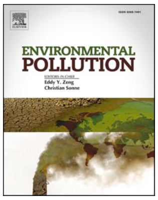
Environmental Pollution 286 (2021) 117461

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol



Evaluating the fate of hexabromocyclododecanes in the coastal environment: Fugacity analysis using field data

Yoonsub Kim [a], Hwang Lee [a,b], Mi Jang [c], Sang Hee Hong [c], Jung-Hwan Kwon [a,*]

[a] *Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea*
[b] *Korea National Cleaner Production Center, Korea Institute of Industrial Technology, Hansin Intervalley 24 East B/D 18F, 322 Teheran-ro, Gangnam-gu, Seoul, 06211, Republic of Korea*
[c] *Oil and POPs Research Group, Korea Institute of Ocean Science and Technology, 41 Jangmok 1-gil, Jangmok-myeon, Geoje, 53201, Republic of Korea*

ARTICLE INFO

Handling Editor: Maria Cristina Fossi

Keywords:
Expanded polystyrene
Fugacity
Hexachlorocyclododecanes
Partition constants

ABSTRACT

Abundant use of plastic materials has increased the amount of microplastics (MPs) and related hazardous chemicals in the marine environment. Hexabromocyclododecanes (HBCDs), brominated flame retardants added to expanded polystyrene (EPS), have been detected in biotic and abiotic samples. In this study, the partition constants of HBCDs between plastics and seawater (K_{Psw}) were determined. Fugacities of HBCDs in EPS, seawater, sediment, and mussels were obtained to determine the directions of the diffusive flux. The fugacities in EPS (f_{EPS}) were greater than those in seawater (f_{sw}), sediment (f_{sed}), and mussels ($f_{swmussel\text{-}EPS}$ and $f_{mussel\text{-}rock}$) by three orders of magnitude, indicating that EPS plastics are a significant source of HBCDs. The $f_{mussel\text{-}rock}$ of α-HBCD in rock mussels was greater than f_{sw} by factors of 1.7, whereas the $f_{mussel\text{-}rock}$ of γ-HBCD was smaller than f_{sw} by factors of 16, indicating the bioisomerization from γ-to α-HBCD. The relatively constant concentration ratio of β-HBCD to the total HBCDs indicated that β-HBCD is a sufficient tracer for determining the diffusive flux. The f_{sed} values of HBCDs were greater than f_{sw} by factors of 17–28, implying a probable advective vertical flow of HBCDs from the EPS plastics, which requires further investigation.

1. Introduction

The significant use of plastic products in modern society has caused an increase in plastic debris in the marine environment. One of the main concerns is that the microplastics (MPs) release non-covalently bound hazardous additives with several potential adverse consequences to the marine environment (Hahladakis et al., 2018; Kwon et al., 2017; Teuten et al., 2009). These additives may be found in up to 70% of plastic products (Andrady et al., 2019) and their release rate into the environment depends on their physicochemical properties as well as environmental characteristics (Hahladakis et al., 2018; Kwon et al., 2017; Teuten et al., 2009).

Hexabromocyclododecanes (HBCDs), which are brominated flame retardants widely used since the 1960s, are mainly used for expanded polystyrene (EPS) (Rani et al., 2014). The total global production of HBCDs in 2001 was 16,700 tons (Law et al., 2005). HBCDs were listed as persistent organic pollutants (POPs) in the Stockholm Convention due to their potential for persistence, bioaccumulation, and toxicity (UN, 2013). Although restrictions have been placed on the manufacture, trade, and use of HBCDs, they were used until 2019 in Brazil, Turkey, Czechia and Saudi Arabia, and until 2020 in Korea, while their production and use in China are still ongoing (UNEP, accessed Jan 6, 2021). In 2013, approximately 1536 tons of HBCDs were used in Korea and 238,000 tons have been produced in China to date (Li et al., 2016; UNEP, accessed Jan 6, 2021). The use of EPS in substantial quantities persists in the fish industry, despite its use as buoys having caused severe marine contamination of polystyrene MPs (Lee et al., 2015). Approximately 3974 tons of EPS buoys are discarded from aquaculture facilities in Korea each year, resulting in 74.6% (w/w) of the MPs with a size of 1–5 mm on coastal beaches (Jang et al., 2014; Lee et al., 2015). HBCDs are detected not only in EPS but also in biotic (e.g., mussels) and abiotic samples (e.g., seawater and sediments) (Al-Odaini et al., 2013, 2015; Covaci et al., 2006; Gu et al., 2017; Hong et al., 2013; Jang et al., 2016, 2017; Rani et al., 2014). Studies of Asia-Pacific coastal regions found HBCD concentrations of 0.05–3350 μg g^{-1} in EPS (Jang et al., 2017; Teuten et al., 2009), while 23.1–5160 ng g^{-1} lipid weight was found in mussels (Jang et al., 2016), and 0.08–1.62 ng L^{-1} and 0.0860–49.9 ng g^{-1} of dry weight in seawater and sediment, respectively (Al-Odaini

---

[*] Corresponding author.
E-mail address: junghwankwon@korea.ac.kr (J.-H. Kwon).

https://doi.org/10.1016/j.envpol.2021.117461
Received 17 February 2021; Received in revised form 9 May 2021; Accepted 22 May 2021

et al., 2015; Hong et al., 2013).

