Evaluation of Interactions between Hydrophobic Organic Pollutants and Humic Substances

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Abstract

To better understand the fate and behavior of hydrophobic organic pollutants (HOPs) in aquatic and soil environments, the nature of hydrophobic interactions between HOPs and humic substances (HSs) was evaluated. The partition coefficient of HOPs dissolved in organic carbon (DOC) of HSs (K_{doc}) is known to be an important physicochemical parameter that indicates the magnitude of such interactions. Once K_{doc} is evaluated, methods for the speciation of HOPs (i.e., unbound and bound species with HSs) can easily be selected based on the chemical properties of HOPs, such as the octanol-water partition coefficient. The present review surveys the advantages as well as the disadvantages of methods for analyzing the species of HOPs in aqueous solutions containing HSs. In addition, considering the structural heterogeneous character of HSs, recent issues concerning the influence of the chemical properties of HSs on K_{doc} are also reviewed. The partitioning of HOPs into HSs can also influence the fate as well as the mobility and diffusion of HOPs in subsurface water and soil porefluid. Therefore, recent studies of the influence of HOP partitioning in HSs on biotic and abiotic degradation are also reviewed.

Introduction

Humic substances (HSs) are the most widely distributed terrestrial organic materials on the surface of the earth, and are known to be the major source of dissolved organic carbon (DOC) in aquatic environments. In general, HSs can be classified into two main fractions: humic (HA) and fulvic (FA) acids. HSs have amphiphilic characteristics because they contain both hydrophilic and hydrophobic moieties in their structures (Shinozuka et al., 1987 and 1991). Thus, HSs can act as a surfactant in aqueous solutions and such characteristics are crucially important in determining the fate of hydrophobic organic pollutants (HOPs) in aquatic and soil environments (Chiou et al. 1979 and 1986; Gauthier et al. 1986; Backhus and Gschwend, 1990). In particular, the

affinity of HOPs for HSs can alter the migration rates, biological degradation, photolysis and the volatilization of chemicals. In the past, HSs have not been considered to be an environmental compartment in the development of predictive transport and fate models. However, Caron et al. (1985) has shown that, for DDT, the fraction of HOPs associated with HSs is greater than the fraction associated with suspended sediments or biota.

In an aqueous system containing HSs, to quantify the degree of partitioning HOPs in the DOC of HSs, the partition coefficient (K_{doc}) has been employed as a physicochemical parameter. In general, HSs are regarded to be heterogeneous mixtures, and their chemical composition differs greatly, depending on the origin of the soil. Thus, to compare the K_{doc} values for a variety of HSs and HOPs, the K_{doc} values

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must be normalized to units of organic carbon. K_{doc} values are crucially important in predicting the behavior of HOPs: e.g., soil distribution and the transport of HOPs from soil to an aquatic environment. A number of K_{doc} values for a variety of HOPs have previously been reported (Table 1). K_{doc} values can also be predicted from the octanol-water partition coefficient (K_{OW}) (e.g. Chiou et al., 1986). Thus, the K_{OW} values for HOPs are also listed in Table 1. For evaluating K_{doc}, a speciation analysis of HOPs (i.e., unbound and bound species of HOPs) is required. For this purpose, solubility enhancement, fluorescence quenching, solid-phase extraction, solvent extraction and dialysis have been employed in attempts to measure bound and/or unbound species of HOPs with HSs. The method of choice depends on the types of HOPs, their concentrations, the volume of the sample, the sensitivity or detection limit of the apparatus and so on. In the present review, we first focused on the advantages and disadvantages of methods for evaluating K_{doc}. Secondly, because of the heterogeneous nature of HSs, their chemical composition varies with type. Thus, recent issues concerning the influence of the chemical properties of HSs on K_{doc} are also reviewed.

On the other hand, in aquatic and soil environments, HSs are also thought to be involved in the apparent anomalous effect of solid concentration on the sorptive partitioning of HOPs to suspended sediments and soils (Gschwend and Wu, 1985; Voice et al., 1985). In the case of dissolved HSs, K_{doc} can generally be evaluated by the linear relationships between the concentration of organic carbon in HSs and the ratio of water solubility in the presence to absence of HSs, as described by Chiou et al. (1986). However, in the presence of a solid phase such as soil particles, relationships between the concentrations of organic carbon and the HOPs bound to HSs are nonlinear because of the partitioning of HOPs to both dissolved and adsorbed HSs (Magee et al., 1991; Fukushima et al., 1997). Thus, an interpretation of the partition equilibrium between the three phases (i.e., water, dissolved HS and adsorbed HS to soil particles) should be addressed in the case of transport of HOPs in subsurface environments, such as soil porefluids and the water-soil interface. The focus of the present review is on the environmental significance of HOPs partitioning into both dissolved and adsorbed HSs.

Principal and Method for Evaluating K_{doc}

Solubility enhancement

It has been reported that the presence of aqueous solutions of HSs can result in an enhancement in the apparent water solubility of HOPs. Wershaw et al. (1969) reported that the apparent water solubility of DDT in the presence of 0.5% sodium humate was 200 times larger than that in pure water (5.5 □ g dm⁻³). This can be attributed to partition-like interactions between DDT and hydrophobic regions of dissolved HSs (Chiou et al., 1986 and 1987). The most useful equation for indicating the water solubility enhancement of HOPs in the presence of HSs was proposed by Chiou et al. (1986). The dissolution and partition equilibria of HOP can be written as follows:

$$HOP\,(s) \;\rightleftharpoons\; HOP\,(aq) \qquad (1)$$
$$HOP\,(aq) + HS \;\rightleftharpoons\; HOP\text{–}HS \qquad (2)$$
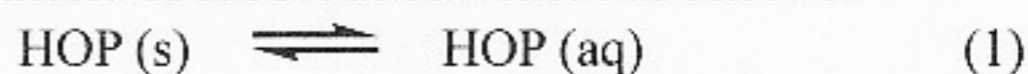
where HOP (s), HOP (aq) and HOP–HS denote HOP in the solid phase, dissolved HOP, and HOP partitioned to dissolved HSs, respectively. The apparent water solubility of HOP in the absence of HSs (S_w^0) and in the presence of HSs (S_w^*) can, respectively, be written as follows:

$$S_w^0 = [HOP]_{aq} \qquad (3)$$
$$S_w^* = [HOP]_{total} = [HOP]_{aq} + [HOP]_{HS} \qquad (4)$$

where $[HOP]_{aq}$ and $[HOP]_{HS}$ represent apparent concentrations of HOP in both aqueous and HS phases based on the total solution volume (mol dm⁻³). In addition, $[HOP]_{total}$ is the total concentration of HOP in the solution (mol dm⁻³). The partition coefficient of HOP between aqueous and HS phases (K_{doc}) can be defined as:

$$K_{doc} = \frac{[HOP]_{doc}}{[HOP]_{aq}[DOC]} \qquad (5)$$

where [DOC] denotes the HS concentration normalized to the dissolved organic carbon (DOC) (kg of C dm⁻³). Combining eqs. (3) – (5), the following relationship between S_w^*/S_w^0 and [DOC] can be derived:

$$S_w^* / S_w^0 = 1 + K_{doc}\,[DOC] \qquad (6)$$

Equation (6) shows that the S_w^* / S_w^0 increase linearly with increasing [DOC]. As shown in Fig. 1, the K_{doc} value can be evaluated from the slope of the liner line.

In the solubility enhancement method, the precision and accuracy of the K_{doc} values are highly dependent on the analytical methods used in measuring the water solubility of an HOP. The key procedures are (1) the preparation of sample solutions and (2)

Table 1. The $\log K_{OW}$ values and the ranges of reported $\log K_{doc}$ values for a variety of HOPs into HSs.

