



## Desorption modeling of hydrophobic organic chemicals from plastic sheets using experimentally determined diffusion coefficients in plastics

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### ABSTRACT

To evaluate rate of migration from plastic debris, desorption of model hydrophobic organic chemicals (HOCs) from polyethylene (PE)/polypropylene (PP) films to water was measured using PE/PP films homogeneously loaded with the HOCs. The HOCs fractions remaining in the PE/PP films were compared with those predicted using a model characterized by the mass transfer Biot number. The experimental data agreed with the model simulation, indicating that HOCs desorption from plastic particles can generally be described by the model. For hexachlorocyclohexanes with lower plastic-water partition coefficients, desorption was dominated by diffusion in the plastic film, whereas desorption of chlorinated benzenes with higher partition coefficients was determined by diffusion in the aqueous boundary layer. Evaluation of the fraction of HOCs remaining in plastic films with respect to film thickness and desorption time showed that the partition coefficient between plastic and water is the most important parameter influencing the desorption half-life.

### 1. Introduction

The exorbitant use of plastic materials in modern society has resulted in a large amount of plastic debris in the environment (Andrady, 2011; Derraik, 2002; Thompson et al., 2004). Plastic particles with sizes of less than five millimeters are termed “microplastics” and are suspected to cause adverse effects on the ecosystem (Andrady, 2011; Derraik, 2002; Engler, 2012). One of the major concerns about microplastics in the aquatic environment is the release of harmful chemicals from the small-sized plastic debris (Hartmann et al., 2017; Koelmans et al., 2016; Kwon et al., 2017). Chemical substances in microplastics include hydrophobic organic chemicals (HOCs) absorbed from water and chemical additives that are intentionally added to the plastics during manufacture, such as flame retardants, UV stabilizers, antioxidants, and plasticizers. Detection of HOCs in plastic particles in the environment has been reported in many recent monitoring studies (Endo et al., 2005; Hirai et al., 2011; Karapanagioti et al., 2011; Rani et al., 2015).

Although roles of microplastics to carry hydrophobic organic pollutants through aquatic food chain would be limited (Koelmans et al., 2016), desorption of HOCs from plastics should be regarded as important process especially for massively used plastic additives (Kwon et al., 2017). The rate of desorption of HOCs from microplastic particles

to the surrounding medium is important not only for quantifying the uptake of chemicals by aquatic organisms via the ingestion of microplastic particles, but also for evaluating the release rate of plastic additives into the aquatic environment. However, desorption of HOCs from microplastic particles has been investigated in only a few studies (Endo et al., 2013; Koelmans et al., 2013; Narváez Valderrama et al., 2016; Teuten et al., 2009). For example, Narváez Valderrama et al. (2016) determined the diffusion coefficients of polybrominated diphenyl ethers (PBDEs) and proposed a model to describe the fraction of PBDEs desorbed during the residence time in the digestive tract. Koelmans et al. (2013) developed a conceptual model that simulates the effects of microplastic particles on bioaccumulation of polychlorinated biphenyls (PCBs). Teuten et al. (2009) measured desorption kinetics of a few organic contaminants (e.g., toluene, *o*-xylene, and tetrachloroethylene) and simulated one-compartment polymer diffusion model. Endo et al. (2013) compared two extreme model cases, i.e., desorption determined by internal diffusion and by aqueous boundary layer diffusion. By monitoring the desorption of selected PCBs from microplastic pellets collected from a beach over the course of 128 days, they showed that the aqueous boundary layer diffusion model better explained the experimental desorption (Endo et al., 2013). However, the importance of two processes—diffusion in the plastic and in the aqueous boundary layer—may depend on environmental conditions

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and chemical properties such as the plastic-water partition coefficient.

In this study, we propose a versatile model to describe the desorption of organic chemicals with a wide range of hydrophobicity from microplastics into water. Polyethylene (PE) and polypropylene (PP) were used as model plastic materials because of their high abundance in the environment (Hidalgo-Ruz et al., 2012; Rios et al., 2007). Six persistent organic pollutants (POPs) (i.e.,  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -hexachlorocyclohexanes (HCH), pentachlorobenzene (PeCB), and hexachlorobenzene (HeCB)) were chosen as model hydrophobic organics (HOCs) covering a wide range of hydrophobicity with experimental partition coefficients between model microplastics and seawater (Lee et al., 2014). The molecular diffusion coefficients of the selected chemicals in the plastic phase were determined using film-stacking experiments. The fractions of HOCs remaining in the plastic phase were measured in batch tests and were compared with the predictions from the convection-diffusion model. Finally, the degree of desorption of hydrophobic chemicals from microplastics is modeled and demonstrated with respect to time and microplastic size to provide an estimate of the desorption half-lives of the HOCs under various environmental conditions.

