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., α-, β-, γ-, and δ-hexachlorocyclohexanes (HCH), pentachlorobenzene (PeCB), and hexachlorobenzene (HeCB)) were chosen as model hydrophobic organics chemicals (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. α- (99.8%), β- (99.5%), γ- (99.8%), and δ-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 (α-, β-, γ-, and δ-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 g cm^{-3} were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). PDMS was cut into rectangular sheets (10 mm × 50 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 μm, density = 0.94 g cm^{-3}) and PP (thickness = 25 μm, density = 0.90 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 mm × 50 mm for determination of the diffusion coefficients and 10 mm × 10 mm for the desorption tests), cleaned using *n*-hexane and methanol for 24 h each and stored in methanol until use.
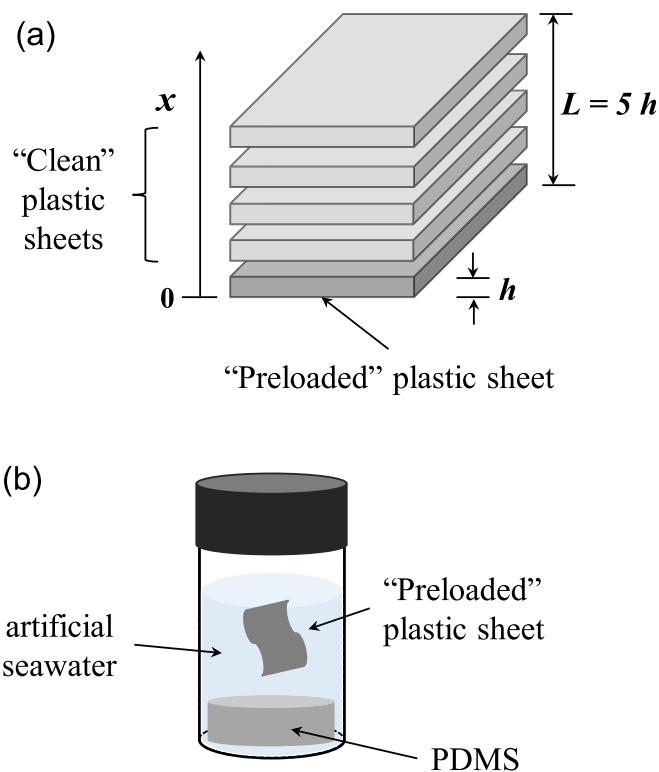

Fig. 1. Schematic diagrams of the experimental systems for measuring (a) diffusion coefficients of HOCs in plastic film and (b) kinetics of desorption of analytes from plastic sheet.

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 μmol L^{-1} of each isomer or CB mixture with 60 μmol 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 mmol m^{-3} (α-

Table 1
Values of log K_{ow}, log K_{PDMSsw}, log K_{PEsw}, and log K_{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	logK$_{ow}$[a]	logK$_{PDMSsw}$[b]	logK$_{PEsw}$[b]	logK$_{PPsw}$[b]	D$_{PE}$ ($\times 10^{-14}$ m^2 s^{-1})		D$_{PP}$ ($\times 10^{-16}$ m^2 s^{-1})
					Literature	This study	This study
α-HCH	3.80	2.77 (2.74, 2.80)	2.41 (2.36, 2.46)	2.69 (2.64, 2.75)	4.27[c], 12.59[d]	1.38 (± 0.10)	5.31 (± 0.42)
β-HCH	3.81	1.81 (1.77, 1.84)	2.04 (1.99, 2.09)	2.18 (2.08, 2.28)	7.41[c], 21.38[d]	1.43 (± 0.06)	4.57 (± 0.23)
γ-HCH	3.55	2.62 (2.58, 2.65)	2.33 (2.28, 2.38)	2.58 (2.52, 2.64)	3.39[c], 10.00[d]	1.00 (± 0.07)	5.44 (± 0.38)
δ-HCH	4.14	2.17 (2.13, 2.20)	2.08 (2.03, 2.12)	2.23 (2.13, 2.34)	4.27[c], 15.85[d]	1.08 (± 0.07)	7.26 (± 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 (± 0.53)	8.01 (± 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[d]	2.76 (± 0.17)	6.01 (± 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. [a]Value suggested by Sangster Research Laboratory. [b]Values taken from Lee et al. (2014); third-phase partitioning method was used. [c]Data from Hale et al. (2010). [d]Data from Rusina et al. (2010). α-, β-, γ-, and δ- HCH = α-, β-, γ-, and δ-hexachlorocyclohexanes, PeCB = pentachlorobenzene, and HeCB = hexachlorobenzene.