Compounds	$\log K_{OW}$ [a]	K_{doc} (dm^3 Kg^{-1} C)	Methods	Literatures
Monoaromatic hydrocarbons				
1,1'-methylenebis-benzene	4.14 [a]	3.30 – 3.65	SPME	Kopinke, F-D., et al., 1995
Stilbene	4.81 [a]	3.60 – 4.20	SPME	Kopinke, F-D., et al., 1995
Polycyclic Aromatic Hydrocarbons (PAHs)				
Naphthalene	3.37 [b]	3.02	Dialysis	McCarthy and Jimenez, 1985
		4.28	SPE	Brown and Peake, 2003
2-Methylnaphthalene	3.87 [a]	3.40 – 3.65	SPME	Kopinke, F-D., et al., 1995
Acenaphthylene	4.00 [c]	3.70 – 4.05	SPME	Kopinke, F-D., et al., 1995
		3.96	SPE	Li and Lee, 2000
		4.34	SPE	Brown and Peake, 2003
Acenaphthene	3.92 [c]	3.45 – 3.80	SPME	Kopinke, F-D., et al., 1995
		3.66	SPE	Li and Lee, 2000
		4.17	SPE	Brown and Peake, 2003
Biphenyl	4.09 [b]	3.27	SPE	Landrum et al., 1984
Fluorene	4.18 [a]	3.50 – 3.95	SPME	Kopinke, F-D., et al., 1995
		3.75	SPE	Li and Lee, 2000
Phenanthrene	4.57 [b]	3.92	SPE	Landrum et al., 1984
		3.92	SPE	Brown and Peake, 2003
		4.70	Fluorescence quenching	Gauthier et al., 1986
		4.64	Fluorescence quenching	Magee et al., 1991
		4.12	SPE	Li and Lee, 2000
		4.67	Centrifugation	Salloum et al., 2002
Anthracene	4.54 [b]	4.1 – 4.5	Fluorescence quenching	Schlautman and Morgan, 1993
		4.30	SPE	Landrum et al., 1984
		4.15	Dialysis	McCarthy and Jimenez, 1985
		4.93	Fluorescence quenching	Gauthier et al., 1986
		4.08 – 5.00	Fluorescence quenching	Perminova et al., 1999
		4.0	SPE	Li and Lee, 2000
		4.41	SPE	Brown and Peake, 2003
Pyrene	5.18 [c]	4.74 – 5.21	Fluorescence quenching,	Gauthier et al., 1986,
		4.70	Solubility enhancement	Schlautman and Morgan, 1993,
		3.96 – 5.17	Solubility enhancement	Chin et al., 1997
		4.11 – 5.38	Fluorescence quenching	Perminova et al., 1999
		4.62	SPE	Li and Lee, 2000
		3.83 – 5.09	SPME	Kopinke, et al., 2001
		4.21 – 4.96	SPME	Mackenzie et al., 2002
		4.87 – 5.54	Fluorescence quenching	
		5.21	SPE	Brown and Peake, 2003
Fluoranthene	5.22 [c]	5.32	Fluorescence quenching	Rav-Acha and Rebhun, 1992
		4.95	Fluorescence quenching	Chen, et al., 1994
		4.43 – 5.26	Fluorescence quenching	Perminova et al., 1999
		4.58	SPE	Li and Lee, 2000
		4.99	SPE	Brown and Peake, 2003
Benzo[a]anthracene	5.91 [c]	5.30 – 5.39	SPE	Landrum et al., 1984
		5.17	Dialysis	McCarthy and Jimenez, 1985
		5.15	SPE	Li and Lee, 2000
		5.30	SPE	Brown and Peake, 2003
Chrysene	5.86 [c]	5.16	SPE	Li and Lee, 2000
		5.39	SPE	Brown and Peake, 2003
Perylene	6.25 [c]	4.1 – 5.1	Fluorescence quenching	Schlautman and Morgan, 1993
Benzo[a]pyrene	6.04 [c]	5.95	SPE	Landrum et al., 1984
		6.12	Dialysis	McCarthy and Jimenez, 1985
		4.68 – 5.54	Dialysis, SPE	Kukkonen and Pellinen, 1994
		4.53	Dialysis	Paolis and Kukkonen, 1997
		5.68	SPE	Li and Lee, 2000
		5.84	SPE	Brown and Peake, 2003
Benzo[b]fluoranthene	5.80 [c]	5.70	SPE	Li and Lee, 2000
		5.80	SPE	Brown and Peake, 2003
Benzo[k]fluoranthene	6.00 [c]	5.56	SPE	Li and Lee, 2000
		5.78	SPE	Brown and Peake, 2003
Dibenzo[a,h]anthracene	6.75 [c]	5.59	SPE	Li and Lee, 2000
		6.16	SPE	Brown and Peake, 2003

Compounds	log K_{OW}[a]	K_{doc} (dm³ Kg⁻¹ C)	Methods	Literatures
Benzo[ghi]perylene	6.50[c]	5.65	SPE	Li and Lee, 2000
		6.11	SPE	Brown and Peake, 2003
Indeno[1,2,3-cd]pyrene	7.04[f]	5.87	SPE	Li and Lee, 2000
		6.54	SPE	Brown and Peake, 2003
Volatile organic chemicals (VOC)				
Trichloroethylene	2.29[d]	0.616 – 2.20	Headspace analysis	Garbarini and Lion, 1985
		1.79	Headspace analysis	Peterson et al, 1988; quoted. Grathwohl. 1990.
Chlorinated benzenes				
1,4-Dichlorobenzene	3.4[e]	2.91	Liquid-liquid extraction	Chin et al., 1990
1,2,3-Trichlorobenzene	4.14[f]	2.0 – 3.0	Solubility enhancement	Chiou et al., 1986
1,2,4-Trichlorobenzene	4.0[e]	3.32	Liquid-liquid extraction	Chin et al., 1990
Pentachlorobenzene	5.18[b]	4.50	SPME	Ramos et al., 1998
Hexachlorobenzene	5.73[b]	4.91	Dialysis	Enfield et al., 1989
		5.1	SPE	Freidig et al., 1998
		4.1 – 5.1	SPME	Ramos et al., 1998
		4.11 – 4.90	SPME	Yabuta et al., 2004
Chlorinated phenols				
2,4,6-Trichlorophenol	3.75[g]	2.81 – 3.03	Gel Permeation	Robinson and Novak, 1994
Pentachlorophenol	4.84 (pH 1.2)[h]	< 3.9	Dialysis	Paolis and Kukkonen, 1997
	3.56 (pH 6.5)[h]			
	3.32 (pH 7.2)[h]			
	3.86 (pH 13.5)[h]			
Polychlorinated dibenzo-p-dioxins (PCDDs)				
1,2,3,7-tetrachloro dibenzo-*p*-dioxin	6.9[i]	5.39 – 6.55	SPE	Webster et al., 1986
1,3,6,8-tetrachloro dibenzo-*p*-dioxin	7.1[i]	2.05-2.38	SPE	Servos and Muir, 1989
2,3,7,8-tetrachloro dibenzo-*p*-dioxin	6.8[c]	4.71 – 5.59	Dialysis, SPE	Kukkonen and Pellinen, 1994
		6.9	Centrifugation	Walters and Guiseppi-Elie, 1988 (Walters et al., 1989)
1,2,3,4,7-pentachloro dibenzo-*p*-dioxin	7.40[c]	4.85 – 6.38	SPE	Webster et al., 1986
1,2,3,4,7,8-hexachloro dibenzo-*p*-dioxin	7.80[c]	5.41 – 6.32	SPE	Webster et al., 1986
1,2,3,4,6,7,8-heptachloro dibenzo-*p*-dioxin	8.00[c]	6.09 – 7.19	SPME	Yabuta et al., 2004
		6.35 – 7.65	SPME	Tanaka et al., 2004
Polychlorinated biphenyls (PCBs)				
2,2',5-trichlorobiphenyl	5.6[i]	4.85	Liquid-liquid extraction	Chin et al., 1990
2,2',5'-trichlorobiphenyl	4.73[k]	3.66 – 4.16	Solubility enhancement	Uhle et al., 1999
2,4,4'-trichlorobiphenyl	5.62[k]	3.54 – 4.40	Solubility enhancement	Chiou et al., 1986
3,3',4,4'-tetrachlorobiphenyl	6.26[k]	4.17 – 5.97	Dialysis, SPE, SPME	Kukkonen and Pellinen, 1994,
		4.57 – 4.71	Solubility enhancement	Uhle et al., 1999
2,2',5,5'-tetrachlorobiphenyl	6.1[j]	4.86	Gas purging	Hassett and Milicic, 1985
2,2',5,6'-tetrachlorobiphenyl	5.5[k]	3.63 – 4.16	Solubility enhancement	Uhle et al., 1999
2,5,2',5'-tetrachlorobiphenyl	6.26[f]	4.40	SPE	Landrum et al., 1984
2,2',3,5',6-pentachlorobiphenyl	6.4[j]	3.70 – 4.60	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4',5-pentachlorobiphenyl	6.5[k]	3.75 – 4.75	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4,5'-pentachlorobiphenyl	6.5[j]	3.75 – 4.87	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',4,5,5'-pentachlorobiphenyl	6.4[j]	3.86 – 4.86	Liquid-liquid extraction	Lara and Ernst, 1989
2,3,3',4',6-pentachlorobiphenyl	6.3[k]	3.79 – 4.80	Liquid-liquid extraction	Lara and Ernst, 1989
2,4,5,2',5'-pentachlorobiphenyl	6.11[b]	4.07 – 4.87	Solubility enhancement	Chiou et al., 1986
2,2',3,3',6,6'-hexachlorobiphenyl	6.7[k]	4.27 – 5.05	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',5,6-hexachlorobiphenyl	7.3[k]	4.41 – 5.18	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4,4',5'-hexachlorobiphenyl	6.7[j]	4.60 – 5.22	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4',5,5'-hexachlorobiphenyl	—	4.58 – 5.22	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,5,5',6-hexachlorobiphenyl	6.7[k]	4.41 – 5.11	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',4,4',5,5'-hexachlorobiphenyl	6.9[j]	4.62 – 5.26	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,4',5-heptachlorobiphenyl	6.7[j]	4.99 – 5.63	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,5,5'-heptachlorobiphenyl	6.7[j]	4.97 – 5.71	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4',5,6-heptachlorobiphenyl	—	4.90 – 5.54	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4,4',5',6-heptachlorobiphenyl	—	4.92 – 5.53	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4,4',5,5'-heptachlorobiphenyl	7.2[i]	5.09 – 5.73	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,4',5,5',6-heptachlorobiphenyl	7.0[k]	4.90 – 5.51	Liquid-liquid extraction	Lara and Ernst, 1989