## 2. Materials and methods

### 2.1. Materials and chemicals

High-purity chemical standards were used as the model HOCs.  $\alpha$ - (99.8%),  $\beta$ - (99.5%),  $\gamma$ - (99.8%), and  $\delta$ -HCH (98.2%), PeCB (98%), and HeCB (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), or Fluka (Buch, Switzerland). All experiments were conducted using mixtures of compounds having similar chemical structures, i.e., HCH mixture ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH) and chlorinated benzene mixture (PeCB and HeCB). Artificial seawater was prepared at 3.5% (w/w) by dissolving artificial sea salt purchased from Sigma-Aldrich in de-ionized water. The partitioning properties of all the HOCs are listed in Table 1.

Medical-grade polydimethylsiloxane (PDMS) sheets with a thickness of 1.0 mm and density of  $1.17 \text{ g cm}^{-3}$  were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). PDMS was cut into rectangular sheets ( $10 \text{ mm} \times 50 \text{ mm}$ ) before use. The sheets were cleaned using *n*-hexane and methanol for 2 h each and stored in methanol until use.

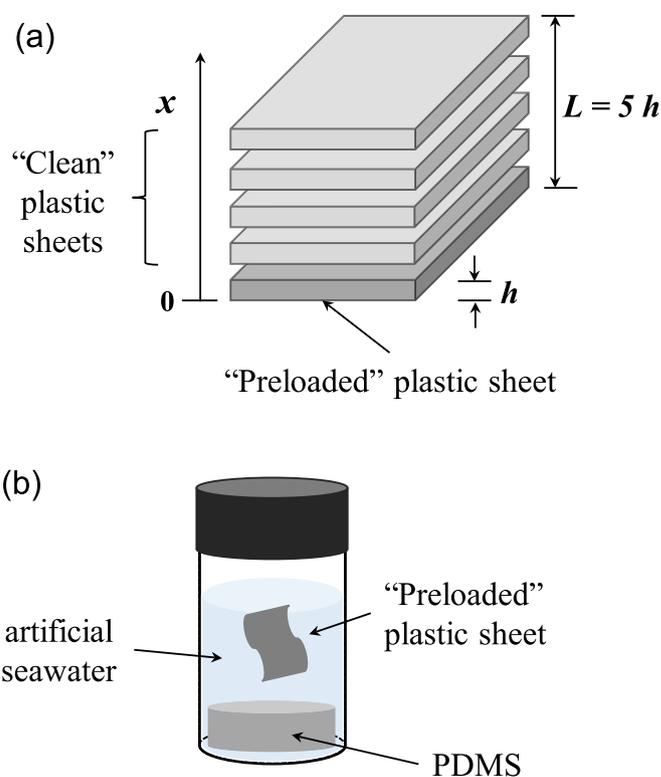
Films of PE (thickness =  $75 \mu\text{m}$ , density =  $0.94 \text{ g cm}^{-3}$ ) and PP (thickness =  $25 \mu\text{m}$ , density =  $0.90 \text{ g cm}^{-3}$ ), purchased from Goodfellow Cambridge Ltd. (Huntingdon, UK), were used for determination of the diffusion coefficients and evaluation of the chemical desorption. The plastic films were cut into rectangular sheets ( $10 \text{ mm} \times 50 \text{ mm}$  for determination of the diffusion coefficients and  $10 \text{ mm} \times 10 \text{ mm}$  for the desorption tests), cleaned using *n*-hexane and methanol for 24 h each and stored in methanol until use.

**Table 1**

Values of  $\log K_{\text{ow}}$ ,  $\log K_{\text{PDMSsw}}$ ,  $\log K_{\text{PEsw}}$ , and  $\log K_{\text{PPsw}}$  for the selected chemicals and summary of diffusion coefficients of the selected chemicals determined in this study with those reported in the literature.