Commercial HBCD mixtures consist mainly of α- (10%–13%), β- (1%–12%), and γ-HBCD (75%–89%). These technical mixtures are added to EPS as flame retardants (Covaci et al., 2006). Furthermore, bioisomerization of γ-to α-HBCD occurs (Law et al., 2006). Although the concentrations of HBCD in coastal environments have been monitored, their partition properties among environmental media have not been conducted to provide a comprehensive understanding of their environmental fate. In environmental systems, chemicals flow from high to low fugacity. When additives such as HBCDs are found concentrated in plastic materials, EPS MPs are an important source of HBCDs, whereas other plastic materials such as polyethylene (PE) and polypropylene (PP) are efficient sinks of HBCDs (Jang et al., 2016; Rochman et al., 2014; Teuten et al., 2009). However, the partition constants of HBCDs between plastics and seawater (K_{Psw}) have not been extensively determined, making it difficult to evaluate the fate of HBCDs in the coastal environment.

This study aimed to quantitatively evaluate the fate of HBCDs in the coastal environment. Values of K_{Psw} were obtained for α-, β-, and γ-HBCD using the three-phase equilibrium method applied in a previous study (Lee et al., 2014). PE, PP, polystyrene (PS), and EPS were chosen as representative plastics in the coastal environment because they are most widely used plastic materials and detected as MPs. A fugacity analysis was conducted by comparing the fugacity levels of HBCDs in the environmental media, presenting the direction of their diffusive flux in the coastal environment.

2. Materials and methods

2.1. Chemicals

The α-, β-, and γ-HBCD, and isotope-labeled standards of ^{13}C-α-, β-, and γ-HBCD were purchased from Wellington Laboratories (Guelph, ON, Canada). Artificial sea salt was purchased from Sigma-Aldrich (St. Louis, MO, USA) and used to make artificial seawater at 35‰. Medical grade polydimethylsiloxane (PDMS) sheets (thickness = 1 mm, density = 1.17 g cm^{-3}) were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). The PE (thickness = 75 μm, density = 0.94 g cm^{-3}), PP (thickness = 25 μm, density = 0.90 g cm^{-3}), and PS (thickness = 29 μm, density = 1.05 g cm^{-3}) films were purchased from Goodfellow Cambridge Ltd. (Huntingdon, UK). EPS sheets (thickness = 300 μm, density = 0.025 g cm^{-3}) were prepared by cutting bulk EPS purchased from a local market. PDMS sheets were used in the phase equilibrium method owing to the ease of handling and its chemical inertness. They were cut into disks (diameter = 6 mm) and the PE, PP, and PS films were cut into square sheets (1 cm × 1 cm). EPS sheets were cut into rectangular sheets (4 cm × 1 cm). PDMS disks, PE, and PP sheets were cleaned using *n*-hexane and methanol for 24 h each and stored in methanol until use. The PS and EPS sheets were cleaned in a Soxhlet extractor using methanol for 12 h and stored in methanol until use. HBCDs were not detected above the detection limits in cleaned PDMS, PE, PP, PS, and EPS.

2.2. Partition constants between PDMS and seawater (K_{PDMSsw})

The K_{PDMSsw} values were measured using the aqueous boundary layer (ABL) permeation method (Kwon et al., 2007). Further details regarding the theory and experimental procedure for the ABL permeation method can be found in previous studies (Kwon et al., 2007; Lee et al., 2012) and the Supplementary Material. In summary, a donor PDMS disk loaded with HBCDs was prepared using a methanol:water ratio of 6:4 (v/v). The donor and acceptor disks were separated using a 6 mm thick artificial seawater layer. The thickness of ABL was estimated to be 12.5 μm because this experiment was conducted in accordance with the experimental design indicated in previous studies (Fig. S1a) (Kwon et al., 2007; Lee et al., 2012; Lee et al., 2014). The mass transfer rate was obtained by measuring the concentration of the donor (C_d) and acceptor (C_a) disks and plotting log [$1-2C_a/(C_a + C_d)$] vs. time. The value of K_{PDMSsw} was derived using the mass transfer rate. The disks were extracted using 1 mL dichloromethane for 24 h, which was exchanged with acetonitrile for a high-performance liquid chromatography (HPLC) analysis. All experiments were conducted at 25 °C.

2.3. Partition constants between plastics and seawater (K_{Psw})

Owing to the strong hydrophobicity of HBCDs, a significant amount of time is required to reach equilibrium in the plastics-seawater system. Thus, K_{Psw} was obtained using a phase equilibrium method to overcome this experimental difficulty (Lee et al., 2014). To determine the partition constants between EPS and seawater (K_{EPSsw}), the equilibrium distribution ratio between EPS and PDMS ($K_{EPS\text{-}PDMS}$) was calculated using Eq. (1), whereas the equilibrium distribution ratios between the plastic material and a solvent mixture (methanol:water = 6:4, v/v) (K_{Psm}) and those between PDMS and the solvent mixture (K_{PDMSsm}) were used to derive K_{Psw} (Eq. (2)). Concentrations of α-, β-, and γ-HBCDs in the solvent mixture were 20.5, 11.6, and 12.5 mg L^{-1}, respectively. Methanol only causes a limited swelling of PS, thus, it was presumed that it did not significantly alter the sorptive properties of polymers (Gilbert et al., 2016; Lee et al., 2003).

$$K_{EPSsw} = K_{PDMSsw} K_{EPS-PDMS} \tag{1}$$

$$K_{Psw} = K_{PDMSsw} \frac{K_{Psm}}{K_{PDMSsm}} \tag{2}$$

An EPS sheet was placed between the two pre-loaded PDMS sheets. The EPS and PDMS sheets were firmly in contact with the magnets (Fig. S1b, Supporting Information). After the designated time intervals based on a preliminary experiment, the EPS and PDMS sheets were extracted using 1 mL and 1.5 mL of dichloromethane, respectively. To determine K_{Psw}, each vial containing PE, PP, PS, or PDMS and the solvent mixture was agitated at 150 rpm using a shaking incubator (Fig. S1c). After the designated time intervals, a plastic sheet (or PDMS disk) was removed and rinsed using 1 mL of methanol:water (6:4, v/v) and 1 mL of distilled water. The plastic sheet (or PDMS disk) was extracted using 1 mL of dichloromethane, which was exchanged with acetonitrile for PE, PP, and PDMS. Because PS and EPS dissolve in dichloromethane, 19 mL of hexane was added to the solution to recrystallize the PS and EPS. The crystals were then filtered through a polytetrafluoroethylene (PTFE) filter (0.45 μm). After the removal of PS and EPS, a mixture of hexane and dichloromethane was exchanged with acetonitrile. All experiments were conducted at 25 °C.