Compounds	log K_{OW}[a]	K_{doc} (dm^3 Kg^{-1} C)	Methods	Literatures
2,2',3,3',4,4',5,5'-octachlorobiphenyl	7.4[k]	5.36 – 5.94	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,4',5,6-octachlorobiphenyl	—	5.22 – 5.78	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,5,5',6-octachlorobiphenyl	—	5.23 – 5.91	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,5,5',6'-octachlorobiphenyl	—	5.31 – 5.91	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,5',6,6'-octachlorobiphenyl	—	5.10 – 5.68	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',5,5',6,6'-octachlorobiphenyl	7.1[j]	4.99 – 5.61	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	7.2[j]	5.69 – 6.15	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	8.16[k]	5.44 – 5.98	Liquid-liquid extraction	Lara and Ernst, 1989
2,2',3,3',4,4',5,5',6,6'-nonachlorobiphenyl	8.26[k]	5.61 – 6.19	Liquid-liquid extraction	Lara and Ernst, 1989
Aroclor1254		4.8 – 6.7	Solubility enhancement	Voice and Weber, 1985
Pesticides				
p,p'-DDT	6.36[b]	4.39 – 5.61	Solubility enhancement,	Carter and Suffet, 1982 Caron et al, 1985, Chiou et al., 1986
	5.83	SPE	Landrum et al., 1984	
	5.57	SPME	Ramos et al., 1998	
Lindane	3.70[b]	1.5 – 3.0	Solubility enhancement	Caron et al., 1985, Chiou et al., 1986
Parathion	3.83[m]	4.72	SPE	Johnson et al., 1991
Diazinon	3.3[m]	4.83	SPE	Johnson et al., 1991
Fenvalerate	6.2[n]	4.60	SPE	Day, 1991
		4.30	SPE	Fan et al., 1997
Insecticide				
α-Chlordane	6.0[o]	4.38	Liquid-liquid extraction	Chin et al., 1990
Herbicides				
Atrazine	2.5[p]	1.9 – 2.8	Ultrafiltration	Kulikova and Perminova, 2002
Antimicrobials				
4-Quinolones				
Flumequine	1.72[q]	3.17 – 4.44	SPME	Holten Lützhøft, et al., 2000
Oxolinic acid	0.68[r]	3.82 – 4.52	SPME	Holten Lützhøft, et al., 2000
Sarafloxacin	—	4.71 – 5.26	SPME	Holten Lützhøft, et al., 2000
Endocrine Disruptors				
17β-Estradiol	3.94, 4.01[f]	4.57 – 4.94	Fluorescence quenching	Yamamoto et al., 2003
17α-Ethynylestradiol	3.67, 4.12[f]	4.55 – 4.80	Fluorescence quenching	Yamamoto et al., 2003
Estriol	2.45, 2.81[f]	4.64 – 4.99	Fluorescence quenching	Yamamoto et al., 2003
p-Nonylphenol	5.76, 5.99[f]	4.70 – 4.96	Fluorescence quenching	Yamamoto et al., 2003
p-tert-Octylphenol	5.28, 5.85[f]	4.63 – 4.94	Fluorescence quenching	Yamamoto et al., 2003
Dibutylphthalate	4.57, 4.61[f]	4.65 – 4.95	Fluorescence quenching	Yamamoto et al., 2003
Organometals				
Monobutyl tin	—	3.15 – 3.25	SPME	Poerschmann et al., 1997
Dibutyl tin	—	3.45 – 3.80	SPME	Poerschmann et al., 1997
Triethyltin	0.6[s]	– 0.2	Dialysis	Arnold et al., 1998
Tripropyltin	—	1.3	Dialysis	Arnold et al., 1998
Tributyl tin	—	3.65 – 4.25	SPME	Poerschmann et al., 1997
	3.3	Dialysis	Arnold et al., 1998	
Tripentyl tin	—	5.0	Dialysis	Arnold et al., 1998
Triphenyl tin	—	2.7	Dialysis	Arnold et al., 1998
Tetraethyl tin	—	2.6 – 3.2	SPME	Poerschmann et al., 1997
Tetrabutyltin	—	3.80 – 4.45	SPME	Poerschmann et al., 1997
Copper(II)-oxinate	—	2.8 – 3.9	Solubility enhancement	Fukushima et al., 1994

Literatures of log K_{OW}: [a] Howard, 1993; [b] Schwarzenbach et al., 1993; [c] Mackay et al., 1992b; [d] Hansch and Leo, 1979; [e] Oliver and Charlton, 1984; [f] the same as the paper of log K_{doc}; [g] Suntio et al., 1988; [h] IPCS, 1987; [i] Shiu et al., 1988; [j] Shiu and Mackay, 1986; [k] Mackay et al., 1992a; [l] Brodsky et al., 1988; [m] Tomlin, 1994; [n] Schimmel et al., 1983; [o] Montgomery, 1993; [p] Iglesias-Jimenez et al., 1996; [q] Takács-Novác and Avdeef, 1996; [r] Takács-Novác et al., 1992; [s] Wulf and Byington, 1975 (log K_{OW} of hydroxide complex form in aqueous solution).
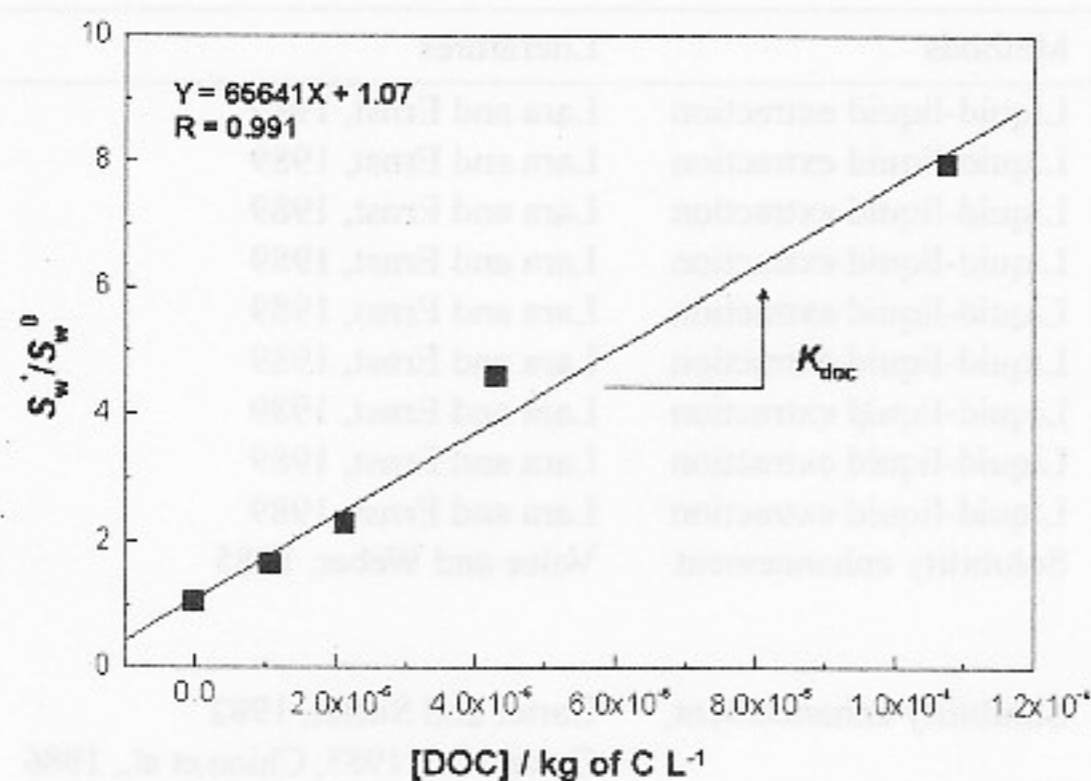
Figure 1. The relationship between S_w^*/S_w^0 for pyrene and [DOC]. Measurement conditions: pH 5, ionic strength 0.01, temp. 25°C. The S_w^0 value was evaluated to be 0.59 μmol dm^{-3}, and was used for the parameter in eq. (6). HA, derived from Bibai peat soil, was used. The solid line was obtained by the linear regression analysis.

the separation of excess HOPs from the solutions. Chiou et al. (1986) reported that repeated centrifugation and aspiration can completely eliminate excess HOPs. For the preparation of a test solution, Danielsen et al. (1995) and Chin et al. (1997) added HOPs in an organic solvent (e.g. acetone) to the centrifuge tube and then evaporated the solvent before adding aqueous solutions containing HSs. Because this method allows the amounts of HOPs to be minimized, the repeated centrifugation and aspiration procedures can be omitted. For separating HOPs from the sample solution, Tanaka et al. (1997) used a filtration technique instead of centrifugation and aspiration. This is a simple and rapid technique for separating excess HOPs from the sample solution. However, Kopinke et al. (1997) pointed out that the adsorption of HOPs by filtration equipment, such as the filter and funnel, was a significant factor during the filtration. To avoid such problems, the use of a glass fiber filter (< 0.4 μm) and rinsing the equipment with an aliquot of the equilibrium solution before the filtration are recommended. Due to these procedures, the water solubility of pyrene in pure water was determined to be 0.59 – 0.63 μmol dm^{-3}, and these values were in good agreement with the reported value (0.67 μmol dm^{-3}) (Kopinke et al., 1997).

The solubility enhancement method is a simple technique for evaluating K_{doc} values, compared to dialysis (Carter and Suffet, 1982; McCarthy and Jimenez, 1985) and reverse-phase separation (Landrum et al., 1984). In these methods, the deter-

mination of K_{doc} is based on the separation of unbound and bound species of HOPs to HSs. The separation of these species is difficult because of the loss of some HS fractions from the dialysis bag and some sorption of HOP–HS complexes to the reverse-phase materials. Therefore, these methods result in the underestimation of K_{doc} values (Mott, 2002).

There are some limitations to the solubility enhancement method. Enhancing water solubility is significant in HOPs that have a lower solubility in water and with a higher K_{ow} (e.g., p,p'-DDT, PCBs, PAHs). Thus, a significant enhancement in water solubility is not observed in less hydrophobic HOPs, such as lindane and 1,2,3,-trichlorobenzene (Chiou et al., 1986). If water solubility enhancement was not observed in the presence of HSs, the K_{doc}[DOC] term in eq. (6) could be much lower than 1. Assuming that [DOC] in the solubility enhancement method does not exceed 100 mg dm^{-3} (10^{-4} Kg C dm^{-3}), K_{doc} could be much lower than 10^4. To satisfy this condition, K_{doc} values should be lowered by one order of magnitude. Thus, the solubility enhancement method cannot be used for HOPs with log K_{doc} < 3. In addition, the relationships between log K_{doc} and log K_{OW} (Table 2 in Burkhard, 2000) suggest that the solubility enhancement method is not applicable to HOPs of which the log K_{OW} values are less than 3.6.

