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Sorption capacity of plastic debris for hydrophobic organic chemicals

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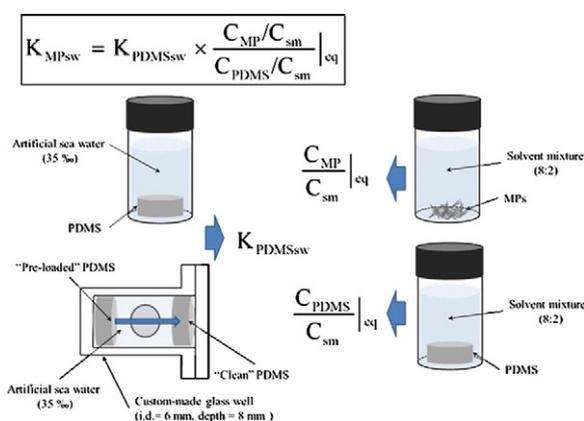
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HIGHLIGHTS

- Sorption capacity of microplastic debris was evaluated.
- A third-phase partitioning method was used to determine partition coefficients.
- Partition coefficients between plastics and seawater were determined for HOCs.
- The sorption capacities of three plastics were comparable to that of 1-octanol.
- Marine microplastics may play an important role in the global fate of POPs.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of microplastics (MPs) in the ocean is an emerging world-wide concern. Due to high sorption capacity of plastics for hydrophobic organic chemicals (HOCs), sorption may play an important role in the transport processes of HOCs. However, sorption capacity of various plastic materials is rarely documented except in the case of those used for environmental sampling purposes. In this study, we measured partition coefficients between MPs and seawater (K_{MPsw}) for 8 polycyclic aromatic hydrocarbons (PAHs), 4 hexachlorocyclohexanes (HCHs) and 2 chlorinated benzenes (CBs). Three surrogate polymers – polyethylene, polypropylene, and polystyrene – were used as model plastic debris because they are the major components of microplastic debris found. Due to the limited solubility of HOCs in seawater and their long equilibration time, a third-phase partitioning method was used for the determination of K_{MPsw} . First, partition coefficients between polydimethylsiloxane (PDMS) and seawater (K_{PDMSsw}) were measured. For the determination of K_{MPsw} , the distribution of HOCs between PDMS or plastics and solvent mixture (methanol:water = 8:2 (v/v)) was determined after apparent equilibrium up to 12 weeks. Plastic debris was prepared in a laboratory by physical crushing; the median longest dimension was 320–440 μm . Partition coefficients between polyethylene and seawater obtained using the third-phase equilibrium method agreed well with experimental partition coefficients between low-density polyethylene and water in the literature. The values of K_{MPsw} were generally in the order of polystyrene, polyethylene, and polypropylene for most of the chemicals tested. The ranges of $\log K_{MPsw}$ were 2.04–7.87, 2.18–7.00, and 2.63–7.52 for polyethylene, polypropylene, and polystyrene, respectively. The partition coefficients of plastic debris can be as high as other frequently used partition

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coefficients, such as 1-octanol–water partition coefficients (K_{ow}) and $\log K_{MPsw}$ showed good linear correlations with $\log K_{ow}$. High sorption capacity of microplastics implies the importance of MP-associated transport of HOCs in the marine environment.

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1. Introduction

Plastics are released into the environment via various pathways, and a significant amount of plastic material ultimately reaches the marine environment (e.g., Andrady, 2011; Cole et al., 2011; Derraik, 2002; Moore, 2008; Thompson et al., 2004). Plastic debris undergoes size reduction as a result of physical and chemical processes, such as abrasion by waves and chemical transformation by ultraviolet light. Tiny plastic particles smaller than a few millimeters are often referred to as “microplastics” (Graham and Thompson, 2009). Microplastics floating over water are transported by ocean currents and are found in regions where water circulation is relatively stationary or on seashores (Claessens et al., 2011; Hidalgo-Ruz et al., 2012; Hirai et al., 2011; Martins and Sobral, 2011; Van et al., 2012). A number of heavily produced low density plastics (e.g., polyethylene, polypropylene, and polystyrene) have been identified as the main components of microplastics, and these have various shapes and sizes, ranging from a few micrometers to a few millimeters (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Martins and Sobral, 2011).

