# Releases of Brominated Flame Retardants (BFRs) from Microplastics in Aqueous Medium: Kinetics and Molecular-size Dependence of Diffusion

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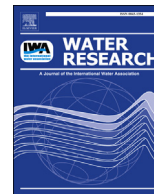**Shuangcheng Tao**
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# Releases of brominated flame retardants (BFRs) from microplastics in aqueous medium: Kinetics and molecular-size dependence of diffusion

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## ARTICLE INFO

## ABSTRACT

Microplastics (<5 mm) are increasingly detected in aquatic environment, and the high levels of brominated flame retardants (BFRs) contained in them can potentially impact water quality. This study characterized the release kinetics of polybrominated diphenyl ethers (PBDEs) and 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) from millimeter-sized microplastic pellets in water at environmentally relevant temperatures. Leaching rates of BFRs from the microplastic pellets made of acrylonitrile butadiene styrene (ABS) were found to be controlled by their diffusion within the plastic matrix, and their diffusion coefficients ($D$) in the plastic matrices ranged from $10^{-28.30}$ to $10^{-20.84}\,\mathrm{m^2\,s^{-1}}$. The apparent activation energies of the BFRs' diffusion coefficients were estimated to be in the range of 64.1 –131.8 kJ mol$^{-1}$ based on their temperature dependence and the Arrhenius equation. The diffusion coefficients of the BFRs decrease with their molecular diameters, while the activation energies for diffusion increase with the molecular diameters, which are indicative of significant steric hindrance for BFR diffusion within the plastic matrices. A semi-empirical linear relationship was observed between $\mathrm{Log}_{10}D$ and the glass transition temperature ($T_g$) of plastics, which allows prediction of the diffusion coefficients of BFRs in other types of microplastics commonly found in marine environment. The half-lives of BFR leaching (i.e., 50% depletion) from the microplastic pellets would range from tens of thousands to hundreds of billions of years at ambient temperatures if their physical and chemical structures could remain intact. Although the release fluxes of BFRs from microplastics are extremely low under the model conditions, a range of physical and chemical processes in the natural environment and the digestive systems of organisms that ingested them could potentially accelerate their leaching by causing breakdown and swelling of the plastic matrices.

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## 1. Introduction

With properties that can be engineered to meet the demand of almost any applications, plastics have increasingly displaced wood, metal, and glass in a wide range of products over the past several decades. The global production of plastics has exceeded 300 million tonnes in 2014 (Lebreton et al., 2017), and the industry is expected to continue to grow. Up to 10% of the plastics used by the society are believed to end up in the oceans, where they can last very long times because of their chemical stability (Andrady, 2011). Abundant waste plastics have been found in oceans and polar regions (Derraik, 2002; Waller et al., 2017). Recently, microplastics, which are plastic pieces of less than 5 mm in size, as defined by the National Oceanic and Atmospheric Administration (NOAA), have emerged as an important concern in the marine environment (Castillo et al., 2016). Microplastics are generated from the disintegration of large pieces of plastic materials, such as monofilament line, plastic strapping, and plastic bags, under the action of external forces and solar radiation (Andrady, 2011; Derraik, 2002). They can be subsequently suspended in the sea water or deposit to the ocean bottom and become components of the sediments.

Microplastics occurring in oceans pose potential risk to marine

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ecosystems, and they have been found in organisms of different trophic levels in the marine food chain (Besseling et al., 2012; Gaylor et al., 2013). Once ingested by marine organisms, microplastics can produce mechanical damage and block the eating organ, resulting in reduction of nutrient absorption, starvation, injury, and even death of the organisms (Andrady, 2011; Derraik, 2002; Spear et al., 1995). In addition, microplastics also act as a source of organic pollutants. Ingestion of microplastics by biota could lead to increased exposure to plastic additives, such as brominated flame retardants (BFRs) (Gandara e Silva et al., 2016; Narváez Valderrama et al., 2016; Tanaka et al., 2015).

Polybrominated diphenyl ethers (PBDEs) are a major class of BFRs that have been widely used in electronic and electrical products. They were later discovered to have significant negative effects on human health, and the use of those with high biological toxicity, including penta-BDEs, octa-BDEs, and deca-BDE (BDE-209), were gradually phased out in the 2000s. Nonetheless, PBDEs, including the banned ones, continue to exist in the plastics of a wide variety of current-use and discarded electrical and electronic products, and are thus widely detected in environmental matrices. Meanwhile, new BFRs, such as 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), have been developed as substitutes. Unfortunately, these alternative BFRs have also been increasingly detected in the environment (Yang et al., 2012).