Fluorescence quenching

Fluorescence quenching is known to be a rapid, elegant, sensitive and reproducible method that dose not require complicated pretreatment processes or large amounts of HSs. Thus, this method has been widely applied to the determination of the K_{doc} values of fluorescent HOPs, such as PAHs. In principle, the fluorescence intensity of HOPs decreases with increasing concentrations of HSs, and the fluorescence quenching is believed to be due to the binding of HOPs to HSs. It should be noted that the fluorescence of HSs is included in the observed intensity of a sample solution containing both HOPs and HSs. Therefore, the background intensity in the presence of HSs should be subtracted from the observed intensity.

The K_{doc} values can quantitatively be evaluated according to a Stern-Volmer equation (Gauthier et al., 1986). In the presence of HSs, the partition equilibrium of HOPs can be represented as follows:

$$HOP + HS \rightleftharpoons HOP\text{--}HS \qquad (7)$$

$$K_{doc} = \frac{[HOP\text{-}HS]}{[HOP]_f[DOC]} \qquad (8)$$

where $[HOP]_f$ and $[HOP–HS]$ are the concentrations of free and bound species of HOPs (mol dm^{-3}), respectively. The concentration of HOPs in the absence of HSs ($[HOP]_0$) can correspond to the total concentration of HOPs, as shown in eq. (9):

$$[HOP]_0 = [HOP]_f + [HOP–HS] \qquad (9)$$

The $[HOP]_0$ also indicates the total concentration of HOPs. Combining eqs. (8) and (9), the linear relationship between $[HOP]_0 / [HOP]_f$ and [DOC] can be derived as:

$$[HOP]_0 / [HOP]_f = 1 + K_{doc}[DOC] \qquad (10)$$

If the fluorescence intensity can be attributed to the concentration of free HOP, the following equation (Stern-Volmer equation) can be derived:

$$F_0 / F = 1 + K_{doc}[DOC] \qquad (11)$$

where F_0 and F show the fluorescence intensity of HOPs in absence and presence of HSs, respectively. According to eq. (11), the K_{doc} value can then be calculated from the slope of the linear relationship between F_0 / F and [DOC] (Fig. 2).
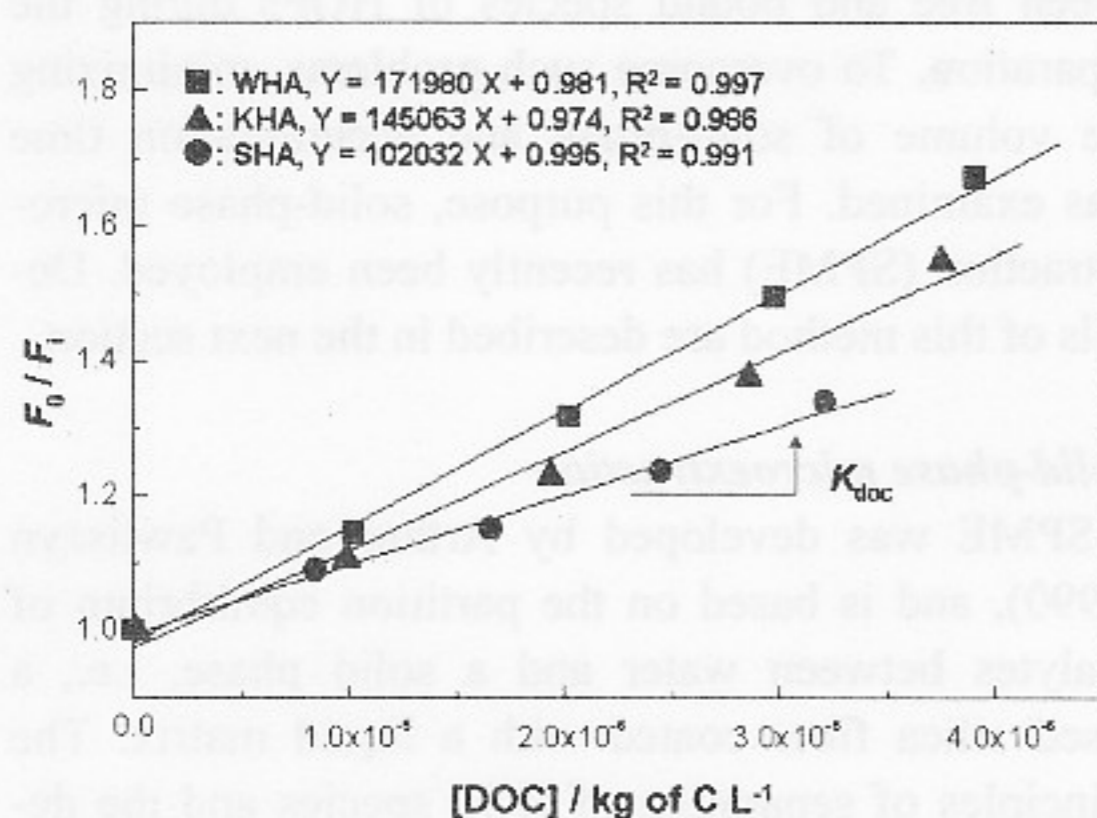
Figure 2. A Stern-Volmer plot of the fluorescence quenching of pyrene by humic acids. The solution conditions: pH 5 (0.01 mol dm^{-3} acetate buffer), ionic strength 0.01, temp. 25°C. The excitation and emission wavelength were set at 333 nm and 377 nm. F_i was corrected by eq. (12). HAs: SHA from Shinshinotsu peat soil (●), KHA from Kalimantan tropical peat (▲), and WHA from Wako Pure Chemicals commercial product (■). The solid lines were obtained by the linear regression analysis.

In general, fluorescence quenching consists of both static and dynamic processes. Although only the binding of a fluorophore (HOPs) to the quencher (HSs) could be considered in the case of a static process, collisions between fluorophores and

quenchers should also be considered in a dynamic process. When only static quenching is predominant, the linear Stern-Volmer equation can be used to evaluate the K_{doc} value. K_{doc} values have been evaluated at lower concentrations of HSs by the Stern-Volmer equation by considering only static quenching (Backhus and Gschwend, 1990; Gauthier et al., 1987; Chen et al., 1994).

Another problem associated with the fluorescence quenching method is absorption of excitation and emission light by the color of the sample solutions. This is generally called, "an inner filter effect", and in order to correct for it, the absorbance values at the excitation (A_{ex}) and emission (A_{em}) wavelengths should be considered. Gauthier et al. (1986) proposed that the fluorescence intensity of an aqueous solution in the presence of HSs should be corrected by considering the inner filter effect:

$$F_{cor} = \frac{2.3A_{ex}}{1-10^{-A_{ex}}} \times 10^{0.4A_{em}} \times \frac{2.3 \times 0.1A_{em}}{1-10^{-0.1A_{em}}} \times F_{obs} \qquad (12)$$

where F_{cor} and F_{obs} represent the corrected and observed fluorescence intensities, respectively.

In addition, dissolved O_2 in the sample solutions poses a significant problem in the fluorescence quenching method. Danielson et al. (1995) reported that the K_{doc} value for pyrene, as determined by the fluorescence quenching method, was 1.6 – 2.7 times larger than the value determined by the solubility enhancement method. Peuravuori (2001) also showed that the fluorescence quenching method resulted in an overestimation in K_{doc} values, compared to the solubility enhancement method. Such overestimation can be due to dissolved O_2, which acts as an efficient dynamic quencher for a number of fluorescent substances (Danielson et al., 1995; Green and Blough, 1996; Tiller and Jones, 1997). To eliminate dissolved O_2 from the sample solutions, Peuravuori (2001) carried out deaeration by N_2 gas purging for 2 min. Nevertheless, an overestimation of K_{doc} was observed. Tiller and Jones (1997) and Backhus et al. (2003) suggested that purging for 0.5 – 1 h may be sufficient to reduce O_2 levels in 2 – 3 cm^3 volumes of sample solutions at concentrations less than 2 mg dm^{-3}. These reports indicate that the deaeration of sample solutions is necessary for precise and accurate determination of K_{doc} values.