Hydrophobic organic chemicals (HOCs) that are persistent and travel long distance tend to sorb to organic phases such as particulate and dissolved organic matter, sediments, and synthetic polymers. Thus, the accumulation of microplastics in the ocean (Browne et al., 2011; Moore, 2008; Thompson et al., 2004, 2009) may affect local or global transport of HOCs in the marine environment (Rios et al., 2007; Teuten et al., 2009). In addition, sorption of HOCs to marine microplastics may affect food-web bioaccumulation and bioavailability of HOCs (Rios et al., 2007). HOCs associated with microplastics may be taken up by aquatic organisms and absorbed in gastrointestinal tracts, similar to uptake processes of sediment-bound HOCs. On the contrary, sorption of HOCs to microplastics may lower the free aqueous concentration and decrease the bioavailability of HOCs. Although it is well known that sorption of HOCs to dissolved organic matter, such as humic acids, lowers the bioaccumulation potential and toxicity of HOCs by reducing bioavailability (e.g., Escher and Hermens, 2002; McCarthy and Jimenez, 1985), the overall contribution of microplastics for bioaccumulation or toxicity of HOCs is unclear. Whereas many studies have been conducted to evaluate sorption/desorption processes of HOCs to various organic phases under laboratory and field conditions (e.g., Cornelissen et al., 2005; Goss, 2011; Karickhoff et al., 1979; Kim and Kwon, 2010), only a few studies have been conducted to assess the effects of sorption of HOCs to microplastics, and for the quantitative evaluation of equilibrium partitioning between microplastics and seawater (Hirai et al., 2011; Teuten et al., 2007; Van et al., 2012). Due to a limited number of partitioning studies, partition or distribution coefficients have been reported for only a few HOCs and plastic phases. Because the equilibrium partition coefficient is one of the most fundamental properties governing the fate of HOCs in the marine environment, it is necessary to understand equilibrium distribution of HOCs between various plastic phases and seawater.

However, there are experimental difficulties relating to the measurement of partition coefficients of HOCs between plastic and seawater, due to low solubility of HOCs and associated problems. The time required for phase-equilibrium in conventional batch equilibrium experiments increases with increasing partition coefficient (Kwon et al., 2007). To circumvent problems with low solubility and long experimental durations, researchers have developed third-phase partitioning methods. For example, partitioning between dissolved organic matter and water has been precisely

quantified by measuring partition coefficients between a polymeric phase and water, and between the polymeric phase and a solution containing dissolved organic matter (Kim and Kwon, 2010; Kim et al., 2010; ter Laak et al., 2005).

The primary objective of this research is to obtain reliable partition coefficients for HOCs between microplastics and seawater under laboratory conditions. Polyethylene (PE), polypropylene (PP), and polystyrene (PS) were chosen as model plastic phases for this evaluation, because they are intensively used; they are also the three most frequently found microplastics in the marine environment (Heo et al., 2013; Hidalgo-Ruz et al., 2012; Martins and Sobral, 2011). As model HOCs, 8 polycyclic aromatic hydrocarbons (PAHs), 4 hexachlorocyclohexanes (HCHs) and two chlorinated benzenes were chosen. To obtain partition coefficients of the selected HOCs, poly(dimethylsiloxane) (PDMS) was used as a third-phase. Partition coefficients between PDMS and seawater (K_{PDMSsw}) were measured for the selected HOCs. To compare relative sorption capacity of PDMS and microplastics, the partitioning of HOCs between PDMS (or microplastics) and the methanol/water solvent mixture was evaluated. Then, partition coefficients between microplastics and seawater were calculated based on the measured values. The partition coefficients were compared to partition coefficients between low-density polyethylene and water (K_{LDPEw}) and K_{ow} .

2. Material and methods

2.1. Materials and chemicals

High purity chemical standards were used for all HOCs. Phenanthrene (PHE, 98%), fluoranthene (FLU, 98%), anthracene (ANT, 99%), and pentachlorobenzene (PeCB, 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). α -HCH (99.8%), chrysene (CHR, 99.9%), benzo[a]pyrene (BaP, 99.1%), dibenz[a,h]anthracene (DBaH, 99.9%), and benzo[ghi]perylene (BghiP, 99.6%) were purchased from Supelco (Bellefonte, PA, USA). Pyrene (PYR, 99%), β - (99.5%), γ - (99.8%), δ -HCH (98.2%), and hexachlorobenzene (HeCB, 99%) were purchased from Fluka (Buch, Switzerland). All partitioning experiments were conducted using mixtures of similar compounds: PAHs mixture 1 (PHE, ANT, FLU, and PYR), PAHs mixture 2 (CHR, BaP, DBaH, and BghiP), HCHs (α -, β -, γ -, and δ -HCHs), and chlorinated benzenes (PeCB and HeCB). Artificial seawater was prepared at 3.5% (w/w) by dissolving artificial sea salt obtained from Sigma-Aldrich. Medical grade PDMS sheets with a thickness of 1 mm and a density of 1.17 g cm⁻³ were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). For partitioning experiments, the PDMS was cut into disks of diameter 6 mm, cleaned in a Soxhlet extractor using *n*-hexane and methanol for 2 h each, and stored in methanol until use.

2.2. Preparation of microplastic debris

Microplastic debris was obtained by grating commercial labwares made of PE, PP, and PS using a bastard-cut hand file. The obtained plastic debris was passed through a 250 μ m sieve (mesh No. 60, Chunggye Industrial MFG Co., Seoul, Republic of Korea) to screen larger debris. Then, it was washed with *n*-hexane and methanol for 24 h each, and dried at room temperature until use. The size of the prepared plastic debris was measured using an optical microscope (IX71, Olympus, Japan) equipped with 4 \times lens (Olympus). The longest dimension was determined visually, using the image taken. In order to compare the visual estimation results to those obtained by dynamic light scattering, the

particle size distribution of polystyrene powder was also measured using LS 13 320 laser diffraction particle size analyzer (Beckman Coulter Inc., Brea, CA, USA). The density of plastics was measured using a volumetric method (ASTM, 2009).