As BFRs are mechanically added into the polymer blocks of plastics without formation of chemical bonds, they can escape from the plastic matrix over time, despite of their low volatilities and poor water solubilities (Gaylor et al., 2013). Plastics can gradually lose structural integrity during use and after being disposed of through processes such as weathering, wear-and-tear, and pulverization, resulting in breakaway of small fragments from the bulk plastic body (Andrady, 2011; Teuten et al., 2009). Consequently, releases of the additives from the plastics can be significantly accelerated due to the physical and/or chemical disintegration of their matrices (Gaylor et al., 2013).

To date, research on pollution of microplastics has focused mainly on their ecological effect, and to a less extent, on their role as a sink for hydrophobic organic chemicals (HOCs) in the marine environment (Bakir et al., 2014a; Mato et al., 2001). The release of plastic additives, BFRs in particular, from microplastics in aquatic environment has received little attention. This study was conducted to evaluate the release kinetics of BFRs from millimeter-sized pellets of acrylonitrile butadiene styrene (ABS), a common type of microplastic found in the environment (Castillo et al., 2016), in water at environmentally relevant temperatures. Although the types of microplastics in the environment are diverse, the release rates obtained and the dependence of diffusion coefficient on molecular size of the diffusant and the glass transition temperature ($T_g$) of the plastic matrix observed could provide important insights for assessing the release kinetics of BFRs from other types of microplastics and thus help assess their risk in aquatic environment.

## 2. Materials and method

### 2.1. Materials

Approximately spherical plastic pellets (Fig. S1) made of ABS in the size ranges of 10–20, 30–40, and 50–100 meshes (0.841–2.000, 0.420–0.595, and 0.149–0.297 mm, respectively) were obtained by grinding the plastic rear covers of two computer displays and then sieving with wire meshes (Supplementary data). Their BFR contents were determined by exhaustive extraction (sequential microwave-assisted extraction for five times) and quantitation using gas chromatography-mass spectrometry (GC-MS) (Supplementary data). The contents of BFRs in the microplastic

pellets are summarized in Table S1. Low-density polyethylene (LDPE) sheets (50 μm thick) were purchased from Maolu Plastic (Changzhou, China). Stripes of LDPE (2 cm × 3 cm) were successively pre-cleaned by soaking in dichoromethane for 48 h, methanol for 24 h, and triple-distilled water for 24 h. The pre-cleaned LDPE stripes were cleaned again in triple-distilled water immediately before being used to ensure cleanness. All laboratory glassware used was soaked in chromic acid mixture for 12 h, then cleaned with tap water and triple-distilled water successively, finally oven-dried at 450 °C for 4 h prior to use.

### 2.2. BFR release experiment

Kinetics of BFR releases from the plastic pellets was investigated in sealed glass bottles using LDPE film as the "infinite sink". Approximately 1.00 g (±0.1 mg) of plastic pellets were wrapped in copper wire of 180 mesh and inserted into 100 mL wide mouth glass bottles wrapped with aluminum foil, followed by three stripes of pre-cleaned LDPE film. The bottles were then filled with triple-distilled water, sealed, and equilibrated in dark constant temperature chambers (10 and 30 °C). To avoid potential breakdown of the microplastic pellets, no mechanical mixing was used during the course of leaching experiment. Although marine water could be a more realistic environmental medium to study the leaching behaviors of the BFRs from the plastic pieces, it has been demonstrated that there was little difference in the leaching of BDE-209 from high-density polyethylene (HDPE) plates soaked in distilled water, seawater, and acidic pepsin solution (Tanaka et al., 2015). Triple-distilled water was used in this study because the diffusion within the polymeric matrix was believed to be the rate-limiting step in the overall release processes and it eliminated the need to control microbial growth during the experimental period.