Solid-phase extraction

Solid-phase extraction (SPE) is a well known pre-

treatment technique for concentrating and purifying analytes from sample solutions prior to HPLC and GC. The advantages of SPE compared to liquid-liquid extraction are (1) the consumption of organic solvents can be decreased and (2) the extraction time can be reduced. There are a variety of sorbents available for SPE: e.g., reversed phase, normal phase, ion exchange, and size exclusion. For isolating HOPs from aqueous solutions, reversed-phase sorbents are commonly used because such the sorbents are composed of hydrophobic materials (Octadecyl (C-18), Octyl (C-8), and Graphitized carbon, etc.), which include nonpolar interactions and van der Waals forces. Among the reversed-phases, C-18 sorbents have been frequently used because of their strong hydrophobicity and high capacity. In addition, automation systems for SPE combined with HPLC or GC are frequently employed. Online SPE systems can improve experimental accuracy, thus saving manipulation time for column conditioning and elution steps, which minimizes the exposure of analysts to highly toxic compounds (e.g. chlorinated benzenes, biphenyls and dioxins). Thus, the SPE method has been used for the evaluation of K_{doc} values of HOPs to HSs. In principle, as shown in Fig. 3, the C-18 sorbent can retain unbound species of HOPs, and bound HOPs and unbound HSs pass through the SPE column. Unbound species of HOPs can be eluted by an appropriate solvent and the concentration of unbound HOPs ([HOP]$_f$) can then be determined by HPLC or GC technique. K_{doc} values can be calculated by the linear relationships between [HOP]$_0$/[HOP]$_f$ and [DOC], as shown in eq. (10).
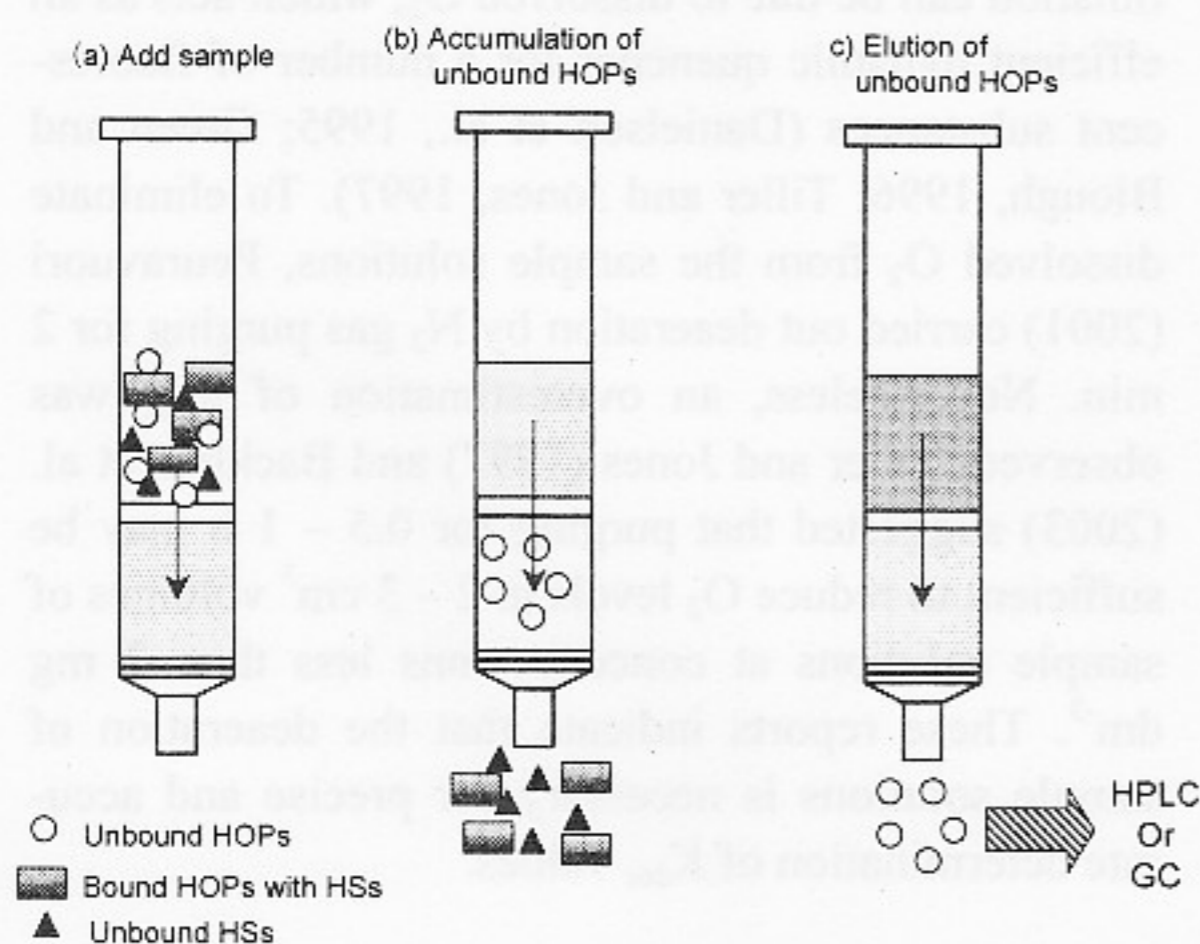
Landrum, et al. (1984) first demonstrated the SPE technique using a C-18 Sep-Pak cartridge (Waters) to determine K_{doc} values for PAHs and PCBs. This study was based on the hypothesis that the bound species of HOPs, which are less hydrophobic than unbound HOPs, could pass through the SPE column (Gardner and Landrum, 1983). Johnson, et al. (1991) also applied SPE using the Sep-Pak to evaluate K_{doc} values of pesticides. To determine both unbound and bound species of PAHs, Li and Lee (2000) developed a tandem-cartridge SPE system which combined reversed-phase separation and dynamic ion-exchange extraction. However, the SPE also includes some drawbacks: e.g., high blank values (Hoke, et al., 1986; Green and LePape, 1987), long equilibration and sampling times, large amounts of sample solution (1 – 10 L), adsorption of HOPs to the plastic cartridge and lower extraction efficiency (Ramos, et al., 1998).

In the SPE method, the large volume of the solid-phase needed and long accumulation time frequently lead to a disturbance in the equilibrium between free and bound species of HOPs during the separation. To overcome such problems, minimizing the volume of solid-phase and accumulation time was examined. For this purpose, solid-phase microextraction (SPME) has recently been employed. Details of this method are described in the next section.

Solid-phase microextraction

SPME was developed by Arthur and Pawliszyn (1990), and is based on the partition equilibrium of analytes between water and a solid phase, i.e., a fused silica fiber coated with a liquid matrix. The principles of separation of HOP species and the determination of K_{doc} are basically similar to the SPE method. Schematic diagrams for the separation and measurement when the SPME method is used are shown in Fig. 4. The SPME needle is first injected into a vial through a teflon-faced septum of the vial cap, and the fiber is then exposed to a sample solution (2 – 20mL) by pushing a plunger (Fig.4 a). Unbound species of HOPs accumulate on the fiber by stirring or agitating the solution (Fig.4 b). The equilibration period is usually 10 – 60 min. The fiber is introduced into the injection port of a GC, followed by thermal desorption and then analyzed (Fig.4 c). The evaluation of K_{doc} is based on eq. (10), as for the SPE method. Examples of the relationships between [HOP]$_0$/[HOP]$_f$ and [DOC] for hexa-
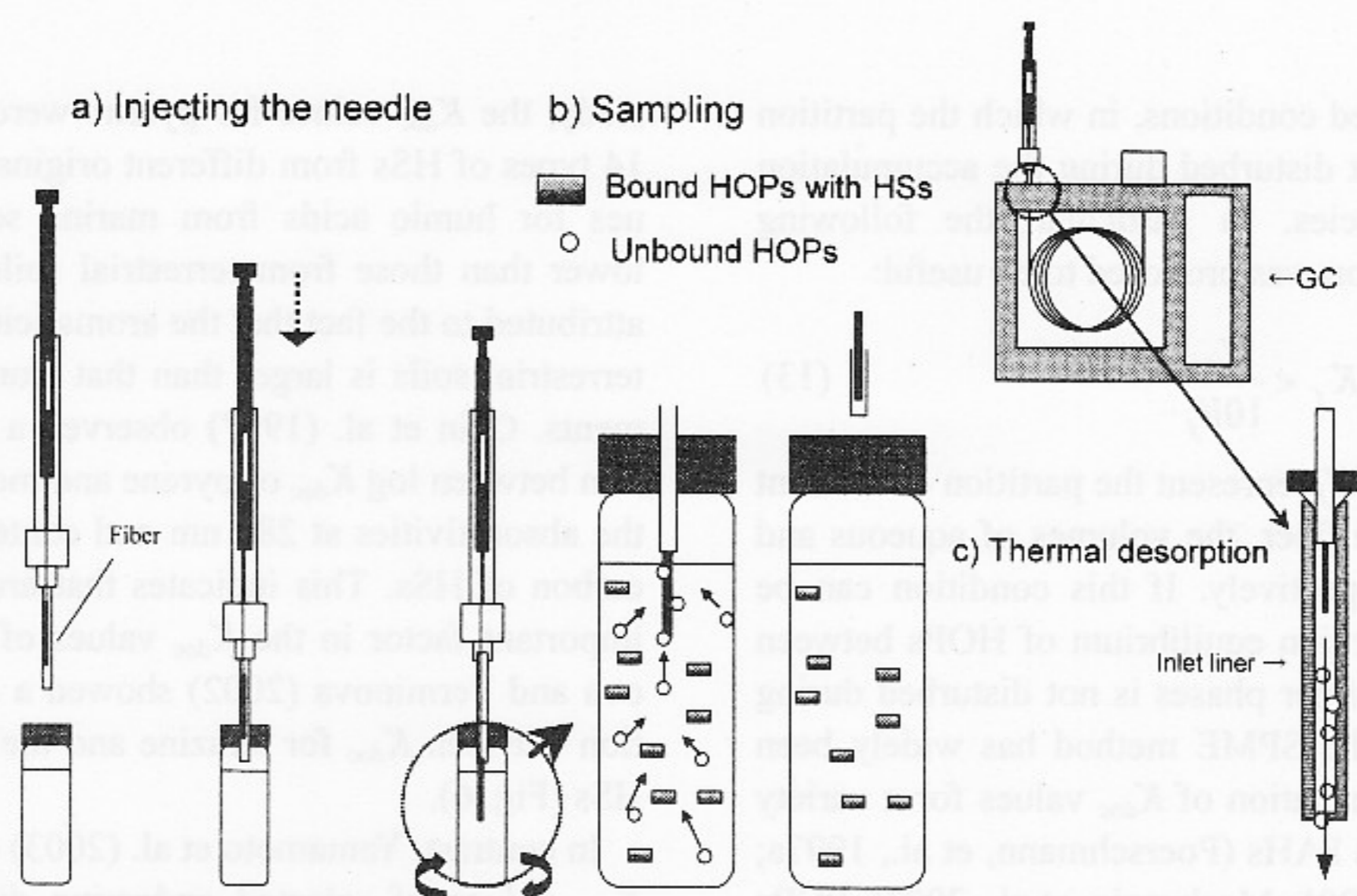

Figure 3. Separation of unbound and bound species of HOPs by an SPE column.

a) Injecting the needle **b) Sampling**

▨ Bound HOPs with HSs
○ Unbound HOPs

←GC

c) Thermal desorption

Fiber

Inlet liner →

Figure 4. Schematic diagrams of the separation and measurement of unbound HOPs in the presence of HSs using the SPME method.