2.3. Determination of partition coefficients between PDMS and seawater (K_{PDMSsw})

Values of K_{PDMSsw} were measured using the aqueous boundary layer (ABL) permeation method (Kwon et al., 2007) for PAHs and chlorinated benzenes, whereas the batch equilibrium method was used for less hydrophobic HCHs because equilibrium between PDMS and seawater is easily obtained for them and the ABL permeation method is not desirable for chemicals with low partition coefficients (Kwon et al., 2007). The experimental procedure for the ABL permeation method has been extensively described in earlier literature (Kwon et al., 2007; Lee et al., 2012); its theoretical basis is described in the Supplementary Material. In short, a PDMS donor disk (6 mm diameter, 1 mm thickness) was loaded with a mixture of HOCs using methanol:water (6:4, v/v) for 24 h. A clean PDMS acceptor disk of the same size was separated from the donor disk by 6 mm artificial seawater. The aqueous solution between the two disks was agitated using a stainless steel disk (5.08 mm diameter, 0.635 mm thick) at 300 rpm using a VP710F tumble stirrer (V&P Scientific Inc., San Diego, CA, USA). The corresponding thickness of the aqueous boundary layer was estimated at 12.5 μm , as the experimental dimensions in this case were identical to those used in the previous studies (Kwon et al., 2007; Lee et al., 2012). The mass transfer rate constant was obtained by measuring the changes in the concentration of both the donor and the acceptor PDMS disks, and was in turn used to derive K_{PDMSsw} . The donor and acceptor disks were extracted using 1 mL organic solvents for 2 h. *n*-Hexane was used for the analysis of CBs and acetonitrile was used for the analysis of PAHs. Almost all HOCs were extracted after the first extraction of PDMS disks and less than 5% of HOCs were extracted at the second extraction. The initial concentration in the PDMS donor disks ranged from 90 $\mu\text{mol L}^{-1}_{PDMS}$ (PYR) to 8 mmol L^{-1}_{PDMS} (HeCB). All experiments were conducted at 25 ± 2 °C.

Values of K_{PDMSsw} for HCHs were obtained by measuring the equilibrium concentrations in PDMS and seawater in a batch solution. Four different initial concentrations of HCHs were prepared by dissolving them in artificial seawater. The maximum concentrations of HCHs were 650, 100, 600, and 600 $\mu\text{g L}^{-1}$ for α -, β -, γ -, and δ -HCH, respectively,

sufficiently lower than their aqueous solubilities. After apparent equilibrium between PDMS and seawater was obtained in 36 h, both the aqueous solution and PDMS were extracted using *n*-hexane and the concentrations in the extracts were quantified using a gas chromatography–electron capture detector (GC-ECD). The extraction recoveries for all HCHs in water were between 90 and 110%.

2.4. Determination of partition coefficients between plastic debris and seawater (K_{MPsw})

Because direct determination of K_{MPsw} requires very long equilibration time due to high partition coefficients and slow diffusion in plastic phase, K_{MPsw} values were obtained using a third-phase equilibrium method (Kim and Kwon, 2010; Kim et al., 2010; Lee et al., 2012; ter Laak et al., 2005). Fig. 1 describes a schematic diagram of the determination of K_{MPsw} using equilibrium between PDMS and solvent mixture and between microplastic debris and solvent mixture. A methanol:water (8:2 v/v) mixture was used as the solvent mixture, because methanol does not result in significant swelling of PDMS (Lee et al., 2003) and sample plastics. Furthermore, plastic materials sink by gravity in the solution, because the solution density is approx. 0.85 g cm^{-3} . K_{MPsw} can be calculated using partitioning ratios as follows:

$$K_{MPsw} = \frac{K_{MPsm}}{K_{PDMSsm}} K_{PDMSsw} \quad (1)$$

where K_{MPsm} and K_{PDMSsm} are partition coefficients between MP and solvent mixture and between PDMS and solvent mixture, respectively.

Each vial containing PDMS (or plastics) and solvent mixture was agitated at 25 °C and 150 rpm using a shaking incubator in the dark. The mass of the 6-mm PDMS disk was 39 mg and that of microplastics was approximately 10 mg in a 4 mL solvent mixture. Under this condition, the initial concentration of HOCs in the solvent mixture did not change significantly by sorption to PDMS or microplastics. PDMS disks were taken out after the designated number of hours, and extracted using either acetonitrile for HPLC analyses or *n*-hexane for GC analyses as described above. After the designated number of days, solvent mixture was filtered through a glass filter (0.45 μm) to separate microplastics. Filtered microplastics were washed by flowing 1 mL of distilled water through the glass filter two times to remove residual solvent on the surfaces of plastics. The mass of air dried microplastics was measured and the HOCs sorbed to plastics were extracted using

