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# Determination of the partition coefficient between dissolved organic carbon and seawater using differential equilibrium kinetics<sup>☆</sup>

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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'-tetrachlorobiphenyl (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 obtained by comparing their  $k_2$  with that of PCB 28. The calculated log  $K_{DOCsw}$  values were 6.57–7.35 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 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-

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 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).

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  $K_{pw}$  (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 ( $K_{PDMSsw}$ ),  $K_{DOCsw}$  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 hydrocarbons (PAHs) (phenanthrene, 3-methylphenanthrene, 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<sup>-1</sup> 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 μL cm<sup>-1</sup>. 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 was 35 μg mL<sup>-1</sup> in isoctane. Phenanthrene, 3-methylphenanthrene, 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 μg mL<sup>-1</sup>. 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<sup>-1</sup>. 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):

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

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:

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