(a)

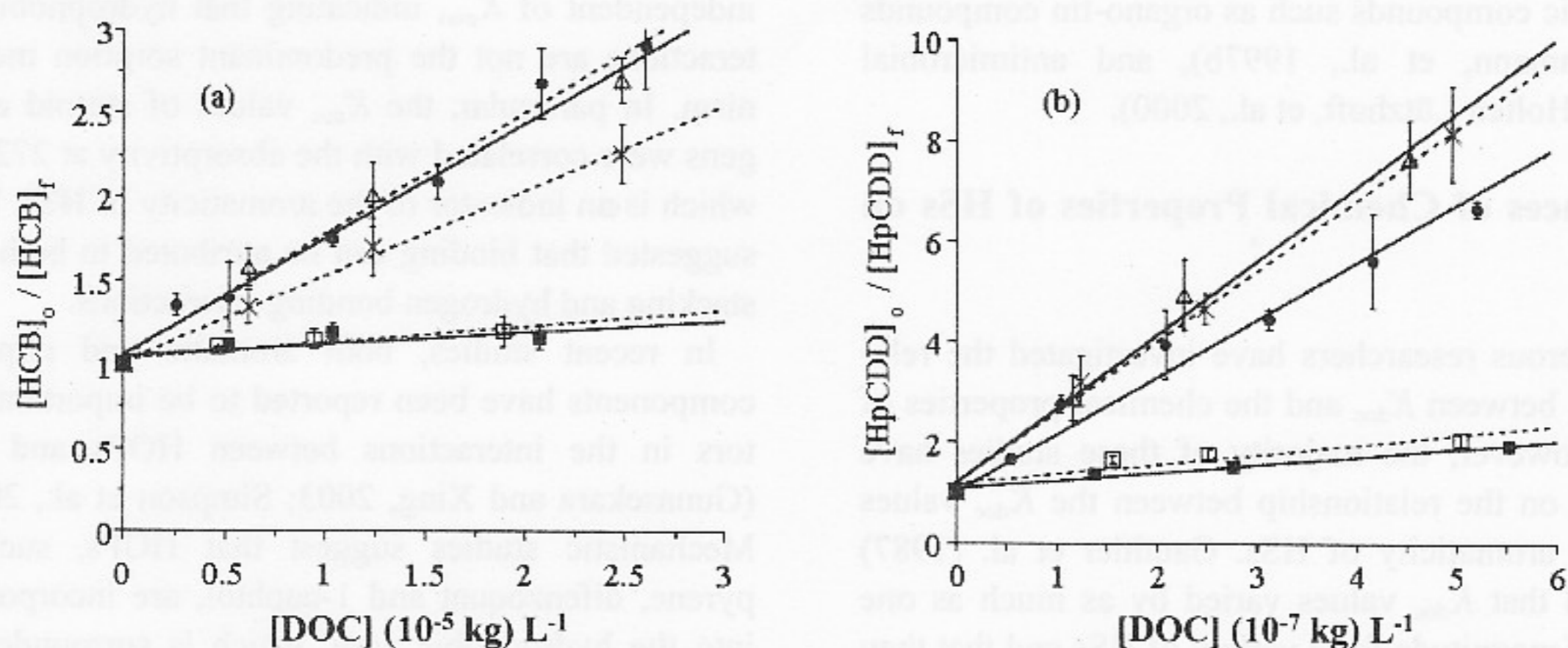[HCB]$_0$ / [HCB]$_f$

[DOC] (10^{-5} kg) L^{-1}

(b)

[HpCDD]$_0$ / [HpCDD]$_f$

[DOC] (10^{-7} kg) L^{-1}

Figure 5. Relationships between [DOC] and [HCB]$_0$/[HCB]$_f$: (a) or [HpCDD]$_0$/[HpCDD]$_f$: (b) (Yabuta et al., 2004). Types of HSs: HA from Aldrich (●); HA from Tohro ando soil (×); HA from Bibai peat soil (△); FA from Dando brown forest soil (□); FA from Inogashira ando soil (■).

chlorobenzene (HCB) and 1,2,3,4,6,7,8-hepta-chlorodibenzo-p-dioxin are shown in Fig. 5 (Yabuta et al., 2004). Different types of solid phases are applicable for HOPs with a variety of volatility and polarity: e.g., polydimethylsiloxane (PDMS) for nonpolar compounds; carbowax for polar compounds; polyacrylate for polar semivolatile compounds. The film thickness of the fibers can be in the range of 7 – 100 μm, which corresponds to a fiber volume of 0.026 – 0.61 μdm^3. The advantages of this technique, compared to the SPE method, include not only simplicity, but also the fact that no organic solvent is needed, which minimizes the sample volume

and avoids analysts being exposed to toxic compounds. In the case of SPE, more than 90% of HOPs can be extracted from an aqueous solution, but only 1 –·2% is injected into the GC. In contrast, SPME can take up 2 – 20% of the HOPs, all of which are injected into the GC (Thurman and Mills, 1998). This also indicates that further minimizing the sample volume is possible in the SPME method.

In the SPME method, the issue whether the concentrations of HOPs species are varied by disturbing the partition equilibrium during the accumulation of unbound HOPs to the SPME fiber is a serious question. Langenfeld, et al. (1996) and Poerschmann, et

al. (1997a) derived conditions, in which the partition equilibrium is not disturbed during the accumulation of unbound species. In particular, the following boundary condition was proposed to be useful:

$$K_f < \frac{V_W}{10 V_f} \qquad (13)$$

where K_f, V_W and V_f represent the partition coefficient of HOPs into the fiber, the volumes of aqueous and fiber phases, respectively. If this condition can be satisfied, the partition equilibrium of HOPs between the aqueous and fiber phases is not disturbed during the extraction. The SPME method has widely been applied to the evaluation of K_{doc} values for a variety of HOPs, such as PAHs (Poerschmann, et al., 1997a; Kopinke, et al., 2001; Mackenzie, et al., 2002), PCBs (Ramos, et al., 1998), and chlorinated benzenes (Ramos, et al., 1998) and chlorinated dibenzo-p-dioxins (Yabuta, et al., 2004; Tanaka, et al., 2004), as well as ionogenic compounds such as organo-tin compounds (Poerschmann, et al., 1997b), and antimicrobial agents (Holten Lützhøft, et al., 2000).

Influences of Chemical Properties of HSs on K_{doc}

Numerous researchers have investigated the relationship between K_{doc} and the chemical properties of HSs. However, the majority of these studies have focused on the relationship between the K_{doc} values and the aromaticity of HSs. Gauthier et al. (1987) reported that K_{doc} values varied by as much as one order of magnitude for a variety of HSs and that they were strongly correlated with aromaticity, which can be measured by the following three methods, i.e., ^{13}C NMR, absorptivity at 272 nm and H/C ratio. In this
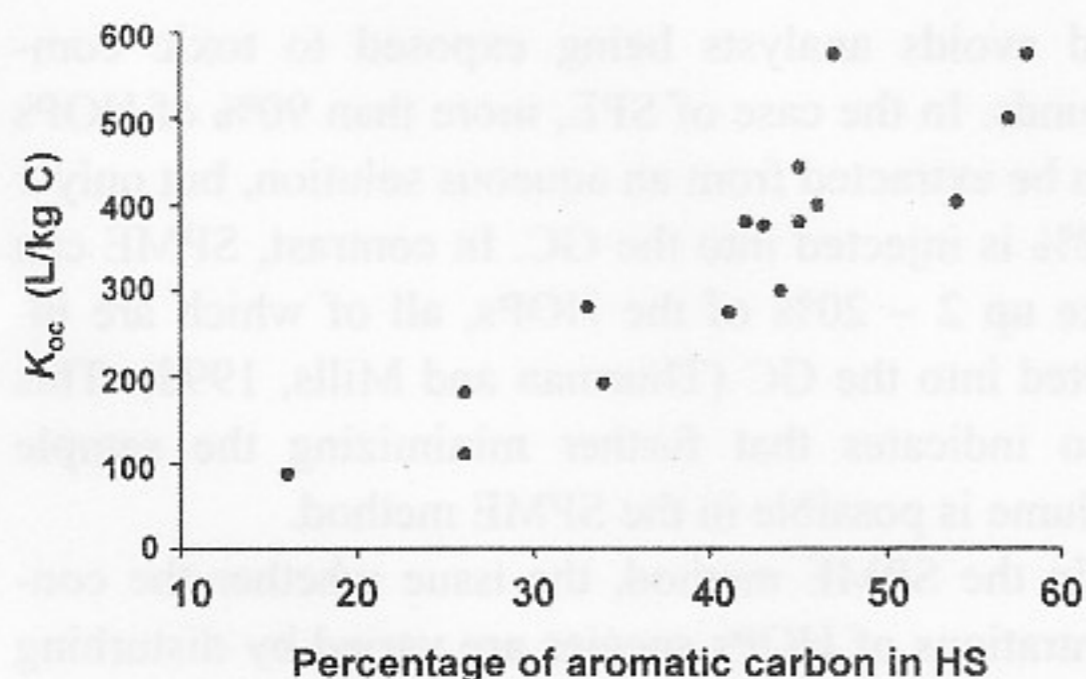
study, the K_{doc} values for pyrene were evaluated for 14 types of HSs from different origins. The K_{doc} values for humic acids from marine sediments were lower than those from terrestrial soils. This can be attributed to the fact that the aromaticity of HSs from terrestrial soils is larger than that from marine sediments. Chin et al. (1997) observed a direct correlation between log K_{doc} of pyrene and molecular weight, the absorptivities at 280 nm and content of aromatic carbon of HSs. This indicates that aromaticity is an important factor in the K_{doc} values of HOPs. Kulikova and Perminova (2002) showed a strong correlation between K_{doc} for atrazine and the aromaticity of HSs (Fig. 6).