2.4. Fugacity analysis

Reported field data in seawater, sediment, and mussels were used to calculate the fugacity of HBCDs in the coastal environment (Al-Odaini et al., 2015; Hong et al., 2013; Jang et al., 2016). All sampling points for each matrix used for fugacity calculation was situated inside the Jinhae Bay (Fig. S2) and samples were collected within 3 years (from 2010 to 2013). The number of samples are 26 for seawater (14 stations), 19 for sediment (19 stations), 7 for mussel-rock (6 stations), 28 for mussel-EPS (11 stations), and 48 for EPS (11 stations), respectively. In case of mussels, more than 30 individuals were used for one sample of HBCD analysis. Therefore, the field data are considered sufficient to represent the HBCD concentration in this area. EPS buoys that are commonly used in aquaculture farms contain 0.0256–419 (median: 1.52), 0.00737–232 (median: 0.651), and 0.0673–4690 (median: 15.0) μg g^{-1} of α-, β-, and γ-HBCD, respectively (Jang et al., 2016), the concentrations in seawater were 0.0221–0.330 (median: 0.0748), 0.0100–0.159 (median: 0.0315), and 0.0207–0.693 (median: 0.0923) ng L^{-1} (Hong et al., 2013). The concentrations in the sediment were n.d.−6.96 (median: 0.632), n.d.−3.96 (median: 0.410), and 0.0860–39.0 (median: 2.94) ng g$^{-1}_{dw}$ for α-, β-, and γ-HBCD, respectively (Al-Odaini et al., 2015). The concentrations in mussels inhabiting rocks were 0.237–0.632 (median: 0.430), n.d.–0.0564 (median: 0.0205), and 0.0193–0.155 (median: 0.0505) ng $g^{-1}{}_{ww}$, and those for the mussels inhabiting the EPS buoys were 0.0937–10.1 (median: 0.921), n.d.–2.48 (median: 0.123), and 0.132–86.6 (median: 0.793) ng $g^{-1}{}_{ww}$ for α-, β-, and γ-HBCD, respectively (Jang et al., 2016). Because environmental monitoring studies (Al-Odaini et al., 2015; Hong et al., 2013; Jang et al., 2016) have been conducted in different years at different sampling locations, the median values were used for fugacity analysis to demonstrate fugacity gradients in the coastal regions.

The fugacity of HBCDs in each medium (f_{medium}) was calculated using the following equations:

$$f_{EPS} = C_{EPS}\frac{K_H}{K_{EPSsw}}, \tag{3}$$

$$f_{sw} = C_{sw}K_H, \tag{4}$$

$$f_{sed} = C_{sed}\frac{K_H}{K_d}, \text{ and} \tag{5}$$

$$f_{mussel} = C_{mussel}\frac{K_H}{BAF}, \tag{6}$$

where C_{EPS} (μg g^{-1}), C_{sw} (ng L^{-1}), C_{sed} (ng $g^{-1}{}_{dw}$), and C_{mussel} (ng $g^{-1}{}_{ww}$) represent the concentration of HBCDs in the EPS plastics, seawater, sediment, and mussels, respectively. K_{EPSsw} is the partition constant between EPS and seawater (L kg^{-1}_{EPS}), K_H is the Henry's law constant (Pa m^3 mol^{-1}), K_d is the partition coefficient between sediment and water (L kg^{-1}_{sed}), and BAF is the bioaccumulation factor (L $kg^{-1}{}_{ww}$). Values of K_d were calculated by multiplying the partition coefficient between organic carbon and water (K_{oc}) and the fraction of organic carbon (f_{oc}) of the sediment, which was set to 0.02 (Cho et al., 2013). K_H, K_{oc}, and BAF were estimated using EPI Suite™ equations (US EPA, 2012) based on the experimental octanol-water partition constant (K_{ow}) (Guerra et al., 2011). Because estimated K_d values assuming that HBCDs are sorbed only to organic carbon, estimated fugacities in sediment have relatively larger uncertainties. It should be also noted that the temperature correction was not made for fugacity calculation because temperature of environmental samples was not specified. Although partition constants may change by a factor of 2–4 within the environmental temperature range of 15 °C (Bahadur et al., 1997; Lei et al., 2000), the effects of temperature were neglected because the range of monitored concentration outweighed and determine the fugacity gradients among media.