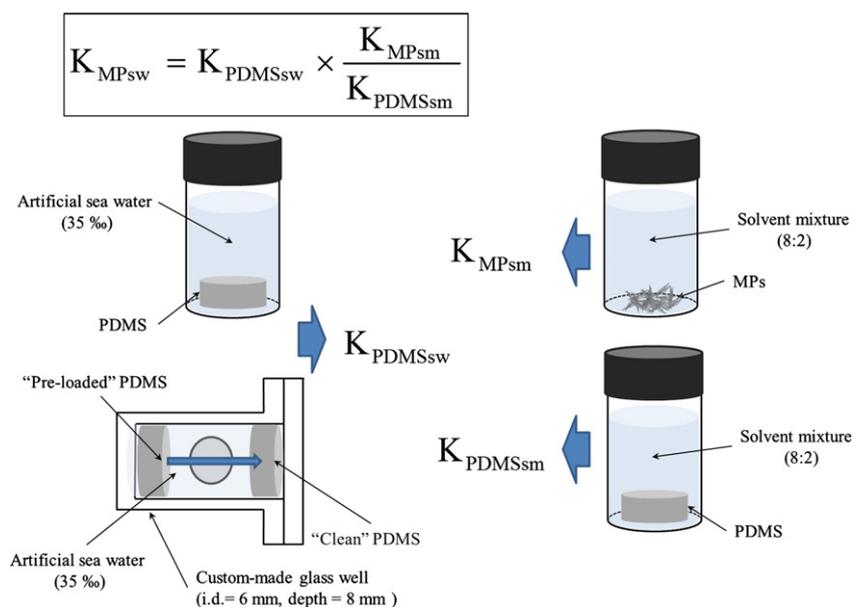


Fig. 1. Schematic diagram of the determination of microplastic–seawater partition coefficients using a third-phase partitioning method.

n-hexane for 1 day. *n*-Hexane extracts were then subjected to GC analyses for CBs and HCHs. For PAHs, *n*-hexane was exchanged by acetonitrile for HPLC analyses. Because preliminary sequential extraction showed that almost all extractable HOCs (>95%) were extracted from microplastics at the first extraction, the chemical concentration in microplastics was measured using the first extraction.

2.5. Instrumental analyses

For chemical analyses of HOCs, chlorinated benzenes (CBs) and HCHs were quantified using a GC-ECD, and PAHs were analyzed using an HPLC-fluorescence detector. One microliter of the extracted samples containing CBs or HCHs was injected into a GC system equipped with a Hewlett-Packard 5890 Series II gas chromatograph, an electronic pressure control (EPC), a split/splitless capillary inlet, and an ECD. One microliter of *n*-hexane solution was injected at the split ratio of 10:1. Mixtures of chlorinated benzenes and HCHs were separated on an HP-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent J&W Scientific, Folsom, CA). The column oven temperature was held at 120 °C for 3 min, followed by an increase to 200 °C at 5 °C min⁻¹, held for 5 min, an increased to 280 °C at 45 °C min⁻¹, and held for 1 min. The injector and the ECD temperature were 200 and 320 °C, respectively.

The concentration of PAHs was quantified using an HPLC system equipped with a Waters 600E pump (Milford, MA, USA), an auto-sampler (Waters 717+), and a fluorescence detector (Waters 2475). Mixtures of PAHs were separated on a Fortis C18 column (4.6 × 150 mm, 5 μm particle size; Fortis Technologies Ltd., Neston, UK) in isocratic mode, using deionized water:methanol (6:4 or 8:2 v/v). The total flow rate of eluent was 1 mL/min. The excitation and emission wavelengths were 260 and 420 nm for PAH mixture 1 (PHE, ANT, FLU, and PYR) and 290 and 430 nm for PAH mixture 2 (CHR, BaP, DBaH, and BghiP).

3. Results and discussion

3.1. Physical characterization of microplastics

Fig. 2 shows microscopic images of laboratory prepared microplastics for (a) polyethylene (PE), (b) polypropylene (PP), and (c) polystyrene (PS). As shown, the shape of microplastics was fragment-type and the median (25 and 75 percentile) sizes of the longest dimension were estimated 420 (310, 540), 440 (340, 550), 320 (250, 420) μm for PE, PP, and PS, respectively. The median diameter of PS measured by laser diffraction was 306 μm, close to the median value obtained by microscopic analysis. The experimental densities (± standard error) of the three microplastics were 0.963 (±0.016), 0.920 (±0.013), and 1.090 (±0.006) g·cm⁻³ for PE, PP, and PS, respectively. Because high-density polyethylene (HDPE) has density above 0.94 g·cm⁻³ (Baker and Mead, 2000), the PE material used in this study can be classified as HDPE with high crystallinity. The measured densities of three plastics

are at the high ends of the range of reported densities (Table S1, Supplementary Material).

