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Determination of the partition coefficient between dissolved organic carbon and seawater using differential equilibrium kinetics^{*}

Du Yung Kim, Jung-Hwan Kwon^{*}

Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 02841, Republic of Korea

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ABSTRACT

Because the freely dissolved fraction of highly hydrophobic organic chemicals is bioavailable, knowing the partition coefficient between dissolved organic carbon and water (K_{DOCw}) is crucial to estimate the freely dissolved fraction from the total concentration. A kinetic method was developed to obtain K_{DOCw} that required a shorter experimental time than equilibrium methods. The equilibrium partition coefficients of four polychlorinated biphenyls (PCBs) (2,4,4'-trichlorobiphenyl (PCB 28), 2,2',3,5'-tetra-chlorobiphenyl (PCB 44), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153)) between dissolved organic carbon and seawater (K_{DOCsw}) were determined using seawater samples from the Korean coast. The log K_{DOCsw} values of PCB 28 were measured by equilibrating PCB 28, the least hydrophobic congener, with seawater samples, and the values ranged from 6.60 to 7.20. For the more hydrophobic PCBs (PCB 44, PCB 101, and PCB 153), kinetic experiments were conducted to determine the sorption rate constants (k_2) and their log K_{DOCsw} values were 0.57–7.35 for PCB 44, 6.23–7.44 for PCB 101, and 6.35–7.73 for PCB 153. The validity of the proposed method was further confirmed using three less hydrophobic polycyclic aromatic hydrocarbons. This kinetic method shortened the experimental time to obtain the K_{DOCsw} values of the more hydrophobic polycyclic aromatic hydrocarbons. This kinetic method shortened the experimental time to obtain the K_{DOCsw} values of the more hydrophobic polycyclic aromatic hydrocarbons. This kinetic method shortened the experimental time to obtain the K_{DOCsw} values of the more hydrophobic polycyclic aromatic hydrocarbons. This kinetic method shortened the experimental time to obtain the K_{DOCsw} values of the more hydrophobic PCBs, which did not reach phase equilibrium.

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1. Introduction

Many hydrophobic organic chemicals (HOCs) are regulated by the Stockholm Convention (United Nations Environment Programme, 2009) because of their persistence, bioaccumulation, and toxicity. Although their use has been banned for decades, polychlorinated biphenyls (PCBs), for example, are still detected in environmental samples, such as seawater and marine sediments (Marrucci et al., 2013; Lammel et al., 2015). In seawater, HOCs are present in a freely dissolved state or sorbed to particulate organic carbons (POCs) or dissolved organic carbons (DOCs). Among them, only freely dissolved HOCs are thought to be bioavailable and responsible for the ecotoxicity to aquatic organisms (Landrum et al., 1987). Even after the filtration of POCs, typical liquid-liquid extraction (LLE) might overestimate the concentration of HOCs.

Although many earlier studies developed methods for determining freely dissolved concentration (C_{free}) of HOCs using solid-

* This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author.

E-mail address: junghwankwon@korea.ac.kr (J.-H. Kwon).

the ocean environment still recommend LLE as a standard method to measure the concentration of HOCs in seawater (Ministry of Oceans and fisheries of the Republic of Korea (2014); Ministry of the Environment of Japan (2002a,b); U.S. Environmental Protection Agency (EPA), 2007). C_{free} is calculated by dividing the measured chemical concentration in the polymer at equilibrium by the predetermined equilibrium partition coefficient between the polymer material and water (K_{pw}). Alternatively, C_{free} can be calculated from the total chemical concentration (C_{total}) in the filtered water if the partition coefficient between the DOC and water (K_{DOCw}) is known (Burgess et al., 1996). This calculation of C_{free} using K_{DOCw} may be advantageous over SPME or passive sampling methods because one could use routinely measured C_{total} values under the current analytical guidelines (Yao et al., 2002; Gioia et al., 2008; Duong et al., 2010; Mirza et al., 2012).

phase microextraction (SPME) or passive sampling methods (Ramos et al., 1998; Ter Laak et al., 2005; Monteyne et al., 2013;

Mäenpää et al., 2015), many contemporary analytical guidelines for

Methods for measuring *K*_{DOCw} have been developed over the past several decades. They include reverse phase separation (Landrum et al., 1984), equilibrium dialysis (McCarthy and Jimenez,