2.5. Instrumental analyses

The identification and quantification of the chemicals were performed using an HPLC connected to a triple-quadrupole mass spectrometer TQ5500 (SCIEX, Framingham, MA, USA). The HPLC and mass spectrometer operating conditions were slightly modified from those indicated by previous studies (Al-Odaini et al., 2013; Jang et al., 2016). In summary, the separation of each chemical was achieved on a Zorbax Eclipse C18 reversed-phase analytical column (4.6 × 150 mm i.d., 3 μm particle size, Agilent Technologies). The gradient program consisted of two mobile phases (A = water:methanol, 15:85, B = methanol:acetonitrile, 70:30). Mass spectrometry analyses were performed in the multi-reaction monitoring and atmospheric chemical ionization negative mode. Quantification was based on the transitions 639/79 and 652/79 for α-, β-, and γ-HBCD and ^{13}C-α-, β-, and γ-HBCD, respectively. The instrumental detection limits were quantified as 0.5, 1.0, 2.5 ng mL^{-1} for α-, β-, and γ-HBCD, respectively. Because the measured concentrations of all laboratory-prepared samples were greater than the lowest external standard (5 ng mL^{-1}), it was regarded that all measurement was conducted within the linear dynamic range of the instrument. Before the instrumental analysis, 20 ng of each ^{13}C-α-, β-, and γ-HBCD were spiked into samples to correct any variations in instrumental analysis.

Extraction recovery was assessed using polymers prepared by spiking 3 and 5 μL of HBCD solution with concentrations of 9.61, 5.22, and 7.49 mg L^{-1} for α-, β-, and γ-HBCD, respectively. Measurements were conducted in triplicate for each initial spiking volume. Table S1 presents the extraction recoveries of HBCDs from PDMS, PE, PP, PS, and EPS.

3. Results and discussion

3.1. Determination of partition constants

Fig. 1a presents the mass transfer kinetics obtained by measuring the concentrations of both the donor (C_d) and acceptor PDMS disks (C_a). The solid lines indicate the mass transfer kinetics obtained by a linear regression analysis of the experimental values. The values of log K_{PDMSsw} were 4.01, 4.14, and 4.66 for α-, β-, and γ-HBCD, respectively (Table 1). The concentration ratio of C_{EPS}/C_{PDMS} was measured to obtain $K_{EPS\text{-}PDMS}$. $K_{EPS\text{-}PDMS}$ values were obtained from the average of the last four data points, including the 12-day data. Although it seems that equilibrium was reached after 12 days (Fig. 1b), there might be an uncertainty considering that the 38-day results show slightly higher values than the 21-day values.

C_P/C_{sm} and C_{PDMS}/C_{sm} were measured to obtain K_{Psm}/K_{PDMSsm} (Figs. S3 and S4). K_{PEsm} was obtained using the average of the last three data points, including the 42-day data. Because PP and PS were thinner than PE, a shorter time was required to reach equilibrium (Fig. S3). The average of the last four data points was used to obtain K_{PPsm} and K_{PSsm}. A period of 12 h was sufficient to reach equilibrium for K_{PDMSsm}, which was obtained using the average of the last four data points, including the 12-h data (Fig. S4). K_{Psw} values were then calculated using Eq. (2).

Table 1 summarizes the partitioning properties of HBCDs. The logarithmic values of K_{Psw} were 4.37–5.24, 3.77–4.57, 3.41–4.10, and 3.18–3.91 for PE, PP, PS, and EPS, respectively. The sorption capacities of PS and EPS were slightly lower than those of PE and PP owing to the difference in the state of each plastic at ambient temperature. The glass transition temperatures (T_g) of PE and PP were reported to be approximately 200 K and 279 K, respectively, indicating a rubbery state at 25 °C (Lee et al., 1998; Yang et al., 2016). Rubbery regions of PE and PP have relatively greater flexibility, allowing them to have higher sorption capacity. PS and EPS, however, are in a glassy state (T_g of PS = 373 K) at 25 °C, restricting molecular vibrational and short-range rotational motions (Endo and Koelmans, 2019).

The values of log K_{EPSsw} were 3.18, 3.32, and 3.91 for α-, β-, and γ-HBCD, respectively, similar to those of log K_{PSsw}, which were 3.41, 3.84, and 4.10 for α-, β-, and γ-HBCD, respectively. The foaming process during the production of EPS generates pores (average pore diameter = 39.3 nm) (Zhang et al., 2018). Although the existence of pores increases the surface area of EPS significantly greater than that of PS, it is not likely to affect partition constants because the large pores apparently do not alter micropores less than 2 nm where HBCDs are sorbed. A previous study indicated that the micropores were not detected in the virgin EPS whereas they were found in weathered beach EPS (Zhang et al., 2018). Insignificant differences between log K_{EPSsw} and log K_{PSsw} could be due to the lack of significant differences in their sorption sites. However, changes in the EPS sorption properties with weathering needs to be investigated because EPS could be degraded much more easily than PS, and micropores affecting the sorption phenomena may be formed during the dynamic degradation of EPS under environmental conditions.

3.2. Fugacity analysis

Fig. 2a illustrates the median fugacities of the HBCDs in the coastal environment. The range of β-HBCD fugacities, which is the main tracer of the fugacity analysis, is presented in Fig. 2b and those of α- and γ-HBCDs are shown in Fig. S5. The values of f_{EPS} were 1.71 × 10^{-13}–2.81 × 10^{-9} (median: 1.02 × 10^{-11}), 3.50 × 10^{-14}–1.10 × 10^{-9}