3.2. Determination of $K_{PDMS_{SW}}$

Equilibrium partition coefficients of HCHs between PDMS and seawater were determined from the slopes of the equilibrium concentration in PDMS (C_{PDMS}) compared to that in artificial seawater (Fig. S1, Supplementary Material). As shown in Fig. S1, narrow 95% confidence intervals for the slopes were obtained. Determination of kinetic rate constants for the ABL permeation method is shown in Fig. S2, Supplementary Material. All measured values of log $K_{PDMS_{SW}}$ are listed in Table 1. Because partition coefficients between PDMS and deionized water ($K_{PDMS_{DW}}$) for the selected HOCs have already been measured in earlier studies (Brown et al., 2001; Kwon et al., 2007; Leslie et al., 2002; Maruya et al., 2009; Mayer et al., 2000; Ouyang et al., 2008; Paschke and Popp, 2003; Poerschmann et al., 2000; Potter and Pawliszyn, 1994; Ramos et al., 1998; Shurmer and Pawliszyn, 2000; ter Laak et al., 2005; Valor et al., 2001; Witt et al., 2009; You et al., 2007; detailed values are presented in Table S2, Supplementary Material), the measured values of $K_{PDMS_{SW}}$ in this study were compared with $K_{PDMS_{SW}}$ in the literature (Fig. S3, Supplementary Material). Values of log $K_{PDMS_{SW}}$ in this study agreed well with median log $K_{PDMS_{SW}}$ values reported in literature except for β- and δ-HCHs. While log $K_{PDMS_{SW}}$ values of 2.59 (Paschke and Popp, 2003) and 2.66 (Valor et al., 2001) were reported for β-HCH, log $K_{PDMS_{SW}}$ obtained in this study (1.81) was approximately one order of magnitude lower than those values. For δ-HCH, log $K_{PDMS_{SW}}$ in this study (2.17) agreed well with 2.03 obtained by Paschke and Popp (2003), but deviated much from 3.30 by Valor et al. (2001). Values of log $K_{PDMS_{SW}}$ in this study were very close to the median literature values especially for less hydrophobic PAHs, chlorinated benzenes and α- and γ-HCHs. However, the measured log $K_{PDMS_{SW}}$ values for more hydrophobic PAHs (i.e., BaP, DBaH, and BghiP) were slightly greater than median values of log $K_{PDMS_{SW}}$. Because the theoretical difference between log $K_{PDMS_{SW}}$ and log $K_{PDMS_{DW}}$ should be about 0.05–0.2 with Setschenow constant of 0.1–0.4 L mol⁻¹ (Endo et al., 2012), it was difficult to evaluate “salting-out” effects in this study due to the wide range of log $K_{PDMS_{SW}}$ values in the literature.

3.3. Determination of partition coefficients between plastic debris and seawater

Preliminary experiments showed that a very long time is required to attain phase equilibrium between plastic debris and seawater for the selected HOCs. Thus, in order to minimize experimental duration and any potential artifacts with this, concentration ratios (C_{PDMS}/C_{SM} for PDMS and solvent mixture and C_{MP}/C_{SM} for MP and solvent mixture) were separately measured to derive $K_{MP_{SM}}/K_{PDMS_{SM}}$ (Fig. 1). Fig. 3 shows changes (a) in C_{PDMS}/C_{SM} and (b) in C_{PEMP}/C_{SM} , with increasing shaking time for PAHs mixture 1 using polyethylene as examples. All other kinetic results are shown in Fig. S4–S7, Supplementary Material. As

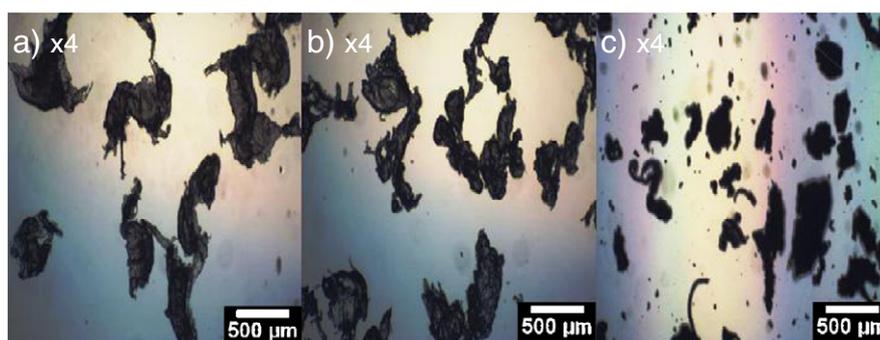


Fig. 2. Microscopic images of microplastics prepared in the laboratory. (a) polyethylene (PE), (b) polypropylene (PP), (c) polystyrene (PS).

Table 1
Values of log K_{PDMSsw} , log K_{PEsw} , log K_{PPsw} , and log K_{PSsw} for the selected HOCs with their log K_{ow} values.

