionation of HA induced by the sorption on particulate matters affects the distribution of DEHP into water among different particulate matters. For example, ferrihydrite prefers hydrophilic fraction in HA, which leads to the increase of hydrophobicity of HA remaining in water. As a result,  $K_{eq}$  values (binding constant between HA and DEHP) apparently decreased in the ferrihydrite/HA/DEHP system. Although these results are similar to those obtained for other non-polar organic solutes, this is the first paper studying the interaction between humic substances and DEHP, or phthalic esters. It is expected that  $K'_{ow}$ ,  $K_{eq}$ , and other parameters obtained for DEHP in this study will enable us to estimate approximately the distribution coefficients of DEHP, or phthalic esters, in solid-water system in natural aquifer.

## Acknowledgements

We thank the members of the Radioisotope Center in the Natural Science Center for Basic Research and Development (N-BARD) in Hiroshima University for their assistance for the experiments using the facility. This research was supported by a grant-in-aid for scientific research from the Japan Society for the Promotion of Science.

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