Chemicals	$\log K_{\text{ow}}^{\text{a}}$	$\log K_{\text{PDMSsw}}^{\text{b}}$	$\log K_{\text{PEsw}}^{\text{b}}$	$\log K_{\text{PPsw}}^{\text{b}}$	$D_{\text{PE}}$ ( $\times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ )		
					Literature	This study	This study
$\alpha$ -HCH	3.80	2.77 (2.74, 2.80)	2.41 (2.36, 2.46)	2.69 (2.64, 2.75)	4.27 <sup>c</sup> , 12.59 <sup>d</sup>	1.38 ( $\pm 0.10$ )	5.31 ( $\pm 0.42$ )
$\beta$ -HCH	3.81	1.81 (1.77, 1.84)	2.04 (1.99, 2.09)	2.18 (2.08, 2.28)	7.41 <sup>c</sup> , 21.38 <sup>d</sup>	1.43 ( $\pm 0.06$ )	4.57 ( $\pm 0.23$ )
$\gamma$ -HCH	3.55	2.62 (2.58, 2.65)	2.33 (2.28, 2.38)	2.58 (2.52, 2.64)	3.39 <sup>c</sup> , 10.00 <sup>d</sup>	1.00 ( $\pm 0.07$ )	5.44 ( $\pm 0.38$ )
$\delta$ -HCH	4.14	2.17 (2.13, 2.20)	2.08 (2.03, 2.12)	2.23 (2.13, 2.34)	4.27 <sup>c</sup> , 15.85 <sup>d</sup>	1.08 ( $\pm 0.07$ )	7.26 ( $\pm 0.35$ )
PeCB	5.17	4.51 (4.40, 4.60)	4.63 (4.49, 4.75)	4.50 (4.39, 4.59)		5.54 ( $\pm 0.53$ )	8.01 ( $\pm 0.55$ )
HeCB	5.31	4.90 (4.79, 4.99)	5.22 (5.08, 5.34)*	5.01 (4.89, 5.10)	20.89 <sup>d</sup>	2.76 ( $\pm 0.17$ )	6.01 ( $\pm 0.35$ )

\*Value might be underestimated due to limited equilibration time. Partition coefficient values in parentheses are the lower and upper 95% confidence limits. Diffusion coefficient values in parentheses represent standard error. <sup>a</sup>Value suggested by Sangster Research Laboratory. <sup>b</sup>Values taken from Lee et al. (2014); third-phase partitioning method was used. <sup>c</sup>Data from Hale et al. (2010). <sup>d</sup>Data from Rusina et al. (2010).  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -HCH =  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -hexachlorocyclohexanes, PeCB = pentachlorobenzene, and HeCB = hexachlorobenzene.



**Fig. 1.** Schematic diagrams of the experimental systems for measuring (a) diffusion coefficients of HOCs in plastic film and (b) kinetics of desorption of analytes from plastic sheet.

### 2.2. Film-stacking experiments for measuring diffusion coefficients

The diffusion coefficients of the selected chemicals were measured via a film-stacking experiment. One film of custom-cut PE or PP sheet was loaded with a test chemical mixture. The polymer sheet was submerged in a vial containing 4 mL of *n*-hexane with the dissolved chemical mixture (HCH mixture with  $20 \mu\text{mol L}^{-1}$  of each isomer or CB mixture with  $60 \mu\text{mol L}^{-1}$  of each chemical) and the vial was agitated at 150 rpm in a shaking incubator for 24 h. Preliminary experiment showed that 24 h was found to be sufficient to uniformly load test chemicals in polymer sheet due to good swelling of polymer sheets in *n*-hexane. The polymer sheet was removed and rinsed twice with gently flowing 2 mL methanol:water (8:2, v/v) to remove residual *n*-hexane on the polymer surfaces, followed by careful removal of the washing solvent using a lint-free tissue. The initial concentrations of chemicals in polymer sheets were measured by extracting them using *n*-hexane. The initial concentration in the PE sheets ranged from  $16 \text{ mmol m}^{-3}$  ( $\alpha$ -

HCH) to 500 mmol m<sup>-3</sup> (PeCB) and that in the PP sheets ranged from 41 mmol m<sup>-3</sup> (α-HCH) to 760 mmol m<sup>-3</sup> (PeCB). Four clean polymer sheets of the same size were superimposed from a preloaded polymer sheet (Fig. 1a). Five superimposed polymer piles were wrapped with clean aluminum foil and a pressure of approximately 40 kPa was applied at 25 °C. The polymer sheets were separated after allowing diffusion for 24 h and the chemicals in the individual sheets were extracted using 4 mL of *n*-hexane by shaking for 24 h at 150 rpm in a shaking incubator. Preliminary experiments showed that 24 h is sufficient to obtain reliable concentration in the third sheet and thus to calculate the diffusion coefficient. The extract was then subjected to gas chromatography-electron capture detector (GC-ECD) analysis for quantification of the chemical concentration.