Chemical	log K_{ow} ^a	log K_{PDMSsw} (K_{PDMSsw} in L_{sw}/L_{PDMS})	log K_{PEsw} (K_{PEsw} in L_{sw}/kg_{PE})	log K_{PPsw} (K_{PPsw} in L_{sw}/kg_{PP})	log K_{PSsw} (K_{PSsw} in L_{sw}/kg_{PS})
PAHs					
PHE	4.52	3.87 (3.76, 3.95)	4.44 (4.33, 4.54)	4.00 (3.88, 4.11)	5.39 (5.27, 5.49)
FLU	5.20	4.37 (4.27, 4.45)	5.52 (5.41, 5.62)	4.79 (4.67, 4.90)	5.91 (5.79, 6.01)
ANT	4.50	4.04 (3.94, 4.12)	4.77 (4.67, 4.87)	4.29 (4.18, 4.38)	5.61 (5.51, 5.70)
PYR	5.00	4.37 (4.27, 4.45)	5.57 (5.45, 5.67)	4.80 (4.68, 4.90)	5.84 (5.71, 5.96)
CHR	5.86	4.83 (4.73, 4.92)	6.39 (6.27, 6.50)	5.51 (5.40, 5.61)	6.63 (6.52, 6.72) ^b
BaP	6.35	5.29 (5.17, 5.38)	7.17 (7.03, 7.30) ^b	6.10 (5.97, 6.20) ^b	6.92 (6.80, 7.02) ^b
DBahA	6.75	5.84 (5.74, 5.92)	7.87 (7.72, 8.00) ^b	7.00 (6.89, 7.10) ^b	7.52 (7.41, 7.61) ^b
BghiP	6.90	5.79 (5.68, 5.87)	7.61 (7.46, 7.75) ^b	6.69 (6.56, 6.81) ^b	7.15 (7.03, 7.24) ^b
HCHs					
α -HCH	3.80	2.77 (2.74, 2.80)	2.41 (2.36, 2.46)	2.69 (2.64, 2.75)	3.19 (3.15, 3.23)
β -HCH	3.81	1.81 (1.77, 1.84)	2.04 (1.99, 2.09)	2.18 (2.08, 2.28)	2.63 (2.59, 2.67)
γ -HCH	3.55	2.62 (2.58, 2.65)	2.33 (2.28, 2.38)	2.58 (2.52, 2.64)	3.01 (2.97, 3.05)
δ -HCH	4.14	2.17 (2.13, 2.20)	2.08 (2.03, 2.12)	2.23 (2.13, 2.34)	2.80 (2.75, 2.85)
CBs					
PeCB	5.17	4.51 (4.40, 4.60)	4.63 (4.49, 4.75)	4.50 (4.39, 4.59)	5.10 (4.99, 5.20) ^b
HeCB	5.31	4.90 (4.79, 4.99)	5.22 (5.08, 5.34) ^b	5.01 (4.89, 5.10)	5.28 (5.17, 5.38) ^b

Values in parentheses are the lower and the upper 95% confidence limits. Confidence limits for partition coefficients obtained using ABL permeation method and the third-phase partitioning method were calculated using error propagation.

^a Suggested value by Sangster Research Laboratory.

^b Values might be underestimated due to limited equilibration time.

shown in Figs. 3a and S4, the values of C_{PDMS}/C_{sm} for all HOCs remained unchanged after 6 h. On the contrary, values of C_{MP}/C_{sm} approached steady values after ca. 30 days for PAHs mixture 1 (Figs. 3b, S6a, and S7a). For HCHs, similar trends were observed (Fig. S5–S7). However, slightly increasing trends were observed up to 90 days for PAHs mixture 2 and CBs (Fig. S5–S7). Because values of C_{MP}/C_{sm} are not very high and the size of plastic debris is smaller than that of PDMS, the long equilibration time is likely due to slow diffusion of HOCs into plastic phase. Last four data points were used to derive the equilibrium

ratios of K_{MPsm} and K_{PDMSsm} although K_{MPsm} for more hydrophobic PAHs and CBs might underestimate equilibrium values.

Diffusion coefficients of PAHs in low-density polyethylene (LDPE) were reported 10^{-14} – 10^{-12} $m^2 s^{-1}$ whereas those in PDMS were 2–3 orders of magnitude lower (Rusina et al., 2010). In addition, diffusion coefficients in HDPE are approximately an order of magnitude lower than those in LDPE (Fries and Zarfl, 2012). Because the polyethylene used in this study is classified as HDPE and the diffusion in PS is expected to be slower than in PE, the observed slow kinetics for more hydrophobic chemicals are likely due to slow diffusion in plastic phases.

The obtained partition coefficients between microplastics and seawater are listed in Table 1 as well as their log K_{ow} values for comparison. Sorption capacity of the three plastic materials differed mostly within an order of magnitude for most HOCs tested. Polystyrene had the highest sorption capacity for most HOCs except for the most hydrophobic PAHs (BaP, DBahA, and BghiP). Whereas the sorption capacity of PE was slightly higher than that of PP for PAHs and chlorinated benzenes, PP had higher sorption capacity than PE for HCHs. Different affinities of PAHs to three model plastics agreed with the earlier experiments by Teuten et al. (2007) in which partition coefficients of phenanthrene were in the order of PE > PP > polyvinyl chloride. Similarly, total PAHs concentrations in microplastic pellets deployed for 12 month in San Diego Bay were higher in PE than in PP (Rochman et al., 2013) and concentrations of polychlorinated biphenyls in PE pellets collected in a Japanese beach were higher than those in PP pellets (Endo et al., 2005).

Sorption of HOCs to widely used passive sampling material is typically considered to follow the first-order kinetics. However, sorption of HOCs to microplastics might be limited by diffusion in the plastic phase. This slow diffusion might make that the sorption processes are observed biphasic, fast sorption/desorption in the outer layer followed by slow diffusion into the inner plastic phase. This biphasic model is frequently used for sorption of HOCs to soils or sediments (e.g., Pignatello and Xing, 1996).