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1985), fluorescence quenching (Gauthier et al., 1986), negligible depletive SPME (Ramos et al., 1998), and solid-phase dosing/ extraction using a polymer (Ter Laak et al., 2005; Kim and Kwon, 2010). Solid-phase dosing/extraction is especially useful for highly hydrophobic organic chemicals. In this method, K_{DOCw} is calculated using the equilibrium partition coefficient between the polymer and aqueous solution containing DOCs (K_{paq}) , which can be obtained by equilibrating the polymer with an aqueous solution. To measure the noticeable decrease in the concentration of HOCs in the polymer material, a sufficiently large volume of aqueous solution is required. Because most of the aforementioned methods require equilibration between phases (Ramos et al., 1998; Ter Laak et al., 2005; McCarthy and Jimenez, 1985; Kim and Kwon, 2010), longer equilibration time is required for more hydrophobic organic chemicals. To circumvent the long equilibration time, the rate of mass transfer in the aqueous boundary layer (ABL) may be used to determine K_{nw} (Kwon et al., 2007; Kang et al., 2016). In the film diffusion model, the rate of mass transfer is inversely proportional to K_{pw} ; therefore, K_{pw} is calculated using the experimentally measured transfer rate if the diffusion coefficient and thickness of the ABL are known (Kwon et al., 2007). When K_{pw} and the rate of mass transfer are already known, the thickness of the ABL is determined, and the thickness of the ABL shows small differences under the same experimental condition. Therefore, using the rate of mass transfer and the ABL thickness would be promising to obtain K_{paq} and K_{DOCw} values for HOCs requiring shorter time than equilibrium methods.

In this study, the equilibrium partition coefficients between DOC and seawater (K_{DOCsw}) were determined for four PCBs-2,4,4'-trichlorobiphenyl (PCB 28), 2,2',3,5'-tetrachlorobiphenyl (PCB 44), 2,2',4,5,5'-pentachlorobiphenyl (PCB 101), and 2,2',4,4',5,5'-hexachlorobiphenyl (PCB 153)—as model HOCs using filtered seawater samples collected from Shihwa Lake, Gyeonggi Bay, and Masan Bay in Korea. SPME fibers coated with polydimethylsiloxane (PDMS) were loaded with a PCB mixture and equilibrated in the filtered seawater solution to obtain the distribution coefficient between PDMS fiber and filtered seawater (*K*_{PDMSfsw}). With a known partition coefficient between PDMS and seawater (KPDMSsw), KDOCsw values were obtained for the least hydrophobic PCB 28. Values of K_{PDMSfsw} for the more hydrophobic PCBs (PCB 44, 101, and 153) could not be obtained under equilibrium conditions because of the longer equilibration time. Thus, those values were calculated by comparing the rates of mass transfer of the more hydrophobic PCBs and PCB 28. The proposed kinetic method was further validated by obtaining K_{PDMSfsw} values using both the kinetic method and the classical equilibrium method for three less hydrophobic polycyclic aromatic hvdrocarbons (PAHs) (phenanthrene, 3methylphenanthrene, and pyrene). The freely dissolved fraction of PCBs in each filtered seawater sample was also calculated with the experimentally determined total organic carbon.

2. Materials and methods

2.1. Seawater and dissolved organic carbon samples

Seawater samples were collected to isolate DOC from three sampling locations: Shihwa Lake (January, April, and August 2015), Gyeonggi Bay (August 2015), and Masan Bay (October 2015, June and August 2016) in Korea. Fig. S1 (Supplementary Material) describes all sampling points with their coordinates (Table S1, Supplementary Material). During the sampling campaigns in Shihwa Lake and Gyeonggi Bay, 4 L of surface seawater was collected from each sampling point using pre-baked amber glass bottles. In the case of Masan Bay, 1 L of surface seawater was collected from each sampling point into pre-cleaned polyethylene bottles. Immediately

after sampling the seawater, 50 mg L^{-1} of sodium azide was added to inhibit microbial activity. After the seawater samples were brought to the laboratory, particulate organic matter was removed by filtering the seawater with a GF/F filter (0.7 µm pore size). Filtered seawater samples were pooled for each location, as described by the dashed boxes in Fig. S1, and stored in amber glass bottles at 4 °C until use. The concentration of DOC in each sample was measured using a Shimadzu TOC-L total organic carbon analyzer (Kyoto, Japan) using potassium hydrogen phthalate as the organic carbon standard.

2.2. Materials

A PDMS-coated glass fiber was chosen as the dosing phase and purchased from Polymicro Technologies Inc. (Phoenix, AZ, USA). The thickness of the glass core was 110 µm and the thickness of the PDMS coating was 30 µm. The amount of PDMS over the glass core was 0.13 μ L cm⁻¹. Four selected PCBs (PCB 28, 44, 101, and 153) were purchased from AccuStandard (New Haven, CT, USA). The purity of each PCB was higher than 99%, and the concentration of each PCB $35 \,\mu g \,m L^{-1}$ was in isooctane. Phenanthrene, 3methylphenanthrene, pyrene were purchased from Sigma-Aldrich (St. Louis, MO, USA), Tokyo Chemical Industry (Tokyo, Japan), and Fluka (Buch, Switzerland), respectively. The purity of PAHs were higher than 98%.