In contrast, Yamamoto et al. (2003) determined the K_{doc} values of selected endocrine disruptors (17β-estradiol, estriol, 17α-ethynylestradiol, p-nonylphenol, p-tert-octylphenol, and dibutylphthalate) for HSs. The K_{doc} values of selected endocrine disruptors were independent of K_{ow}, indicating that hydrophobic interactions are not the predominant sorption mechanism. In particular, the K_{doc} values of steroid estrogens were correlated with the absorptivity at 272 nm, which is an indicator of the aromaticity of HSs. They suggested that binding can be attributed to both π–π stacking and hydrogen bonding interactions.

In recent studies, both aromatic and aliphatic components have been reported to be important factors in the interactions between HOPs and HSs (Gunasekara and Xing, 2003; Simpson et al., 2003). Mechanistic studies suggest that HOPs, such as pyrene, difenzoquat and 1-naphtol, are incorporated into the hydrophobic core, which is surrounded by aromatic polymers (Puchaiski et al., 1992; Engebretson and Wandruszka, 1994). Aliphatic moieties in HSs can often serve as binding sites for HOPs, such as phenanthrene and hexafluorobenzene (Salloum et al., 2002; Khalaf et al., 2003). Interactions between HOPs and aliphatic moieties can be attributed to microcrystalline sorption domains, which consist of an aromatic nuclei to which aliphatic chains are linked (Salloum et al., 2002). Khalaf et al. (2003) fractionated HA into eight fractions based on molecular size using ultrafiltration. This study indicated that fractions larger than 100,000 daltons have aliphatic characteristics, while fractions smaller than 30,000 daltons have aromatic characteristics. An investigation by solid-state ^{19}F NMR spectrometry of hexafluorobenzene showed that three sorption sites were present in the smaller fractions, and two sorp-

Figure 6. Correlation between the K_{OC} value of atrazine and the aromaticity of HS (Kulikova and Perminova, 2002)

tion sites were present in the larger fractions.

On the other hand, the importance of oxygen containing functional groups has also been the focus of relationships between K_{doc} and the chemical properties of HSs. Grathwohl (1990) indicated that the K_{doc} values for trichloromethane, 1,1,1-trichloroethane, trichloroethylene and perchloroethylene decreased with increasing content of oxygen-containing functional groups. Paolis and Kukkonen (1997) also observed a relationship between K_{doc} of benzo(a)pyrene and the polarity index ((O+N)/C) or H/O of HSs. The ratio of O+N to C can represent the polar/nonpolar balance (Rutherford et al., 1992). Recently, Tanaka et al. (2004) showed that the K_{doc} for 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin is significantly correlated with carboxylic group content, (N+O)/C and O/C atomic ratios in HSs. In particular, a strong negative relationship between K_{doc} and carboxylic group content was observed, as shown in Fig. 7.
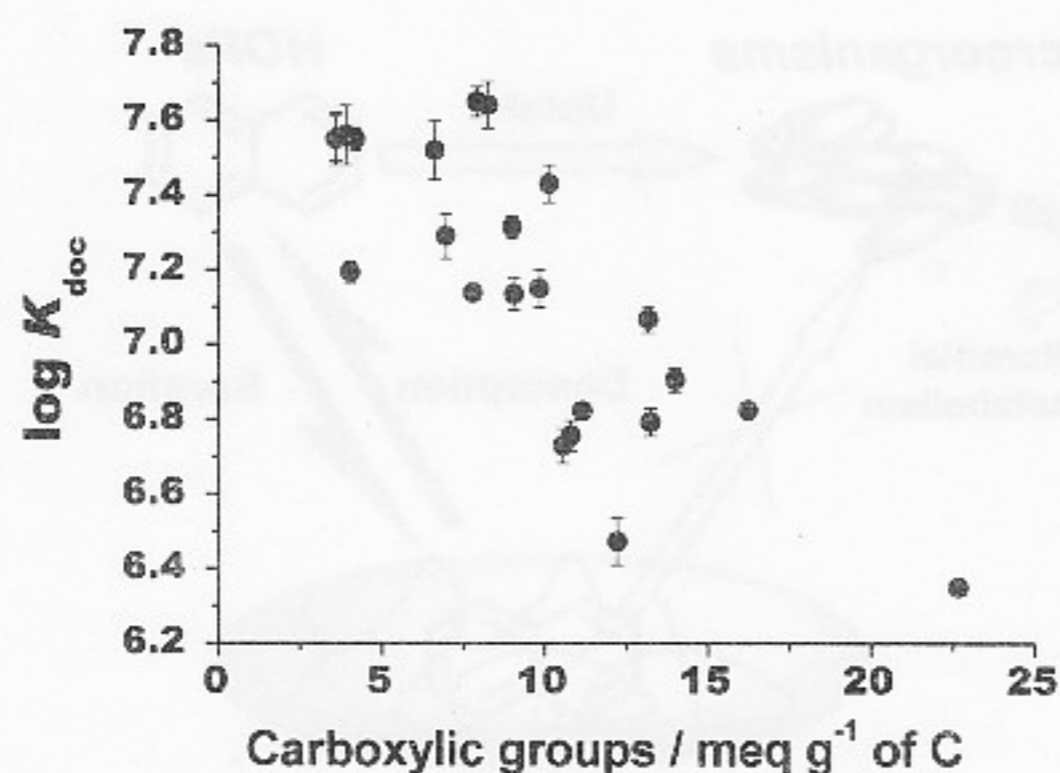

Figure 7. Correlation between log K_{doc} and carboxyl group content

The correlation studies mentioned above show that hydrophobic regions in HSs, which are comprised of aliphatic and aromatic groups, are specific binding-sites for HOPs. The mechanisms for partition and/or sorption have frequently been employed to describe the interactions between HOPs and HSs (Xing, 1998; Khalaf et al., 2003). In the partition model, HSs are regarded to be gel-like polymers, similar to an organic phase, in which HOPs can be extracted from the aqueous phase. Because the HS phase is generally regarded to be homogeneous, the experimental results associated with partitioning are generally linear isotherms. However, the concentration ranges of solutes (HSs and HOPs) are narrow. In the sorption model, HSs are regarded to be mixtures

of macromolecules that contain specific hydrophobic domains such as aromatic and aliphatic regions, and nonlinear relationships can be observed. Thus, the heterogeneous nature of HSs can be reflected in the sorption model rather than the partition model.

Environmental Significance

Mobility of HOPs

Measuring K_{doc} is central to understanding the role of HSs in the facilitated and/or decelerated transport of HOPs in subsurface and surface waters and sedimentary porefluids. In general, HSs can enhance the water solubility of HOPs, thus leading to the facilitation of their transport. Some studies in which the K_{doc} values for dissolved and adsorbed HS are compared have been reported (Laor et al., 1998; Jones and Tiller, 1999). In particular, Laor et al. (1998) reported that the K_{doc} value for dissolved HS was 17 times larger than that for HS adsorbed to clay minerals, such as goethite. Moreover, Kim et al. (2002) investigated the effect of dissolved HS on the leachability of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofrans (PCDD/F) in fly ash. In their study, dissolved HS were found to enhance the leachability of PCDD/F from fly ash. These issues suggest that dissolved HS in soil porefluids plays an important role in enhancing the mobility of HOPs in soil environments.

In contrast, HSs, adsorbed to the surface of a clay mineral, sometimes leads to the uptake of HOPs rather than their dissolution and transport (Terashima et al. 2003). We herein focus on the influences of HSs adsorbed to clay minerals on the distribution of HOPs. Clay minerals (e.g. kaolin, montmolloronite, hematite etc.) have been examined as model mineral surfaces. Terashima et al. (2003) attempted to compare the partition coefficients of HOPs into dissolved and adsorbed HSs. They used pyrene as a model HOP and HS-coated kaolin as an adsorbed HS. To evaluate the distribution coefficient for pyrene into HS-coated kaolin, they derived the simple equation below:

$$\frac{[HOPs]_{total}}{[HOPs]_{aq}} = 1 + K_{OC}^{ads}[OC]_{ads} \qquad (14)$$

where K_{OC}^{ads} and $[OC]_{ads}$ denote the distribution coefficient of HOPs into adsorbed HS and the concentration of organic carbon adsorbed, respectively. Equation (14) is comparable to the Stern-Volmer