3.4. Comparisons with literature values

Partition coefficients obtained in this study for three polymers were compared with reported values of partition coefficients obtained for LDPE used as passive sampling material (Fig. 4). Although polyethylene used in this study has relatively higher density than typical LDPE (Table S1), the measured values agreed well with literature values of partition coefficients between LDPE and water (Adams et al., 2007; Bao et al., 2012; Booij et al., 2003; Cornelissen et al., 2008; Fernandez

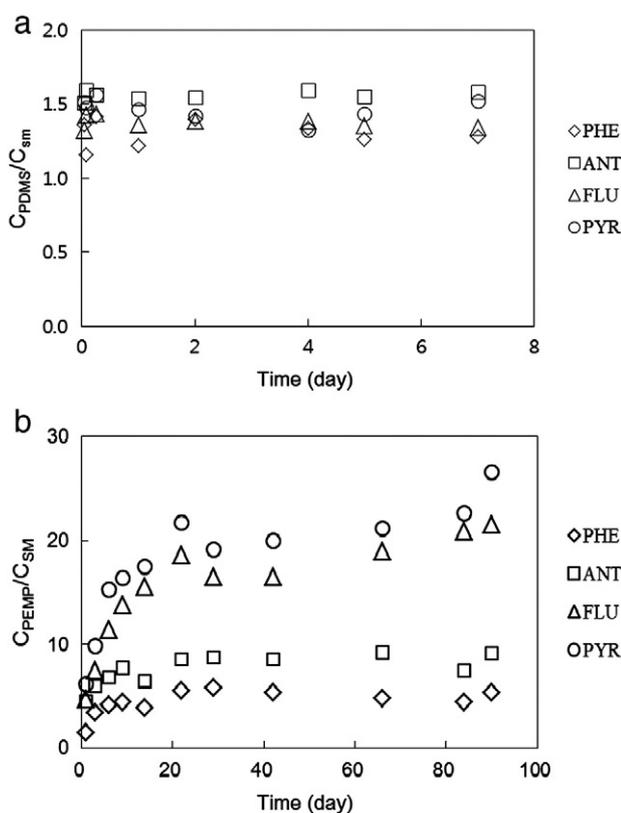


Fig. 3. Changes in (a) C_{PDMS}/C_{sm} and (b) C_{MP}/C_{sm} with increasing shaking time for PAHs mixture 1.

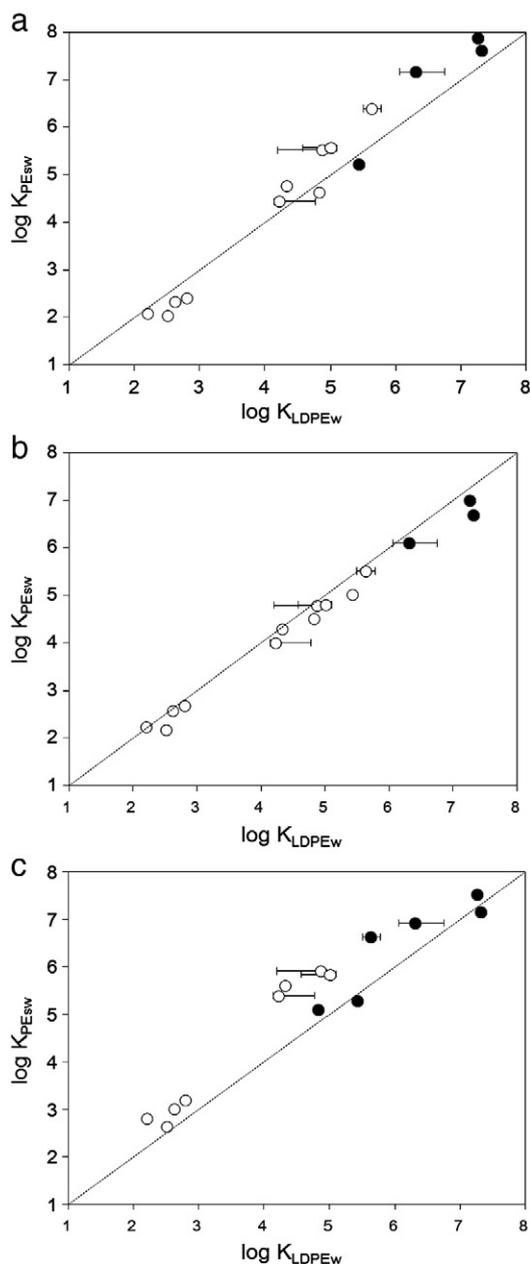


Fig. 4. Relationships between $\log K_{MP_{SW}}$ and $\log K_{LDPEW}$ for (a) polyethylene (PE), (b) polypropylene (PP), and (c) polystyrene. Median values of literature $\log K_{LDPEW}$ were used when multiple values are available. Filled circles indicate $K_{MP_{SW}}$ values that might be underestimated due to limited equilibration time. Horizontal error bars denote the entire range of literature $\log K_{LDPEW}$ values. Dashed lines indicate 1:1 relations.

et al., 2009; Hale et al., 2010; Huckins et al., 1993; Müller et al., 2001; Smedes et al., 2009).