2.3. Experimental methods

2.3.1. Pre-loading polydimethylsiloxane fiber

PDMS fibers were cut into 1.0 cm lengths and cleaned with *n*-hexane for 1 day in a shaking incubator (25 °C, 150 rpm) and then in methanol for 1 day. The loading solution of mixed PCBs was prepared using *n*-hexane as the solvent. The concentration of each PCB in the loading solution was 116 μ g mL⁻¹. For PAHs, the loading solution was made of methanol and water (60:40). The concentration of each PAHs in the loading solution was 50 mg L⁻¹. The cleaned PDMS fibers were submerged in the loading solution and shaken for 2 days at 25 °C and 150 rpm using a shaking incubator. After the loading process, a bundle of fibers was removed and cleaned using 1 mL of methanol followed by 1 mL of distilled water.

2.3.2. Equilibration experiments

Each pre-loaded PDMS fiber with the PCB mixture was placed in a glass vial containing six different volumes of filtered seawater (volume ratios of filtered seawater to PDMS, V_{fsw}/V_{PDMS} , varied from 115 to 1,000,000). The glass vials were placed in a shaking incubator at 25 °C and 150 rpm for 35 days. The experimental period was long enough to equilibrate PCB 28 between DOC and seawater, whereas other PCBs did not attain phase equilibrium. After 35 days, the remaining PCBs in the PDMS fiber were extracted using 200 µL of *n*hexane at 25 °C and 150 rpm for 1 day and analyzed using a gas chromatograph electron capture detector (GC-ECD). $K_{PDMSfsw}$ was obtained using equation (1) (Kim and Kwon, 2010; Kwon et al., 2009):

$$\frac{C_{PDMS}}{C_{PDMS,0}} = \frac{1}{1 + \left(\frac{V_{fsw}}{V_{PDMS}}\right) / K_{PDMSfsw}}$$
(1)

where $C_{PDMS}/C_{PDMS,0}$ is the ratio of the concentration of each PCB in the PDMS fiber after 35 days to the initial concentration of each PCB in the PDMS fiber, and V_{fsw}/V_{PDMS} is the volume ratio of filtered seawater to PDMS. Using the estimated $K_{PDMSfsw}$, K_{DOCsw} was calculated assuming that the mass was conserved:

$$K_{DOCsw} = \frac{\left(K_{PDMSsw} / K_{PDMSfsw}\right) - 1}{m_{DOC} / 10^6}$$
(2)

where K_{PDMSsw} is the partition coefficient between PDMS and seawater without DOCs, m_{DOC} is the concentration of DOC in filtered seawater (mg L⁻¹), and 10⁶ (mg kg⁻¹) is a unit conversion factor.

2.3.3. Kinetic experiments

Longer equilibration times are expected for the more hydrophobic PCBs; therefore, kinetic experiments were conducted to estimate the absorption and desorption rate constants of PCB 28, 44, 101, and 153. Values of K_{DOCSW} were calculated using the rate constants. Using a well-stirred two-compartment model, the changes in the concentration of each PCB in filtered seawater (C_{fSW}) and in PDMS (C_{PDMS}) are described by:

$$\frac{dC_{fsw}}{dt} = -k_1 C_{fsw} \frac{V_{PDMS}}{V_{fsw}} + k_2 C_{PDMS} \frac{V_{PDMS}}{V_{fsw}}$$
(3)

$$\frac{dC_{PDMS}}{dt} = k_1 C_{fsw} - k_2 C_{PDMS} \tag{4}$$

where k_1 is the absorption rate constant ($m^3_w m^{-3}_{PDMS} s^{-1}$), k_2 is the desorption rate constant (s^{-1}), and t is the experimental time (s). The analytical solution for the fraction of remaining PCB in PDMS ($C_{PDMS,O}$) is given by equation (5):

$$\frac{C_{PDMS}}{C_{PDMS,0}} = \frac{k_1 \frac{V_{PDMS}}{V_{fsw}} + k_2 \exp\left(-\left(k_1 \frac{V_{PDMS}}{V_{fsw}} + k_2\right)t\right)}{k_1 \frac{V_{PDMS}}{V_{fsw}} + k_2}$$
(5)