The diffusion coefficient was determined by using Fick's second law of diffusion in one dimension (Eq. (1)):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $D$  is the diffusion coefficient of the test chemical in the polymer [m<sup>2</sup> s<sup>-1</sup>],  $C$  is the concentration of the diffusing chemical at a distance  $x$  from the reference point [mol m<sup>-3</sup>], and  $x$  is the space coordinate normal to the section along which the diffusion takes place [m],  $t$  is the diffusion time [s]. In this experiment, no flux of diffusing chemicals is expected at the edge of the two polymer sheets on both ends of the pile. The analytical solution for  $C$  with respect to  $x$  and  $t$  is given by (Crank, 1975):

$$C = \frac{1}{2} C_0 \sum_{n=-\infty}^{\infty} \left\{ \operatorname{erf} \left( \frac{h + 2nL - x}{2\sqrt{Dt}} \right) + \operatorname{erf} \left( \frac{h - 2nL + x}{2\sqrt{Dt}} \right) \right\} \quad (2)$$

where  $C_0$  is the initial concentration in the homogeneously preloaded polymer sheet,  $\operatorname{erf}$  is the Gauss error function,  $x$  is the distance from the end of the preloaded polymer sheet [m],  $h$  is the thickness of the polymer film [m],  $t$  is the diffusing time [s], and  $L$  is the total thickness of the pile (i.e.,  $L = 5h$ ). The concentrations of the analytes in each plastic sheet after 24 h were assumed to represent those at  $\frac{1}{2}h$ ,  $\frac{3}{2}h$ ,  $\frac{5}{2}h$ ,  $\frac{7}{2}h$ , and  $\frac{9}{2}h$ . With these concentrations, the best-fit value of  $D$  was obtained using the nls function in R version 3.3.1 (R Development Core Team, 2016).

### 2.3. Desorption of analytes from plastic sheets

Desorption of the selected HOCs from the PE or PP sheets was measured in a batch test, as schematically illustrated in Fig. 1b. Because it is ideal to load chemicals uniformly into the plastic phase, *n*-hexane that can swell the PE and PP films was initially used for loading the plastic films with the HOCs as was in the film-stacking experiments for the determination of diffusion coefficients.

In order to provide an infinite sink condition, a sufficiently high volume of PDMS as an absorbing phase was added to the seawater solution (Fig. 1b). The mass of PDMS used for the CBs and HCHs was 580 mg and 1160 mg, respectively, and that of the preloaded plastic sheet was approximately 6 mg (PE) or 2 mg (PP) in 20 mL artificial seawater solution. Based on the partition coefficients between the plastics and seawater and between PDMS and seawater (Lee et al., 2014), at least 90% of the total mass of the selected HOCs should be distributed either in the PDMS phase or in seawater at phase equilibrium. The respective vials containing PDMS and a preloaded plastic sheet were agitated at 25 °C and 100 rpm in the dark using a shaking incubator. Time-course changes in the concentrations of the analytes in the plastic sheet, seawater, and PDMS was monitored over 14 days. After the designated number of days, the plastic sheet was taken and placed in a vial containing 1 mL of *n*-hexane and the vial was shaken for extraction of the chemicals at 150 rpm for one day. Both artificial seawater and PDMS were extracted using *n*-hexane to obtain the initial mass of HOCs in the plastic film ( $M_0$ ) for checking mass balance in test

vials. All extracts were then subjected to GC-ECD analysis.

### 2.4. Desorption models

Assuming that the plastic sheet is infinitely flat, the mass transfer Biot number (which represents the ratio of the mass transfer coefficient in the fluid phase ( $k$ ) to the diffusive mass transfer rate in the plastic phase) is defined as (Tosun, 2007):

$$\operatorname{Bi} = \frac{kL}{D} \quad (\text{for a sheet}) \quad (3)$$

where  $L$  is half of the thickness of the film [m] and  $D$  is the diffusion coefficient in the microplastic phase [m<sup>2</sup> s<sup>-1</sup>] derived from the film-stacking experiment above. The mass transfer coefficient,  $k$ , in water is estimated as (Crank, 1975):