At preset sampling time points, the LDPE stripes were taken out of the sealed bottles and rinsed with triple-distilled water, and then extracted consecutively with 20 mL dichloromethane for 24 h and 20 mL hexane for 24 h. Each extract was concentrated to 5–10 mL by rotary evaporation at 30 °C, passed through a glass column filled with anhydrous $Na_2SO_4$, then further concentrated to 1 mL by nitrogen blowdown. Finally, the extract was solvent-exchanged to about 30 or 1000 μL of hexane, depending on the targeted analytes. The LDPE and water samples were spiked with $^{13}$C-PCB-209 as a recovery standard prior to being extracted, and all experiments were conducted in triplicates. BFRs were analyzed by GC-MS, following the methods reported in our previous work (Sun et al., 2016). The contents of BFRs in the microplastic pellets could be treated as essentially constant because only negligible fractions ($5.94 \times 10^{-7}$-$1.82 \times 10^{-3}$) of them leached out during the experimental period. Instrument detection limits, defined as three times of the signal-to-noise ratios, ranged from 0.01 to 0.15 ng/mL for the targeted analytes (Table S2). All measurement results reported were the averages of triplicated samples. Details of the quality assurance/quality control (QA/QC) procedures are presented in the Supplementary data.

### 2.3. Modeling of BFR leaching kinetics

Fig. 1 schematically illustrates the major mass transfer processes involved in the leaching of BFRs from the microplastic matrix to the LDPE strips in a close system. Leaching of a given BFR molecule occurs via five consecutive steps: diffusion within the plastic matrix, mass transfer across the microplastic-water boundary layer, diffusion in water, mass transfer across the LDPE-water boundary layer, and diffusion in LDPE matrix (Esquerdo et al., 2015; Recasens et al., 1989). In the absence of strong interactions between the fluid and plastic matrix (i.e., no swelling or plasticization of the
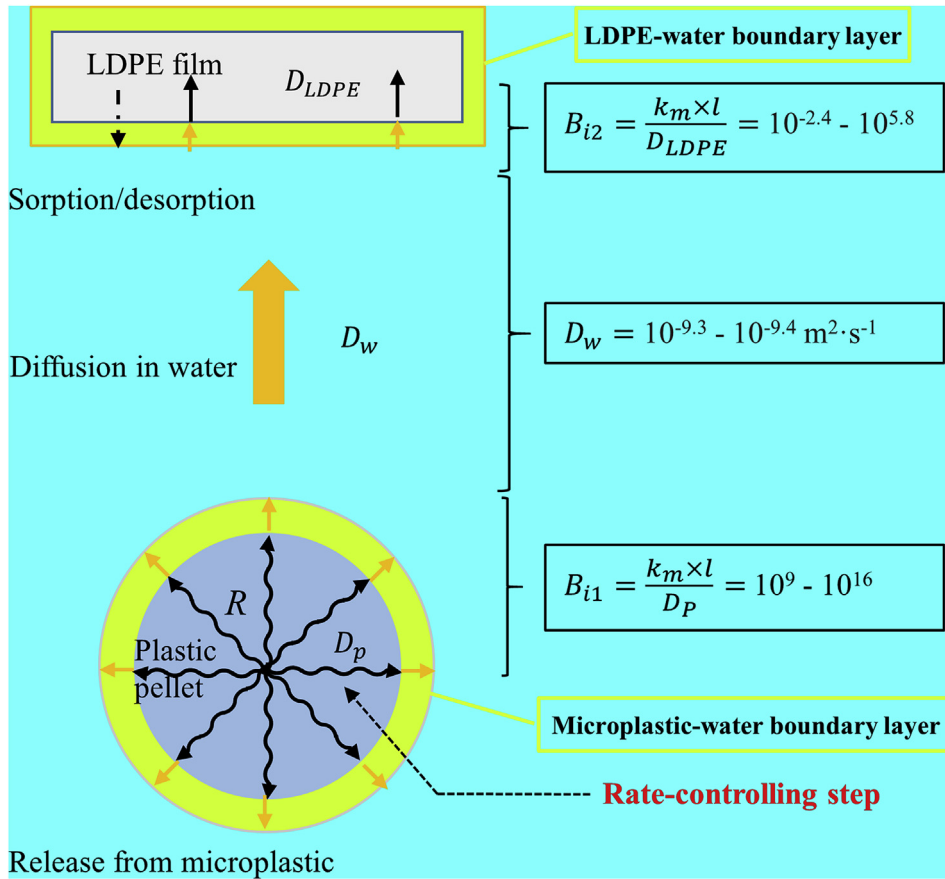
**Fig. 1.** Schematic illustration for the major mass transfer processes of BFRs in the microplastic-water-LDPE system (at 25 °C): Diffusion within the plastic matrix, mass transfer across the microplastic-water boundary layer, diffusion in water, mass transfer across the LDPE-water boundary layer, and diffusion in LDPE matrix. $B_i$ is the mass transfer Biot number, and the subscripts 1 and 2 indicate the mass transfer process across the interface between the microplastic pellet and the liquid boundary layer, and that between the liquid boundary layer and the LDPE film, respectively. $D$ is the diffusion coefficient of the BFR molecules, and the subscripts P, w, and LDPE represent plastic matrix, water, and LDPE film, respectively.