If the diffusion of PCB in the PDMS phase is not rate-limiting, k_2 can be simplified (Kwon et al., 2007; Ter Laak et al., 2009) as:

$$k_2 \cong \frac{D_w}{\delta} \frac{A}{V_{PDMS} K_{PDMSfsw}} \tag{6}$$

$$\delta = R_f \ln\left(1 + \frac{\delta_w}{R_f}\right) \tag{7}$$

where D_w is the molecular diffusion coefficient in seawater (m² s⁻¹), *A* is the surface area of the PDMS fiber (m²), δ is the ABL thickness (m) equivalent to the flat geometry, δ_w is the actual thickness of the ABL around the cylinder (m), and R_f is the outer radius of the PDMS fiber (m). Using the values of $K_{PDMSfsw}$ and k_2 of PCB 28, the reference chemical, the $K_{PDMSfsw}$ values of the more hydrophobic PCBs could be predicted using the relation between the values of k_2 of PCB 28 and the other more hydrophobic PCBs (*i*).

$$\frac{k_{2, ref}}{k_{2, i}} \cong \frac{D_{w, ref}}{D_{w, i}} \frac{K_{PDMSfsw, i}}{K_{PDMSfsw, ref}}$$
(8)

2.4. Model validation using less hydrophobic polycyclic aromatic hydrocarbons

To validate the proposed kinetic method, additional experiments using three PAHs (phenanthrene, 3-methylphenanthrene, and pyrene) were conducted using MB3 filtered seawater sample. The values of $K_{PDMSfsw}$ for all three PAHs were obtained using the equilibration experiment and they were calculated using k_2 values

obtained from the proposed kinetic method. The least hydrophobic PAH, phenanthrene, was used as a reference chemical instead of PCB28 in the main experiments. The equilibration time for the selected PAHs is expected to be shorter than those of PCBs because PAHs are less hydrophobic than PCBs. The most hydrophobic PAH, pyrene, is even less hydrophobic than PCB 28. All experimental procedures were the same as sections 2.3.2. and 2.3.3., except for the volume ration, V_{fsw}/V_{PDMS} (varied from 500 to 100,000), extraction solvent (1 mL of acetonitrile), and experimental time (up to 6 days).

2.5. Instrumental analysis

The concentrations of the four selected PCBs in the PDMS fiber were quantified using a GC-ECD. The extracted sample (1 μ L) was injected into a GC equipped with a Hewlett-Packard 5890 Series II gas chromatograph, electronic pressure control, split/splitless capillary inlet, and an ECD. The mixture of PCBs was separated on an HP-5 column (30 m × 0.25 mm (internal diameter), 0.25 μ m (film thickness), Agilent J&W Scientific, Folsom, CA, USA). The column oven temperature was held at 80 °C for 2 min, increased to 200 °C at 10 °C min⁻¹, held for 2 min, increased to 290 °C at 10 °C min⁻¹, and held for 12 min. The temperatures of the injector and ECD were 250 and 320 °C, respectively.

The concentrations of the three selected PAHs in the PDMS fiber were analyzed using HPLC-FLD. Ten microliter aliquot of the acetonitrile extract was injected into an HPLC system comprised of a quaternary gradient pump (Waters 600E, Milford, MA, USA), a reverse-phase C18 column (150×4.6 mm, 5μ m inner diameter, Fortis, Neston, United Kingdom), and a multi wavelength fluorescence detector (Waters 2475). The analytes were eluted isocratically (acetonitrile:water = 8:2) at the total flow rate of 1 mL min⁻¹. The wavelength of excitation/emission were 260/352 nm for phenanthrene and 3-methylphenanthrene and 260/420 nm for pyrene.

2.6. Data analysis

The values of $K_{PDMSfsw}$ for PCB 28 and phenanthrene, and k_2 of all PCBs and PAHs in the seawater samples were obtained by fitting the experimental data using equations (1) and (5), respectively. A nonlinear least squares fit was conducted with the nls function using the Gauss-Newton algorithm in the R software (R Development Core Team, 2017).

3. Results and discussion

3.1. Equilibration of PCB 28 between the filtered seawater samples and PDMS fiber

Fig. 1 shows the values of $C_{PDMS}/C_{PDMS,0}$ for PCB 28 after 35 days at various volume ratios (V_{fsw}/V_{PDMS}) to determine $K_{PDMSfsw}$ using pooled seawater samples collected from Gyeonggi Bay (August 2015) and Masan Bay (August 2016) as examples. The results for all seawater samples are shown in Fig. S2. The dashed lines indicate the best fits using equation (1). As shown, the differences in $C_{PDMS}/C_{PDMS,0}$ for various volume ratios were sufficient to derive $K_{PDMSfsw}$ values (Fig. 1 and S2), although the values scattered for a few samples. The coefficients of determination (\mathbb{R}^2) ranged from 0.14 to 0.85. The obtained values of log $K_{PDMSfsw}$ ranged from 3.47 to 3.92 (Table 1). The DOC concentrations of the filtered seawater samples were analyzed, and the results are shown in Table 2. The values of m_{DOC} ranged from 2.9 to 8.2 mg L⁻¹. The measured m_{DOC} values did not show any noticeable variations at a given site, regardless of the sampling season, except for the sample labeled MB3. The values of