$$k = \frac{D_w}{K_{pw}\delta_w} \quad (4)$$

where  $D_w$  is the molecular diffusion coefficient in artificial seawater [m<sup>2</sup> s<sup>-1</sup>],  $K_{pw}$  is the plastic-water partition coefficient [–], and  $\delta_w$  is the thickness of the aqueous boundary layer [m]. The value of  $D_w$  was obtained by using the Hayduk-Laudie correlation (Hayduk and Laudie, 1974):

$$D_w (\text{in m}^2 \text{s}^{-1}) = \frac{13.26 \times 10^{-9}}{\mu^{1.4} \operatorname{MLV}^{0.589}} \quad (5)$$

where  $\mu$  is the viscosity of artificial seawater (= 0.97 cP at 25 °C) and MLV is the LeBas molar liquid volume in units of cm<sup>3</sup> mol<sup>-1</sup> (Reid et al., 1977).

The remaining fraction of desorbing substance in a film with thickness  $2L$  ( $M/M_0$ ) under this infinite sink condition is given by (Crank, 1975):

$$\frac{M}{M_0} = \sum_{n=1}^{\infty} \frac{2\operatorname{Bi}^2 \exp\left(-\frac{\beta_n^2 Dt}{L^2}\right)}{\beta_n^2 \{\beta_n^2 + \operatorname{Bi}(\operatorname{Bi} + 1)\}} \quad (\text{for a sheet}) \quad (6)$$

where  $\beta_n$ s are the roots of

$$\beta_n \tan \beta_n = \operatorname{Bi} \quad (7)$$

The remaining mass fraction ( $M/M_0$ ) was plotted with respect to the diffusion time to evaluate the performance of the ideal model described in Eq. (6).

### 2.5. Instrumental analyses

The concentration of chemicals was quantified using 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 electron capture detector. Mixtures of HCHs and CBs were separated on an HP-5 column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Agilent J&C Scientific, Folsom, CA). The column oven temperature was held at 120 °C for 3 min, and subsequently increased to 200 °C at 5 °C min<sup>-1</sup>, held for 5 min, increased to 280 °C at 45 °C min<sup>-1</sup>, and held for 1 min. The injector and the ECD temperature were 200 and 320 °C, respectively.

## 3. Results and discussion

### 3.1. Diffusion coefficients of analytes in PE and PP sheets

Fig. 2 shows the experimentally measured concentrations of the analytes in five sheets after 24 h; the dashed lines were obtained from non-linear regression to obtain the diffusion coefficients of (a) the HCHs in PE and (b) in PP and (c) the CBs in PE and (d) in PP. The analytical solution could very well be fitted to the measured concentrations with resulting diffusion coefficients listed in Table 1. This film-stacking