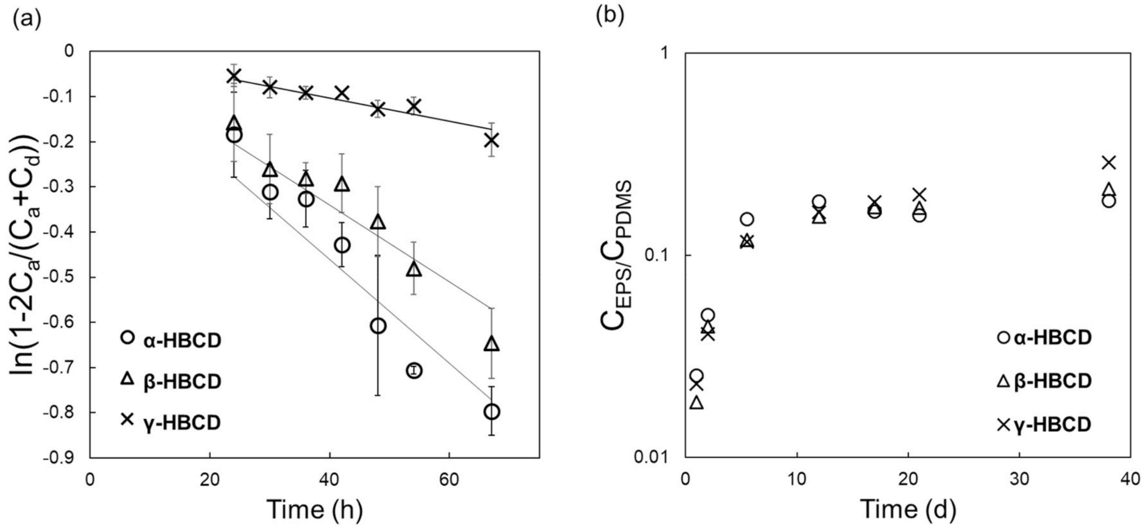


Fig. 1. (a) Mass transfer kinetics of hexabromocyclododecanes (HBCDs) used to obtain the mass transfer coefficient between the donor and the acceptor PDMS disks. Error bars indicate standard deviation of triplicate measurements. (b) Changes in C_{EPS}/C_{PDMS} (expanded polystyrene/polydimethylsiloxane concentration ratio) of HBCDs with increasing contact time.

Table 1
Physicochemical properties of hexabromocyclododecanes (HBCDs).

Chemicals	Log K_{ow} [a]	Log K_{PDMSsw}	Log K_{PEsw} [K_{PEsw} in L_{sw} kg_{PE}^{-1}]	Log K_{PPsw} [K_{PPsw} in L_{sw} kg_{PP}^{-1}]	Log K_{PSsw} [K_{PSsw} in L_{sw} kg_{PS}^{-1}]	Log K_{EPSsw} [K_{EPSsw} in L_{sw} kg_{EPS}^{-1}]
α-HBCD	5.07	4.01 (3.96, 4.07)	4.38 (4.31, 4.45)	3.73 (3.55, 3.86)	3.36 (3.15, 3.50)	3.18 (3.12, 3.25)
β-HBCD	5.12	4.14 (4.09, 4.20)	4.72 (4.66, 4.79)	4.10 (3.98, 4.20)	3.79 (3.53, 3.96)	3.33 (3.25, 3.40)
γ-HBCD	5.47	4.66 (4.62, 4.71)	5.25 (5.17, 5.32)	4.58 (4.48, 4.67)	4.08 (3.71, 4.27)	3.91 (3.77, 4.03)

Values in parentheses are the lower and upper 95% confidence limits. Confidence limits were calculated using error propagation. K_{EPSsw} values might be underestimated due to the insufficient equilibration time.

[a] Guerra et al., 2011

(median: 3.09 × 10^{-12}), and 8.41 × 10^{-14}–5.86 × 10^{-9} (median: 1.88 × 10^{-11}) Pa for α-, β-, and γ-HBCD, respectively. These f_{EPS} values were greater than the fugacities in seawater (f_{sw}), sediment (f_{sed}), and mussels ($f_{mussel\text{-}EPS}$ and $f_{mussel\text{-}rock}$) by at least three orders of magnitude, the $f_{mussel\text{-}EPS}$ values were greater than the $f_{mussel\text{-}rock}$ values by one order of magnitude. Because mussels may uptake HBCDs from the EPS particles in fitting size ranges or from the ventilation of water (Jang et al., 2021), a value of $f_{mussel\text{-}EPS}$ that is higher than that of $f_{mussel\text{-}rock}$ implies the importance of the intake of EPS particles or greater seawater concentrations near mussels inhabited on EPS buoys. Hong et al. showed that the concentration of HBCDs in seawater decreased with the distance from aquaculture farms where EPS buoys were used (Hong et al., 2013). Together with the fugacity analysis in this study, the concentration gradient in seawaters from aquaculture farms suggested that EPS buoys are significant sources of HBCDs in the coastal environment (Hong et al., 2013; Jang et al., 2021).

A thorough investigation of the HBCD isomer fugacities reveals that their environmental distribution is isomer-specific. The $f_{mussel\text{-}rock}$ value of α-HBCD was 12.9 × 10^{-16} Pa, which is 1.7 times greater than that of f_{sw}, indicating that α-HBCD flows from mussels inhabiting rocks to