Fig. 1. Changes in the concentration ratio ($C_{PDMS}/C_{PDMS,0}$) of PCB 28 after equilibrating to the initial concentration with various volume ratios of filtered seawater to PDMS (V_{fsw}/V_{PDMS}) for pooled (a) GB (August 2015) and (b) MB3 (August 2016) samples. Dashed lines show the best fits using equation (1).

Table 1

Aqueous diffusion coefficients (*D_w*), experimental desorption rate constants (*k*₂), log *K_{PDMSSw}*, obtained values of log *K_{PDMSSw}* and log *K_{DOCsw}*, and literature values of *K_{oc}* of four selected PCBs.

Chemical	Sample	D_w^{a} ($ imes 10^{-10} \mathrm{m}^2 \mathrm{s}^{-1}$)	$k_2 (s^{-1})$	log K _{PDMSsw} ^b	log K _{PDMSfsw}	log K _{DOCsw}	Literature log K _{oc}
PCB 28	SI1	6.08	$\textbf{4.87}\times \textbf{10}^{-6}$	5.34	3.92 ± 0.18	6.80 ± 0.20	4.96–8.44 (Jonker and Koelmans, 2002)
	SO1		9.53×10^{-6}		3.73 ± 0.11	7.04 ± 0.13	6.80 (Martinez et al., 2013)
	SI2		$\textbf{2.88}\times10^{-6}$		3.91 ± 0.15	6.60 ± 0.16	5.83 (Durjava et al., 2007)
	SO2		7.92×10^{-6}		3.89 ± 0.09	6.71 ± 0.11	4.86-5.48 (Burgess et al., 1996)
	SI3		8.42×10^{-6}		3.47 ± 0.15	7.14 ± 0.16	5.50 (Baker et al., 1986)
	SO3		$1.11 imes 10^{-5}$		3.59 ± 0.09	7.15 ± 0.12	
	MB1		2.85×10^{-6}		3.80 ± 0.13	6.76 ± 0.15	
	MB2		$5.17 imes10^{-6}$		3.85 ± 0.18	6.64 ± 0.20	
	MB3		1.39×10^{-5}		3.66 ± 0.15	7.20 ± 0.17	
	GB		8.37×10^{-6}		3.77 ± 0.08	6.65 ± 0.11	
PCB 44	SI1	5.79	2.46×10^{-6}	5.52	4.18 ± 0.21	6.70 ± 0.22	6.60 (Martinez et al., 2013)
	SO1		5.70×10^{-6}		3.93 ± 0.16	7.02 ± 0.17	5.06-5.72 (Burgess et al., 1996)
	SI2		$1.68 imes 10^{-6}$		4.13 ± 0.21	6.57 ± 0.22	5.60 (Baker et al., 1986)
	SO2		5.01×10^{-6}		4.07 ± 0.20	6.71 ± 0.21	
	SI3		8.60×10^{-6}		3.44 ± 0.23	7.35 ± 0.24	
	SO3		$3.61 imes 10^{-6}$		4.06 ± 0.24	6.85 ± 0.25	
	MB1		1.97×10^{-6}		3.94 ± 0.16	6.81 ± 0.17	
	MB2		2.95×10^{-6}		4.07 ± 0.21	6.60 ± 0.21	
	MB3		8.94×10^{-6}		3.83 ± 0.21	7.21 ± 0.21	
	GB		$\textbf{4.41} \times \textbf{10}^{-6}$		4.02 ± 0.21	6.57 ± 0.22	
PCB 101	SI1	5.54	$5.01 imes 10^{-7}$	6.14	4.86 ± 0.24	6.65 ± 0.26	5.42-9.18 (Jonker and Koelmans, 2002)
	SO1		1.29×10^{-6}		4.55 ± 0.21	7.01 ± 0.22	7.10 (Martinez et al., 2013)
	SI2		$9.58 imes 10^{-7}$		4.35 ± 0.25	6.97 ± 0.26	6.51 (Durjava et al., 2007)
	SO2		1.50×10^{-6}		4.57 ± 0.33	6.83 ± 0.34	4.98-5.78 (Burgess et al., 1996)
	SI3		1.13×10^{-6}		4.31 ± 0.17	7.11 ± 0.19	5.78–5.83 (Lara and Ernst, 1990)
	SO3		$7.03 imes 10^{-7}$		4.75 ± 0.27	6.78 ± 0.29	6.25 (Swackhamer and Armstrong, 1987)
	MB1		$9.60 imes10^{-7}$		4.23 ± 0.18	7.14 ± 0.20	5.70 (Baker et al., 1986)
	MB2		1.04×10^{-6}		4.51 ± 0.21	6.79 ± 0.22	
	MB3		3.48×10^{-6}		4.22 ± 0.21	7.44 ± 0.23	
	GB		$4.75 imes10^{-7}$		4.97 ± 0.29	6.23 ± 0.30	
PCB 153	SI1	5.32	$3.53 imes 10^{-7}$	6.53	4.99 ± 0.40	6.91 ± 0.42	4.91-5.70 (Burgess et al., 1996)
	SO1		1.20×10^{-7}		5.57 ± 0.47	6.35 ± 0.48	5.99–6.18 (Lara and Ernst, 1990)
	SI2		$5.35 imes 10^{-7}$		4.59 ± 0.55	7.13 ± 0.57	6.48 (Swackhamer and Armstrong, 1987)
	SO2		$6.97 imes 10^{-7}$		4.89 ± 0.72	6.90 ± 0.73	6.88 (Durjava et al., 2007)
	SI3		$\textbf{2.28}\times10^{-7}$		4.98 ± 0.27	6.81 ± 0.30	
	SO3		1.86×10^{-7}		5.31 ± 0.46	6.60 ± 0.48	
	MB1		$8.02 imes 10^{-7}$		4.29 ± 0.21	7.47 ± 0.24	
	MB2		4.19×10^{-7}		4.88 ± 0.23	6.80 ± 0.25	
	MB3		2.65×10^{-6}		4.32 ± 0.31	7.73 ± 0.33	
	GB		$2.80 imes 10^{-7}$		5.19 + 0.98	6.41 + 0.99	