equation, as shown in eq. (10). In their approach, an aqueous solution of pyrene was shaken with HS-coated kaolin. After filtration, the unbound species of pyrene in the filtrate were extracted with hexane and then analyzed by fluorescence spectrophotometry. Figure 8 shows a comparison of the [OC] vs [HOPs]$_{total}$/[HOPs]$_{aq}$ plot for adsorbed and dissolved HSs, in which the slopes of the linear portions indicate the K_{OC}^{ads} and K_{doc} values. The K_{OC}^{ads} values were much larger than the K_{doc} values for humic acid from Shinshinotsu peat soil. These results indicate that the partition of HOPs into adsorbed HS is larger than that into dissolved HS. Thus, dissolved HS cannot always act as solubilizing agent for HOPs.
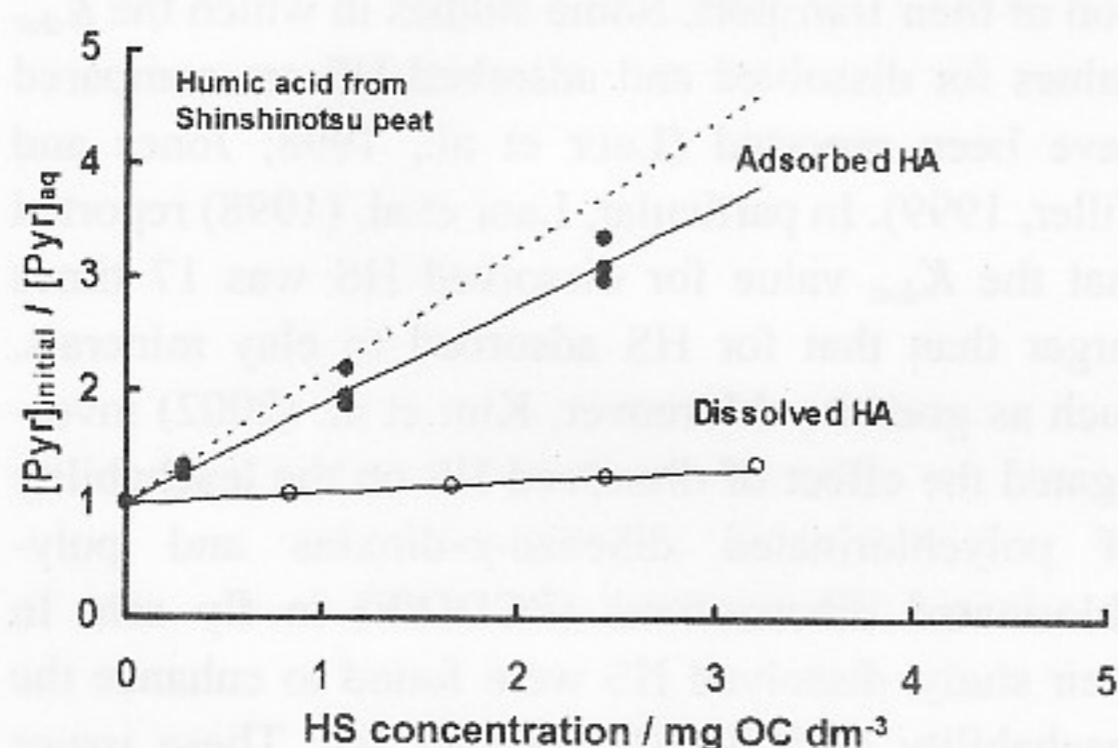

Figure 8. Comparison of partition coefficients for dissolved and adsorbed HA.

As described above, HSs can serve as solubilizing agents (Laor et al., 1998; Jones and Tiller, 1999: Kim et al., 2002) or an accumulator of HOPs to soils (Terashima et al., 2003). It is difficult to compare these different results because of differences in the experimental conditions such as target compounds and the clay mineral used. However, Terashima et al. (2003) proposed that HSs in HS-kaolin complexes may be in a hemi-micelle state as a result of the accumulation of HSs on the surface of the kaolin. Therefore, it is conceivable that the affinity of PAH for the adsorbed HSs would become larger compared with that of the dissolved HSs.

Bioavailability and persistency of HOPs

The partitioning HOPs into HSs are highly related to the attenuation of HOPs via abiotic and biotic degradation processes in aquatic and soil environments. Some reports on the effects of the partitioning of HOPs into HSs on bioavailability have been reported. In particular, Mihelcic and Luthy (1991) re-

ported that the microbial degradation of naphthalene under denitrification conditions in soil-water suspensions is dependent on the partitioning of the solute between soil and water. In their experiments, the degradation efficiency of naphthalene decreased with increasing amounts of soil. Figure 9 shows a conceptual drawing of the processes that occur during the microbial degradation of HOPs in a soil-water suspension. Microorganisms are size-excluded from the micropores of soil particles. However, a solute, such as naphthalene, can enter the micropores and become adsorbed to the surface. Microorganisms cannot degrade HOPs when they are in the micropores of a soil particle. In addition, Perminova et al. (2001) reported that the bioavailability of PAHs to a crustacean, *daphna magna,* was reduced as the result of the partitioning PAHs into HSs. These issues indicate that the partition of HOPs into HSs leads to a decrease in bioavailability.
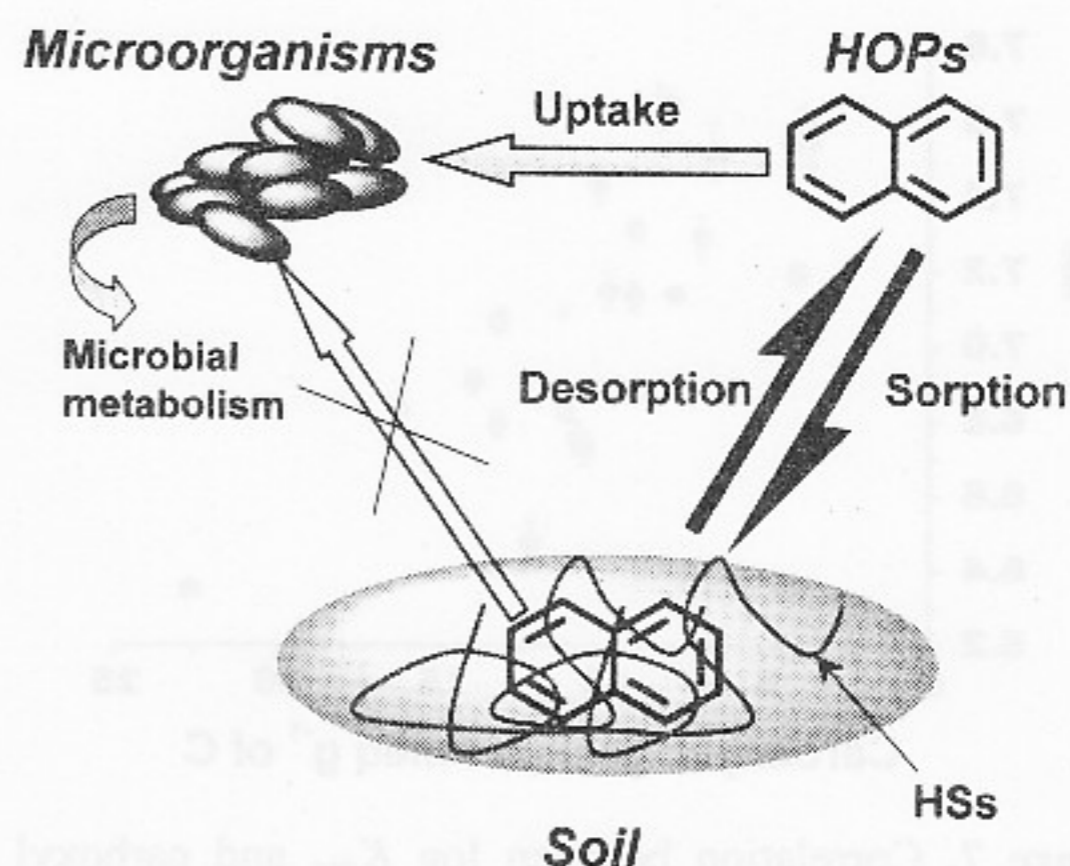

Figure 9. Conceptual drawing of the process occurring during the microbial degradation of HOPs in a soil-water suspension.

For an abiotic system, the photo-Fenton processes via Fe(III)-HSs complexes have been shown to be one of the important remedial processes in surface and subsurface environments (Zepp et al., 1992). In the Fenton reaction, HO· is generated by the degradation of H_2O_2 in the presence of Fe(II) as:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO\cdot + OH^- \quad (15)$$
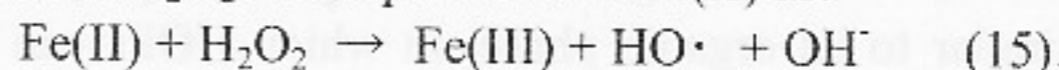
HO· can act as a strong oxidant of HOPs. However, oxidized Fe(III) is precipitated via the formation of hydroxide complexes, which leads to deceleration of the reaction. In the presence of HSs, Fe(III) is bound to HSs and can then be reduced to Fe(II) by HSs again (Fukushima and Tatsumi, 1999). Therefore,

HSs can play an important role in maintaining the catalytic cycle of iron, and this may result in a facilitated degradation. However, Lindsey and Tarr (2000) reported that the degradation of pyrene by the Fenton reaction is inhibited by hydrophobic interactions between pyrene and HSs. HS molecules contain hydrophobic and hydrophilic regions that are physically separated, and the metal binding sites are spatially isolated from the hydrophobic sites (Davies et al., 1997; Sein et al., 1999). Although HOPs such as pyrene can bind to the hydrophobic regions, the formation of HO· can occur at hydrophilic sites in an HS, such as carboxylic acid sites. Thus, the attack of HO· on pyrene may be limited, which results in the inhibition of the degradation of pyrene. These issues show that the partitioning of HSs can retard the attenuation of HOPs via the biotic and/or abiotic degradation processes. This also suggests that the hydrophobic binding of HOPs to HSs increases the persistency of HOPs in environments.

Summary Remarks

In the present review, the advantages and disadvantages of several methods for determining K_{doc} have been discussed. To determine K_{doc} values precisely and accurately, separation and measurement methods should be selected and/or combined based on the chemical properties of HOPs, such as hydrophobicity and K_{OW} value. Numerous methods for determining K_{doc} values have been reported in the 1980s – 1990s. However, the conditions and types of interaction with HSs vary with the type of HOP. Thus, such studies should involve the use of new chemicals and trace chemicals, such as dioxins, which are difficult to analyze.

On the other hand, determining K_{doc} is of crucial importance for predicting the fate and behavior of HOPs in aquatic and soil environments. Recently, the risk management of chemicals has focused on the relationships between the chemical species of HOPs and toxicities. To calculate the distribution of each chemical species, K_{doc} values are required. Although the K_{doc} values discussed in the present review were calculated based on the linear sorption isotherm, the majority of sorption phenomena in the environment might be more complicated. In particular, a non-linear sorption isotherm is observed in the presence of solid particles, such as soil and clay minerals. However, the interpretation of such non-linear sorp-

tion can be regarded as an expansion of linear relationships (Fukushima et al., 1997). Thus, we conclude that the individual K_{doc} value should first be evaluated, which represents the net strength of the interaction between HOPs and HSs. In addition, because K_{doc} varies with the type of HSs, their correlation with the chemical properties of HSs should be elucidated.

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