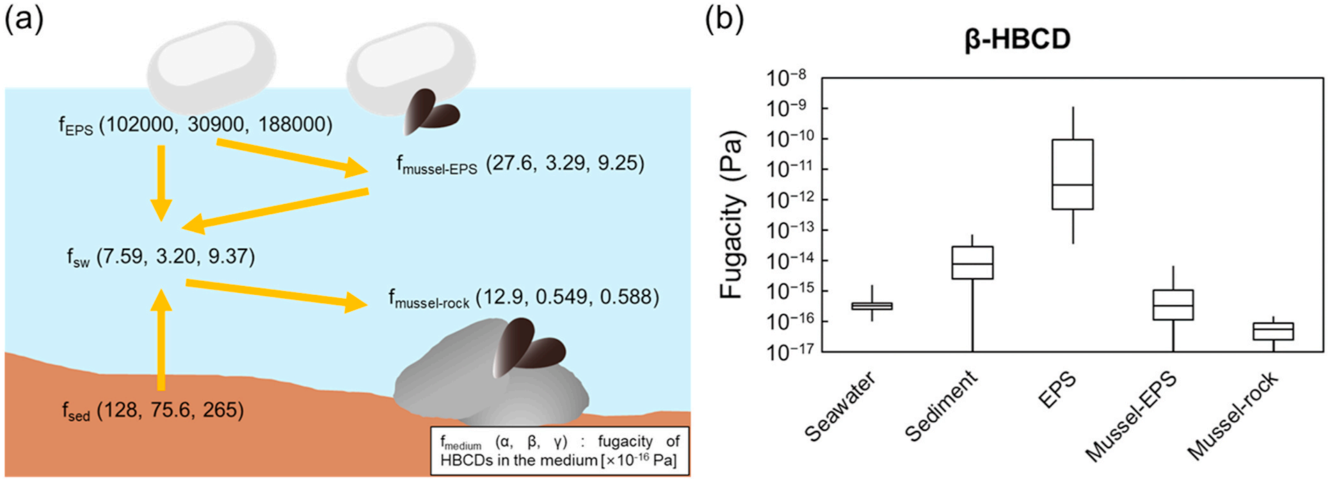


Fig. 2. (a) Median fugacities of HBCDs in the coastal environment. The arrows indicate the mass flow direction of β-HBCD. (b) A box-and-whisker plot of β-HBCD fugacities in environmental media. The lines inside the box indicate the median. The lower and upper box boundaries are the 25th and 75th percentiles, and lower and upper lines indicate the minimum and maximum values.

seawater. However, the $f_{mussel\text{-}rock}$ value of γ-HBCD was lower than that of f_{sw} by a factor of 16, suggesting that γ-HBCD flows in the opposite direction. This difference between isomers could be explained by the bioisomerization of γ-HBCD to α-HBCD in the body and resistance of α-HBCD to biotransformation by the cytochrome P450 (CYP) system (Du et al., 2012; Zegers et al., 2005). The CYP of mussels may have decreased the isomer ratio of γ-HBCD and increased that of α-HBCD. Unlike α- and γ-HBCD, β-HBCD had a relatively constant isomer ratio in the environmental media, indicating that β-HBCD could serve as a good tracer to determine the diffusive flux of a technical mixture of HBCDs added in EPS (Fig. S6). Although the fate of each isomer was different owing to the biological transformations, the HBCDs leached from EPS were transferred to mussels via seawater, considering the slightly lower value of $f_{mussel\text{-}rock}$ for β-HBCD compared to that of f_{sw}.

Notably, calculated fugacities in sediment were greater than those in seawater. If HBCDs were first leached from the EPS plastics to seawater and then transported to other media, a greater value of f_{sw} would be expected than that of f_{sed} or f_{mussel}. However, the median f_{sed} was significantly higher than the median f_{sw} by factors of 17, 24, and 28 for α-, β-, and γ-HBCD, respectively (Fig. 2a), implying a possible advective transport of HBCDs from the EPS plastics to the sediments. Because the concentrations of HBCDs in the sediments collected in the Jinhae Bay, where aquaculture farms are densely populated, were distinctly higher than in those collected outside of the Bay (Al-Odaini et al., 2015), the hypothesis of vertical advective transport of EPS debris requires further investigation. Although EPS has a low density, fragmentation of EPS to smaller particles eliminates trapped air and eventually increases its density to a value close to that of PS. Earlier studies detected EPS MPs in sediments (Abidli et al., 2018; Wu et al., 2020). In addition, EPS can form a biofilm and settle on the sediments and further coagulate with other naturally occurring particles. With an increase in the thickness of biofilm, the density of MPs also increases, and the extracellular polymeric substances secreted by the biofilm could result in the aggregation of MPs with other particles, which may cause vertical sinking (Rummel et al., 2017; Tarafdar et al., 2021; Zhou et al., 2018).

3.3. *Implications of the study*

High fugacity values of HBCDs found in the EPS buoys compared to those in other media indicate that removal of EPS buoys would reduce the level of HBCDs in the coastal environments. Recent regulations in Korea banning the use of EPS buoys for aquaculture purposes (Kang, 2020) are expected to be of significant help in this regard. However, because sediments can be an important secondary source of HBCDs, as observed from the greater value of f_{sed} compared to that of f_{sw}, continued monitoring will be required in contaminated areas.

The fugacity analysis in this study implies that vertical sinking is an important transport process for HBCDs originating from EPS. Because diverse plastic additives are added, and little is known regarding their environmental impacts, the vertical advective flow of persistent chemical additives is important in the assessment of their environmental fate as well as the fate of MPs on a global scale.

4. Conclusions

Partitioning properties of HBCDs were evaluated and their contamination and diffusive flux in the coastal environment were assessed based on fugacities of β-HBCD in EPS, seawater, sediment, and mussels. The highest fugacity in EPS (f_{EPS}) suggests that EPS plastics have been strong sources of HBCDs. Higher fugacities in sediment than those in seawater by factors of 17–28 might be owing to vertical sinking of EPS debris containing high concentration of HBCDs after coagulation with other particles, although this hypothesis requires further investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research was supported by the research project entitled “Environmental Risk Assessment of Microplastics in the Marine Environment” from the Ministry of Oceans and Fisheries of Korea and by the National Research Foundation (NRF) grant funded by the Korean government (MEST) (No. 2020R1A2C2009244).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117461.

Author statement

Yoonsub Kim: Methdology, Investigation, Data curation, Writing – original draft Preparation, Hwang Lee: Methodology, Mi Jang: Investigation, Writing – original draft Preparation, Sang Hee Hong: Supervision, Writing – review & editing, Funding acquisition, Jung-Hwan Kwon: Conceptualization, Methodology, Supervision, Writing – review & editing, Funding acquisition.