^a Calculated using Hayduk and Laudie method (Hayduk and Laudie, 1974).

^b Experimental values from Zeng et al. (2005)

log K_{DOCsw} obtained using equation (2) ranged between 6.60 and 7.20 (Table 1).

3.2. Calculation of the K_{DOCsw} values of the more hydrophobic PCBs

The time-course changes in $C_{PDMS}/C_{PDMS,0}$ up to 35 days are shown in Fig. 2 for all selected PCBs in the filtered seawater sample

labeled SI1. The results of all seawater samples are shown in Fig. S3. For all seawater samples, apparent equilibrium between a PDMS fiber and filtered seawater was achieved for PCB 28 within 35 days. However, equilibrium was not attained for the more hydrophobic PCBs, indicating that the equilibration time increases with respect to the partition coefficient and molecular size.

The values of C_{PDMS}/C_{PDMS}, shown in Fig. 2 and S3 were used to

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Table 2 Total organic carbon concentration (m_{DOC}) measured in the pooled filtered seawater samples.

Sample	$m_{DOC} (\mathrm{mg} \mathrm{L}^{-1})$
SI1	4.09 ± 0.01
SI2	6.42 ± 0.09
SI3	5.26 ± 0.05
SO1	3.64 ± 0.05
SO2	5.33 ± 0.07
SO3	3.94 ± 0.05
MB1	5.82 ± 0.10
MB2	6.85 ± 0.11
MB3	2.94 ± 0.48
GB	8.15 ± 0.09

Values are the mean ± standard deviation.

obtain k_1 and k_2 using equation (5). The fitted k_2 values in all seawater samples are listed in Table 1 (2.88×10^{-6} to $1.39 \times 10^{-5} \, \text{s}^{-1}$ for PCB 28, 1.68×10^{-6} to $8.94 \times 10^{-6} \, \text{s}^{-1}$ for PCB 44, 4.75×10^{-7} to $3.48 \times 10^{-6} \, \text{s}^{-1}$ for PCB 101, and 1.20×10^{-7} to $2.65 \times 10^{-6} \, \text{s}^{-1}$ for PCB 153). As expected, the k_2 values decreased with increasing hydrophobicity and molecular size of the PCBs.

The ABL thickness (δ_w) around the fiber was estimated using k_2 and $K_{PDMSfsw}$ of PCB 28 from the equilibration experiment (Table S2). The values of log $K_{PDMSfsw}$ of the more hydrophobic PCBs (calculated using equation (8)) were 3.44–4.18 for PCB 44, 4.22–4.97 for PCB 101, and 4.29–5.57 for PCB 153 (Table 1). The K_{DOCsw} values obtained using m_{DOC} are also listed in Table 1. The ranges of log K_{DOCsw} of PCB 44, PCB 101, and PCB 153 were 6.57–7.35, 6.23–7.44, and 6.35–7.73, respectively.