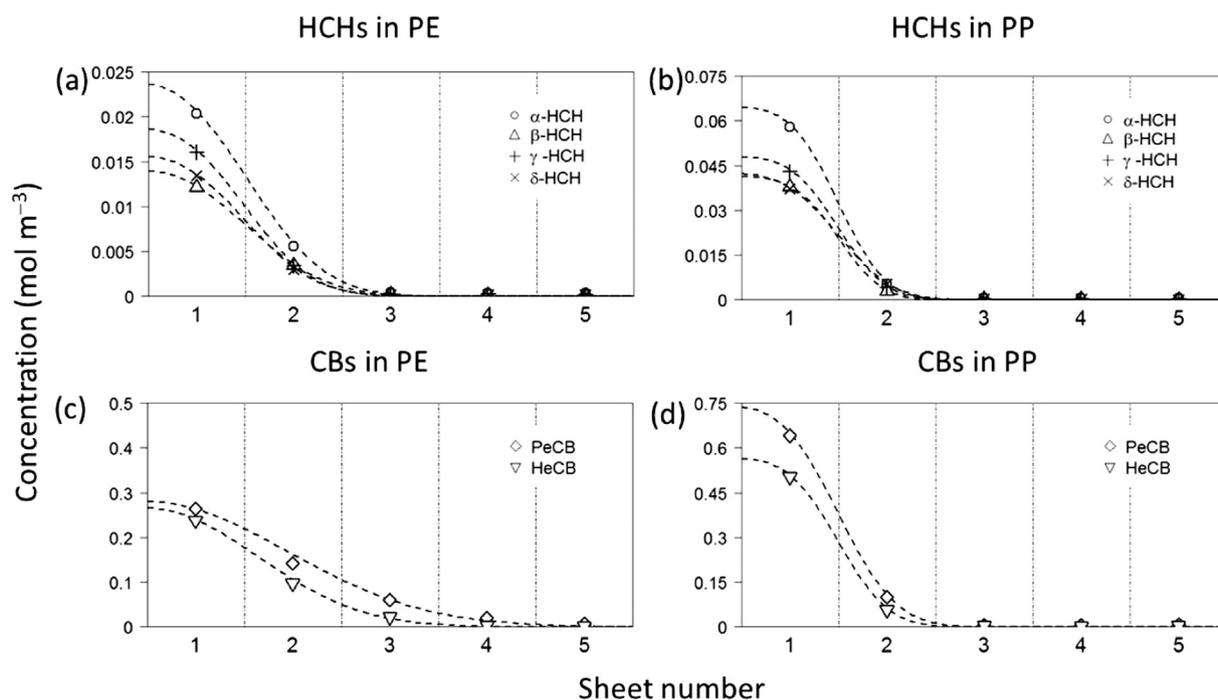


Fig. 2. Determination of diffusion coefficients of (a) HCHs in polyethylene and (b) in polypropylene and (c) CBs in polyethylene and (d) in polypropylene. Dashed lines represent best-fits using non-linear regression employing Eq. (2).

experiment was repeated for all HOCs in PP, resulting that all obtained diffusion coefficients did not deviate from values in Table 1 by a factor of two (data not shown). The diffusion coefficients were consistently higher in PE than in PP for all HOCs analyzed. The diffusion coefficients were of the order of  $10^{-14} \text{ m}^2 \text{ s}^{-1}$  in PE and  $10^{-16} \text{ m}^2 \text{ s}^{-1}$  in PP. The diffusion coefficients in PE ( $D_{PE}$ ) determined herein were approximately one order of magnitude lower than those measured by Hale et al. (2010) and Rusina et al. (2010). This difference might be due to the density of the polymers. The density of the PE sheet used in this study ( $0.94 \text{ g cm}^{-3}$ ) was greater than the value of  $0.91 \text{ g cm}^{-3}$  reported by Rusina et al. (2010). The dependence of the diffusion coefficient on the density of PE was documented by Fries and Zarfl (2012), where the diffusion coefficients in HDPE were approximately one order of magnitude lower than those in LDPE. The slower diffusion in the PP sheet than in the PE sheet could be explained by the higher degree of branched carbons in PP (Baker and Mead, 1999).

### 3.2. Desorption of selected HOCs from plastic sheets

For calculation of the mass transfer Biot number, the thickness of the aqueous boundary layer ( $\delta_w$ ) was estimated to obtain the mass transfer coefficient in artificial seawater (Eq. (4)). The magnitude of the aqueous boundary layer varies with the shear stress on the surface. The thickness of the unstirred aqueous boundary layer on the membrane surfaces was estimated in earlier studies to range from 1 to 5 mm and decreased with stirring (Avdeef, 2003; Avdeef et al., 2004; Kwon et al., 2006). Under gentle agitation, the range of  $\delta_w$  was reported to be between 50 and 100  $\mu\text{m}$  (Kwon et al., 2006). Since the vials containing the PE/PP sheet were gently shaken without any stirring bars,  $\delta_w$  was assumed to range from 100 to 1000  $\mu\text{m}$  for the estimation of  $Bi$ . Fig. 3 shows a comparison of the experimental desorption with three theoretically estimated lines for (a)  $\alpha$ -HCH from the PE sheet and (b) from the PP sheet and (c) PeCB from the PE sheet and (d) from the PP sheet assuming a  $\delta_w$  of 100 (dotted lines), 300 (solid lines), and 1000  $\mu\text{m}$  (dashed lines). The calculated values of  $Bi$  are also shown in Fig. 3 and the values of  $Bi$  for the other HOCs are listed in Table S1 (Supplementary material). The desorption data for all the other chemicals are

presented with the modeling results in Fig. S1 (Supplementary material). The experimental desorption agreed well with the theoretical prediction from the model in the assumed range of  $\delta_w$ . Desorption of the HCHs was much faster than that of the CBs as the partition coefficients for the HCHs are orders of magnitude lower than those for the CBs.