References

Al-Odaini, N.A., Yim, U.H., Kim, N.S., Shim, W.J., Hong, S.H., 2013. Isotopic dilution determination of emerging flame retardants in marine sediments by HPLC-APCI-MS/MS. Anal. Methods 5 (7).

Al-Odaini, N.A., Shim, W.J., Han, G.M., Hong, S.H., 2015. Enrichment of hexabromocyclododecanes in coastal sediments near aquaculture area and a wastewater treatment plant in a semi-enclosed bay in South Korea. Sci. Total Environ. 505, 290–298.

Andrady, A.L., Rajapakse, N., 2019. Additives and chemicals in plastics. In: Takada, H., Karapanagioti, H.K. (Eds.), Hazardous Chemicals Associated with Plastics in the Marine Environment. Springer International Publishing, Cham, pp. 1–17.

Abidli, S., Antunes, J.C., Ferreira, J.L., Lahbib, Y., Sobral, P., Trigui El Menif, N., 2018. Microplastics in sediments from the littoral zone of the north Tunisian coast (mediterranean sea). Estuar. Coast Shelf Sci. 205, 1–9.

Bahadur, N.P., Shiu, W.-Y., Boocock, D.G.B., Mackay, D., 1997. Temperature dependence of octanol-water partition coefficient for selected chlorobenzenes. J. Chem. Eng. Data 42 (4), 685–688, 1997.

Cho, Y.-S., Lee, W.-C., Kim, J.-B., Hong, S.-J., Kim, H.-C., Kim, C.-S., 2013. Establishment of environmental assessment using sediment total organic carbon and macrobenthic polychaete community in shellfish farms. J. Korean Soc. Marine Environ. Safety 19 (5), 430–438.

Covaci, A., Gerecke, A.C., Law, R.J., Voorspoels, S., Kohler, M., Heeb, N.V., Leslie, H., Allchin, C.R., de Boer, J., 2006. Hexabromocyclododecanes (HBCDs) in the environment and humans: a review. Environ. Sci. Technol. 40 (12), 3679–3688.

Du, M., Lin, L., Yan, C., Zhang, X., 2012. Diastereoisomer- and enantiomer-specific accumulation, depuration, and bioisomerization of hexabromocyclododecanes in zebrafish (*Danio rerio*). Environ. Sci. Technol. 46 (20), 11040–11046.

Endo, S., Koelmans, A.A., 2019. Sorption of hydrophobic organic compounds to plastics in the marine environment: Equilibrium. In: Takada, H., Karapanagioti, H.K. (Eds.), Hazardous Chemicals Associated with Plastics in the Marine Environment. Springer International Publishing, Cham, pp. 185–204.

Gilbert, D., Witt, G., Smedes, F., Mayer, P., 2016. Polymers as reference partitioning phase: polymer calibration for an analytically operational approach to quantify multimedia phase partitioning. Anal. Chem. 88 (11), 5818–5826.

Gu, S.Y., Ekpeghere, K.I., Kim, H.Y., Lee, I.S., Kim, D.H., Choo, G., Oh, J.E., 2017. Brominated flame retardants in marine environment focused on aquaculture area: occurrence, source and bioaccumulation. Sci. Total Environ. 601–602, 1182–1191.

Guerra, P., Eljarrat, E., Barceló, D., 2011. Determination of halogenated flame retardants by liquid chromatography coupled to mass spectrometry. TrAC Trends Anal. Chem. 30 (6), 842–855.

Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: migration, release, fate and environmental impact during their use, disposal and recycling. J. Hazard Mater. 344, 179–199.

Hong, S.H., Jang, M., Rani, M., Han, G.M., Song, Y.K., Shim, W.J., 2013. Expanded polystyrene (EPS) buoy as a possible source of hexabromocyclododecanes (HBCDs) in the marine environment. Organohalogen Compd. 75, 882–885.

Jang, Y.C., Lee, J., Hong, S., Mok, J.Y., Kim, K.S., Lee, Y.J., Choi, H.W., Kang, H., Lee, S., 2014. Estimation of the annual flow and stock of marine debris in South Korea for management purposes. Mar. Pollut. Bull. 86 (1–2), 505–511.

Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2016. Styrofoam debris as a source of hazardous additives for marine organisms. Environ. Sci. Technol. 50 (10), 4951–4960.

Jang, M., Shim, W.J., Han, G.M., Rani, M., Song, Y.K., Hong, S.H., 2017. Widespread detection of a brominated flame retardant, hexabromocyclododecane, in expanded polystyrene marine debris and microplastics from South Korea and the Asia-Pacific coastal region. Environ. Pollut. 231 (1), 785–794.

Jang, M., Shim, W.J., Han, G.M., Cho, Y., Moon, Y., Hong, S.H., 2021. Relative importance of aqueous leachate versus particle ingestion as uptake routes for microplastic dditives (hexabromocyclododecane) to mussels. Environ. Pollut. 270, 116272.

Kang, H.M., 2020. Korea to ban styrofoam buoys by 2025. The Korea Bizwire. (Accessed 12 October 2020).

Kwon, J.H., Chang, S., Hong, S.H., Shim, W.J., 2017. Microplastics as a vector of hydrophobic contaminants: importance of hydrophobic additives. Integrated Environ. Assess. Manag. 13 (3), 494–499.

Kwon, J.H., Wuethrich, T., Mayer, P., Escher, B.I., 2007. Dynamic permeation method to determine partition coefficients of highly hydrophobic chemicals between poly (dimethylsiloxane) and water. Anal. Chem. 79 (17), 6816–6822.