As shown, the kinetic measurement of k_2 for the more hydrophobic PCBs requires much less time than that needed to attain

phase equilibrium between the PDMS fiber and filtered seawater including DOC. Therefore, it is beneficial to obtain the equilibrium partition coefficient within a reasonable time less than a month using the kinetic methods when δ is determined using a structurally similar but slightly less hydrophobic chemical (i.e., PCB 28 in this study). Although δ is proportional to $D_w^{1/3}$ (Levich, 1962), the differences in the values of D_w among structurally similar chemicals is not significant because D_w is proportional to $V_m^{-0.589}$ (V_m indicates the molar volume) according to an empirical relationship by Hayduk and Laudie (1974).

3.3. Comparing K_{PDMSfsw} from different methods

Because selected PAHs were less hydrophobic than PCBs, the kinetic experiment showed that apparent equilibrium was attained in 6 days (Fig. S4). The fitted k_2 values are listed in Table 3 (2.93 × 10⁻⁵ s⁻¹ for phenanthrene, $5.31 \times 10^{-6} s^{-1}$ for 3-methylphenanthrene, and $3.34 \times 10^{-6} s^{-1}$ for pyrene). Phenanthrene is the least hydrophobic PAHs selected, having highest k_2 value among three PAHs. Calculated log K_{PDMSfsw} values of 3methylphenanthrene and pyrene using equation (8) were 4.40 and 4.33, respectively (Table 3). Fig. S5 shows the value of C_{PDMS}/ $C_{PDMS,0}$ for three PAHs after 6 days of equilibration time at various V_{fsw}/V_{PDMS} values. The decrease in $C_{PDMS}/C_{PDMS,0}$ was sufficient to obtain $K_{PDMSfsw}$ although the highest V_{fsw}/V_{PDMS} was smaller than PCBs experiment by an order of magnitude. The log K_{PDMSfsw} values from equilibration experiment were 3.69, 4.18, and 4.29 for phenanthrene, 3-methylphenanthrene, and pyrene, respectively (Table 3). The differences of log $K_{PDMSfsw}$ between two methods were 0.22 for 3-methylphenanthrene and 0.04 for pyrene, supporting the validity of the proposed kinetic method.



Fig. 2. Decrease in the concentration in the PDMS fiber with increasing desorption time for (a) PCB 28, (b) PCB 44, (c) PCB 101, and (d) PCB 153 in the SI1 sample (as examples). Dashed lines indicate the best fits using equation (5).

Table 3

Aqueous diffusion coefficients (D_w), experimental desorption rate constants (k₂), and obtained values of log K_{PDMSfsw} using two different experiments for three selected PAHs.

Chemical	Sample	D_w^{a} ($ imes 10^{-10} { m m}^2 { m s}^{-1}$)	$k_2 (s^{-1})$	log K _{PDMSfsw}		
				Equilibration experiment	Kinetic experiment	
phenanthrene	MB3	6.90	$\textbf{2.93}\times \textbf{10}^{-5}$	3.69 ± 0.09		
3-methylphenanthrene		6.49	$5.31 imes 10^{-6}$	4.18 ± 0.07	4.40 ± 0.11	
pyrene		6.62	6.34×10^{-6}	4.29 ± 0.06	4.33 ± 0.11	

^a Calculated using Hayduk and Laudie method (Hayduk and Laudie, 1974).

3.4. Comparison of K_{DOCsw} with literature values

Many earlier studies reported organic carbon-water partition coefficient (Koc) values of various PCBs using natural organic carbons from various sources (Burgess et al., 1996; Baker et al., 1986; Swackhamer and Armstrong, 1987; Lara and Ernst, 1990; Jonker and Koelmans, 2002; Martinez et al., 2013; Durjava et al., 2007). It is well-acknowledged that $\log K_{oc}$ of PCBs depends strongly on the type of organic carbon. Due to strong π - π interactions, PCBs tend to have high log K_{oc} values for black carbons and graphenes (Martinez et al., 2013). However, the characteristic properties of natural organic matter with respect to its role as a sorbent for HOCs still need to be revealed (Schwarzenbach et al., 2017). The magnitude of K_{oc} might vary over a few orders of magnitude for a given PCB congener, as exemplified by Jonker and Koelmans (2002) using several different sources of black carbon. For PCBs, there is a general trend that Koc for the same PCB increases with increasing carbon content in the organic matter, and increased chlorine substitution leads to an increase in K_{oc} for the same organic matter (Jonker and Koelmans, 2002; Martinez et al., 2013).