As illustrated in Figs. 3 and S1, desorption of the HCHs from the PE/PP sheet was independent of  $\delta_w$ , suggesting that desorption of those HOCs is predominantly determined by diffusion within the plastic. In contrast, desorption of PeCB and HeCB depended strongly on  $\delta_w$ . This strong dependence on the aqueous boundary layer thickness was also observed by Endo et al., 2013 where desorption of PCBs from PE pellets was studied. The differences between the two groups of HOCs can be characterized in terms of  $Bi$ . The values of  $Bi$  when  $\delta_w$  is 300  $\mu\text{m}$  are shown in Figs. 3 and S1. Diffusion in the plastic determines the overall desorption at higher  $Bi$ , whereas convective mass transfer through the water boundary layer determines the overall desorption at lower  $Bi$ . Since  $Bi$  depends strongly on the plastic-water partition coefficient, it can be deduced that HOCs with higher partition coefficients tend to desorb slowly, and the overall desorption is dependent on the rate of diffusion in the aqueous boundary layer.

### 3.3. Implications for risk assessment of HOCs from plastic particles

Desorption of HOCs from plastic debris is the most important transport process that determines the leaching of additives from plastic debris and the chemical intake by organisms via ingestion of microplastic particles. Herein, the desorption model was proven to be valid using laboratory experimental data and thus could be used to estimate the time-scale and half-life of desorption of HOCs from plastic particles. Figs. 4 and S2 (Supplementary material) describe the fraction of HOCs remaining in a plastic sheet ( $M/M_0$ ) with respect to the thickness ( $d$ ) and time ( $t$ ) assuming a  $\delta_w$  of 300  $\mu\text{m}$ . The three vertical dashed lines in Figs. 4 and S2 represent 1 h, 1 d, and 30 d, respectively. The relatively less hydrophobic HCHs are expected to desorb much faster. For example, the half-life for desorption of  $\alpha$ -HCH from PE for an infinitely flat sheet with a thickness of 0.1 mm, as indicated by the line at  $M/M_0 = 0.5$ , is only about 1.2 d. On the other hand, the half-life for

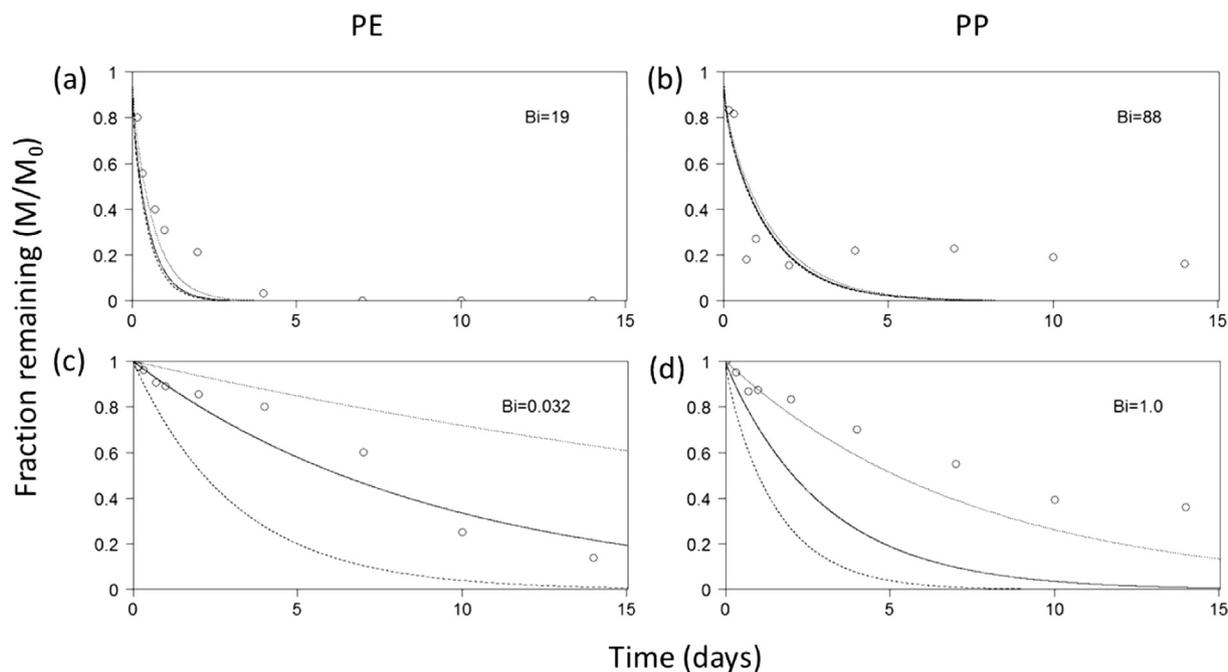


Fig. 3. Fraction of HOCs remaining in the plastic sheet ( $M/M_0$ ) with desorption time ( $t$ ) for (a)  $\alpha$ -HCH from PE sheet and (b) from PP sheet and (c) PeCB from PE sheet and (d) from PP sheet. Lines are values predicted using Eq. (6) where the thickness of the aqueous boundary layer ( $\delta_w$ ) is: 100 (dashed lines), 300 (solid lines), and 1000  $\mu\text{m}$  (dotted lines). Biot numbers were calculated at  $\delta_w = 300 \mu\text{m}$ .