Law, R.J., Kohler, M., Heeb, N.V., Gerecke, A.C., Schmid, P., Voorspoels, S., Covaci, A., Becher, G., Janák, K., Thomsen, C., 2005. Hexabromocyclododecane challenges scientists and regulators. Environ. Sci. Technol. 39 (13), 281A–287A.

Law, K., Palace, V.P., Halldorson, T., Danell, R., Wautier, K., Evans, B., Alaee, M., Marvin, C., Tomy, G.T., 2006. Dietary accumulation of hexabromocyclododecane diastereoisomers in juvenile rainbow trout (*Oncorhynchus mykiss*) I: bioaccumulation parameters and evidence of bioisomerization. Environ. Toxicol. Chem. 25 (7), 1757–1761.

Lee, J.N., Park, C., Whitesides, G.M., 2003. Solvent compatibility of poly (dimethylsiloxane)-based microfluidic devices. Anal. Chem. 75 (23), 6544–6554.

Lee, S., Lee, J.H., Choi, K., Rhee, J.M., 1998. Glass transition behavior of polypropylene/polystyrene/styrene-ethylene-propylene block copolymer blends. Polym. Bull. 40 (6), 765–771.

Lee, H., Kim, H.-J., Kwon, J.-H., 2012. Determination of Henry's law constant using diffusion in air and water boundary layers. J. Chem. Eng. Data 57 (11), 3296–3302.

Lee, H., Shim, W.J., Kwon, J.H., 2014. Sorption capacity of plastic debris for hydrophobic organic chemicals. Sci. Total Environ. 470–471, 1545–1552.

Lee, J., Lee, J.S., Jang, Y.C., Hong, S.Y., Shim, W.J., Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Kang, D., Hong, S., 2015. Distribution and size relationships of plastic marine debris on beaches in South Korea. Arch. Environ. Contam. Toxicol. 69 (3), 288–298.

Lei, Y.D., Wania, F., Shiu, W.Y., Boocock, D.G.B., 2000. HPLC-based method for estimating the temperature dependence of n-octanol-water partition coefficients. J. Chem. Eng. Data 45 (5), 738–742.

Li, L., Weber, R., Liu, J., Hu, J., 2016. Long-term emissions of hexabromocyclododecane as a chemical of concern in products in China. Environ. Int. 91, 291–300.

Rani, M., Shim, W.J., Han, G.M., Jang, M., Song, Y.K., Hong, S.H., 2014. Hexabromocyclododecane in polystyrene based consumer products: an evidence of unregulated use. Chemosphere 110, 111–119.

Rochman, C.M., Lewison, R.L., Eriksen, M., Allen, H., Cook, A.M., Teh, S.J., 2014. Polybrominated diphenyl ethers (PBDEs) in fish tissue may be an indicator of plastic contamination in marine habitats. Sci. Total Environ. 476–477, 622–633.

Rummel, C.D., Jahnke, A., Gorokhova, E., Kühnel, D., Schmitt-Jansen, M., 2017. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. Environ. Sci. Technol. Lett. 4 (7), 258–267.

Tarafdar, A., Lee, J.-U., Jeong, J.-E., Lee, H., Jung, Y., Oh, H.B., Woo, H.Y., Kwon, J.-H., 2021. Biofilm development of *Bacillus siamensis* ATKU1 on pristine short chain low-density polyethylene: a case study on microbe-microplastics interaction. J. Hazard Mater. 409, 124516.

Teuten, E.L., Saquing, J.M., Knappe, D.R., Barlaz, M.A., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhavong, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Phil. Trans. Roy. Soc. Lond. B 364 (1526), 2027–2045.

UNEP. Register of specific exemptions: hexabromocyclododecane. http://www.pops.int/Implementation/Exemptions/SpecificExemptions/Hexabromocyclododecane/RoSE/tabid/5034/Default.aspx. (Accessed 6 January 2021).

US EPA, 2012. Estimation Programs Interface Suite™ for Microsoft® Windows, 4.11. United States Environmental Protection Agency.

Wu, N., Zhang, Y., Li, W., Wang, J., Zhang, X., He, J., Li, J., Ma, Y., Niu, Z., 2020. Co-effects of biofouling and inorganic matters increased the density of environmental microplastics in the sediments of Bohai Bay Coast. Sci. Total Environ. 717, 134431.

Yang, Q., Chen, X., He, Z., Lan, F., Liu, H., 2016. The glass transition temperature measurements of polyethylene: determined by using molecular dynamic method. RSC Adv. 6 (15), 12053–12060.

Zegers, B.N., Mets, A., van Bommel, R., Minkenberg, C., Hamers, T., Kamstra, J.H., Pierce, G.J., Boon, J.P., 2005. Levels of hexabromocyclododecane in harbor porpoises and common dolphins from Western European Seas, with evidence for stereoisomer-specific biotransformation by Cytochrome P450. Environ. Sci. Technol. 39 (7), 2095–2100.

Zhang, H., Wang, J., Zhou, B., Zhou, Y., Dai, Z., Zhou, Q., Chriestie, P., Luo, Y., 2018. Enhanced adsorption of oxytetracycline to weathered microplastic polystyrene: kinetics, isotherms and influencing factors. Environ. Pollut. 243 (B), 1550–1557.

Zhou, Q., Zhang, H., Fu, C., Zhou, Y., Dai, Z., Li, Y., Tu, C., Luo, Y., 2018. The distribution and morphology of microplastics in coastal soils adjacent to the Bohai Sea and the Yellow Sea. Geoderma 322, 201–208.