The obtained values of log *K*_{DOCsw} in this study were in the upper range of or slightly higher than the literature values and the values of K_{oc} were not significantly different among the four PCB congeners, regardless of the number of chlorine substitutions (Table 1). However, literature values of Koc measured using DOC (Baker et al., 1986; Durjava et al., 2007) are not very different from K_{DOCsw} in this study. Considering salting-out effects, the corresponding Koc values in freshwater would be lower by approximately 0.15 log unit, because the Setschnow constants for PCBs measured using NaCl solution were around 0.3 L mol_{NaCl}^{-1} (Endo et al., 2012). Another important aspect to be considered is higher capacity of seawater DOC toward PCBs. Dissolved organic matter in seawater would be more mature than that in freshwater systems. We could not further investigate the properties of organic matter because of the limited volumes of collected seawater samples; however, comparing the sorption capacity of freshwater and seawater organic matter toward HOCs, such as PCBs, warrants further investigations.

3.5. Estimation of the freely dissolved fractions in seawater samples

Fig. 3 demonstrates the freely dissolved fraction (f_{diss}) of PCBs with increasing m_{DOC} of seawater. Dashed lines show the estimated freely dissolved fraction for each value of K_{DOCsw} , and the symbols represent experimental values for the four PCBs in this study. As shown, only 1–10% of the PCBs were present in a freely dissolved state in the filtered seawater, indicating that quantification of the aqueous concentration using LLE for filtered seawater may significantly overestimate the freely dissolved concentration. Due to the variation in K_{DOCsw} measured, experimental f_{diss} did not show a decreasing trend with increasing m_{DOC} (Fig. 3). The typical m_{DOC} value of seawater is around 1 mg L⁻¹ (Ogawa and Tanoue, 2003). However, m_{DOC} may be as high as 10 mg L⁻¹ in organic-rich estuaries (Park et al., 2006). All seawater samples in this study were collected near densely populated areas and industrial complexes in



Fig. 3. Changes in the freely dissolved fraction (f_{diss}) of hydrophobic organic chemicals in a filtered seawater sample with increasing concentrations of dissolved organic carbon (m_{DOC}). Symbols represent experimentally measured values, and lines show the theoretical predications of f_{diss} of hydrophobic organic chemicals with K_{DOCsw} values of 10^5 , 10^6 , 10^7 , and $10^8 L kg^{-1}$.

Korea; therefore, the rather high values of m_{DOC} are likely due to the higher input flux from inland. Within the plausible range of m_{DOC} , as shown in Fig. 3, f_{diss} of the HOCs becomes less than 10% when the value of K_{DOCsw} is above 10⁷, which is a typical order of magnitude for the K_{DOCsw} values of the four PCBs in this study, and instantaneous equilibrium is assumed between the DOC and seawater. Although passive sampling is becoming more popular for determining the freely dissolved concentration of HOCs for risk assessment and evaluating bioaccumulation (Muijs and Jonker, 2012; Jin et al., 2013), routine monitoring data are still obtained using existing monitoring guidelines in many countries (Ministry of Oceans and fisheries of the Republic of Korea, 2014; Ministry of the Environment of Japan, 2002a, b). When the only available monitoring data of HOCs are those obtained using LLE after filtration, the freely dissolved concentration using K_{DOCsw} and m_{DOC} would be very useful to determine the bioavailability of the HOCs. Although the value of m_{DOC} did not significantly vary at each sampling area, regardless of the season, for the limited number of filtered seawater samples in this study, further studies are needed to determine the typical value of m_{DOC} in coastal water with respect to the location, season, etc. In addition, the variation of K_{DOCsw} with respect to the characteristics of the organic matter in seawater warrants further investigations.

4. Conclusions

The K_{DOCsw} values of four selected PCBs with different seawater samples were determined by both the equilibration method and the kinetic method. Because the equilibration time is longer for more hydrophobic PCBs, only PCB 28 was used to measure K_{DOCsw} using the equilibration method. The desorption rate constants of four PCBs and the K_{DOCsw} values of the more hydrophobic PCBs were calculated using a kinetic model. This kinetic method was further validated with less hydrophobic PAHs. The obtained experimental K_{DOCsw} values were generally in the upper range of the literature values, indicating that sorption to organic carbon significantly lowers f_{diss} in Korean coastal waters. For most samples, the estimated f_{diss} values of the PCBs were less than 10%. Experimentally determined K_{DOCsw} can be used to estimate the freely dissolved concentration of HOCs, which is important to assess the bioavailability, bioaccumulation potential, and related risks.

Declarations of interest

None.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.04.114.

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