Although sorption capacity of three different plastic materials varied within approximately an order of magnitude, their partition coefficients ($K_{PE_{SW}}$, $K_{PP_{SW}}$, and $K_{PS_{SW}}$) for PAHs and CBs are close to K_{OW} s within an order of magnitude (Fig. 5). However, $\log K_{MP_{SW}}$ values for HCHs are much smaller than their $\log K_{OW}$ values. Because HCHs have relatively high polarity (Goss et al., 2008) and three plastics are non-polar, the relatively smaller $\log K_{MP_{SW}}$ compared with $\log K_{OW}$ for them may be explained by the absence of polar interactions that are important with 1-octanol.

Relatively high sorption capacity of microplastics for HOCs implies potential roles of microplastic debris in the marine environment. Sorption of HOCs to microplastics might lower the dissolved concentration and thus reduce bioavailability where sufficient quantity of microplastic

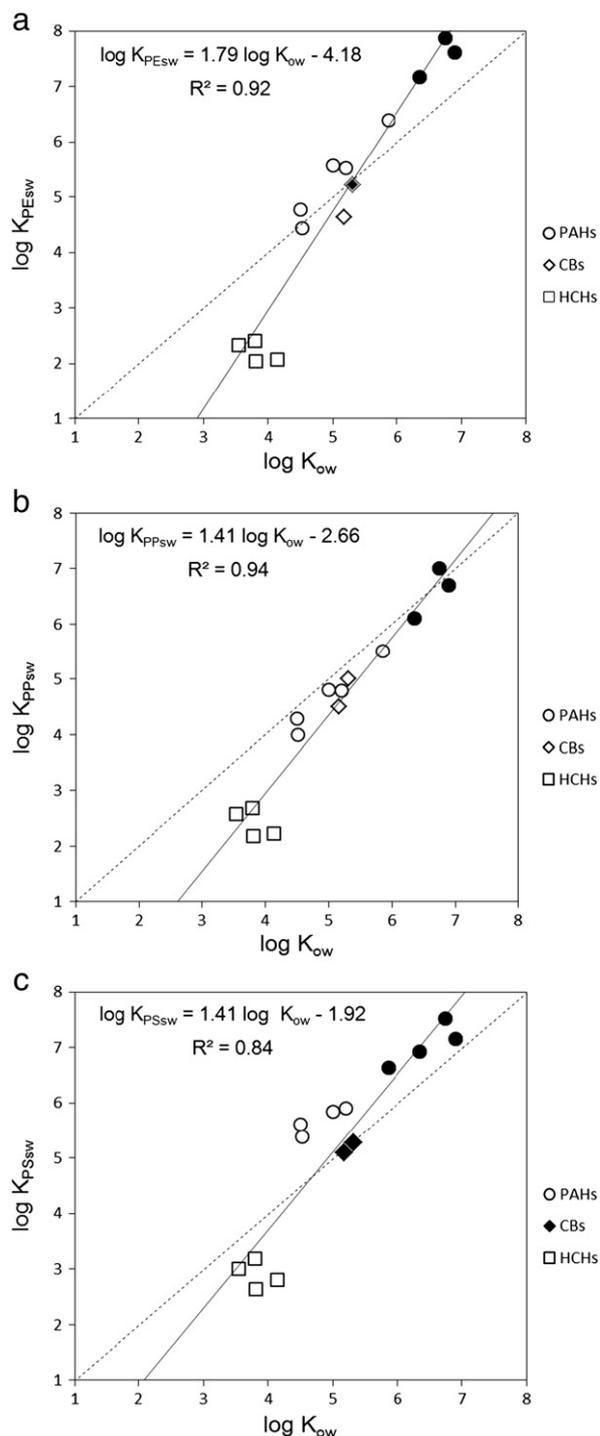


Fig. 5. Relationships between $\log K_{MP_{SW}}$ and $\log K_{OW}$ for (a) polyethylene (PE), (b) polypropylene (PP), and (c) polystyrene (PS). Filled circles and diamonds indicate $K_{MP_{SW}}$ values that might be underestimated due to limited equilibration time. Dashed lines and solid lines indicate 1:1 relations and best-fit linear equations.

exists such as ocean garbage patches. High sorption capacity of microplastics to HOCs would also affect the intermedia transport mechanisms such as evaporation of HOCs from water compartments, enhanced transport of HOCs when desorption is readily available, and plastic-bound uptake of HOCs by fish although it is required for further studies to elucidate the effects of microplastics on these processes. In addition, quantitative partition coefficients will be helpful when monitoring the global distribution of POPs using microplastics used as wide spread passive samplers.

4. Conclusions

The values of K_{MPsw} obtained using a third-phase partitioning method showed that common plastic materials hold high sorption capacities to HOCs comparable to those of 1-octanol or LDPE used for passive sampling purposes. Since microplastics are widespread in the marine environment and undergo slow decomposition, they may play an important role in the fate and transport of HOCs in the marine environment. Because equilibrium partitioning is the most fundamental process governing other kinetic processes, K_{MPsw} obtained in this study would be useful in the evaluation of particle-bound transport processes determining bioavailability and bioaccumulation of HOCs.

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Appendix A. Supplementary material

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