desorption of PeCB from the same sized particles is more than 20 days, although  $M/M_0$  for PeCB strongly depends on  $\delta_w$ . For PE/PP sheets with a thickness greater than 1 mm, the half-life for desorption of PeCB or HeCB is expected to be much longer than one month.

The generalized desorption time-scale is also useful for assessing the bioavailability of HOCs from plastic particles ingested by aquatic organisms or the rate of release of plastic additives from microplastics into water. The release of hydrophobic plastic additives into the environment can be modeled using the model. Because these chemicals are intentionally added to plastic products, their fugacity in the plastic phase should be much greater than that in water or in digestive fluids

by a few orders of magnitude under environmental conditions, satisfying the infinite sink condition assumed in this study. Thus, the estimated desorption time-scale could be used to estimate their release rate into the aquatic environment, although their partition coefficients and diffusion coefficients (as well as a refined estimation of  $\delta_w$  under the environmental conditions) should be known. For chemical additives with very high partition coefficients and low diffusion coefficients, release via the passive diffusion processes under environmental conditions might be slower than the rate of physical and chemical abrasion processes which also lead to the release of additives into the environment. For non-additive HOCs, the limited fugacity gradient between

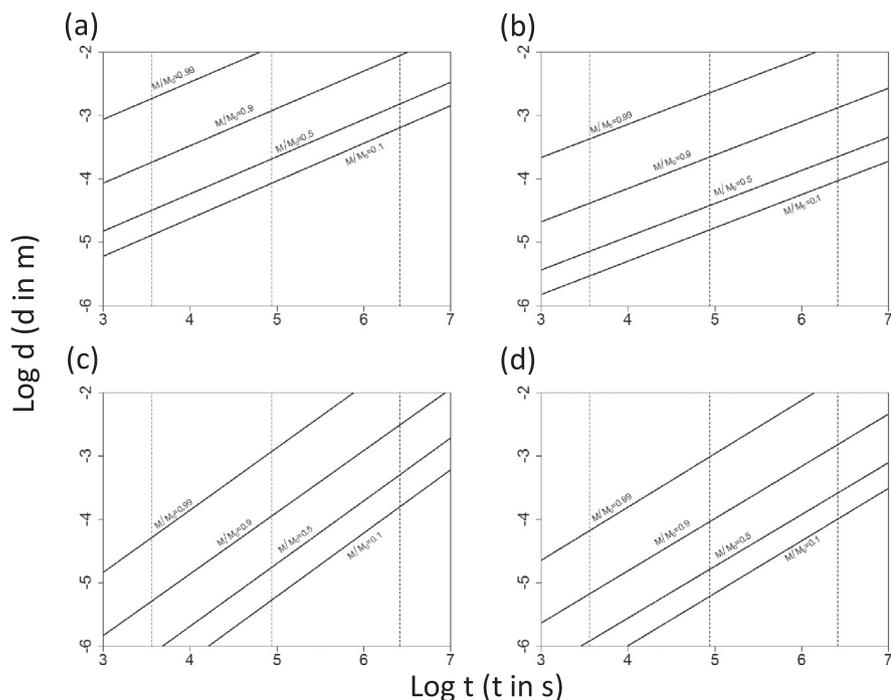


Fig. 4. Variation of the fraction of remaining HOCs ( $M/M_0$ ) with particle diameter and desorption time for (a)  $\alpha$ -HCH from PE and (b) from PP and (c) PeCB from PE and (d) from PP. The thickness of the aqueous diffusion boundary layer was assumed as 300  $\mu\text{m}$ . Three vertical dashed lines indicate 1 h, 1 d, and 30 d (from left).

microplastics and the environment would limit the overall desorption of those HOCs (Bakir et al., 2016; Lee et al., 2017).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2017.11.032>.

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