polymers), leaching of BFRs from the approximately spherical plastic pellets can be considered as governed by the Fick's second Law (Lee et al., 2018; Vitrac et al., 2007):

$$\frac{\partial c(r,t)}{\partial t} = D_p \frac{\partial^2 c(r,t)}{\partial r^2}, \quad 0 < r < R \tag{1}$$

where $c$ is the local concentration of the BFR in the plastic matrix, $D_p$ is the diffusion coefficient in the plastic matrix, and $R$ is the characteristic dimension of the plastic layer and is equal to the radius of the plastic pellets.

The rate controlling step among the various mass transfer processes involved in the release of BFRs from microplastic pellets to water and their subsequent sorption on the LDPE film can be evaluated with the mass transfer Biot number ($B_i$), which represents the ratio of the rate of transport across the liquid boundary layer to the rate of diffusion within the plastic phase. $B_i$ is calculated as (Vitrac et al., 2007):

$$B_i = \frac{k_m l}{D} \tag{2}$$

where $D$ is the diffusion coefficient in the plastic phase ($D_p$ or $D_{LDPE}$), which could be the ABS microplastic pellet or the LDPE film, depending on the mass transfer process studied, and $l$ is the characteristic dimension of the plastic layer, which is the radius ($R$) of the plastic pellets or half of the thickness of the LDPE film. $k_m$ is the

mass transfer coefficient in the plastic-water boundary layer, and can be estimated as (Booij et al., 2003; Crank, 1975):

$$k_m = \frac{D_w}{K_{pw}\delta} \tag{3}$$

where $D_w$ is the diffusion coefficient of BFR in water, $K_{pw}$ is its plastic-water partition coefficient, and $\delta$ is the thickness of the aqueous boundary layer, which can be approximated as the radius of the microplastic pellets for mass transfer from the plastic pellets to water, or half of the thickness of the LDPE film for mass transfer from water to the LDPE film. The value of $D_w$ can be estimated from the Hayduk-Laudie correlation (Hayduk and Laudie, 1974):

$$D_w = \frac{13.26 \times 10^{-9}}{\mu^{1.4} \times v_m^{0.589}} \tag{4}$$

where $\mu$ is the dynamic viscosity of water (Pa·s). $v_m$ is the LeBas molar volume (cm$^3$·mol$^{-1}$) and can be calculated from the molecular structure of the diffusant using a simple additive method (Reid et al., 1977):

$$v_m = 7(N_C + N_H + N_O + N_{DB}) + 31.5 N_{Br} - 7^* \tag{5}$$

where the subscripts C, H, and O stand for atoms of carbon, hydrogen, and oxygen, respectively, and DB stands for double bond, $N$ is the number of these atoms and bonds, and the last value $^*$ is

counted once for diffusants with one or more aromatic rings.

When both the diffusive mass transfer within the solid matrix and the external mass transfer are considered, the released mass fraction ($\frac{M_t}{M_0}$) of a substance from a spherical pellet with a radius $R$ under the "infinite sink" conditions can be calculated as (Crank, 1975):

$$\frac{M_t}{M_0} = 1 - \sum_{n=1}^{\infty} \frac{6B_i^2 \exp\left(-\beta_n^2 D_p t \cdot R^{-2}\right)}{\beta_n^2 \left\{\beta_n^2 + B_i(B_i - 1)\right\}} \tag{6}$$

where $\beta_n$ are the roots of:

$$\beta_n \cot \beta_n + B_i - 1 = 0 \tag{7}$$

As detailed in the Supplementary data, depending on the value of $B_i$, $\frac{M_t}{M_0}$ can be approximated as different functions of $D_p$, $R$, and $t$:

$$\frac{M_t}{M_0} = \begin{cases} a D_p t \cdot R^{-2}, & B_i \leq 1 \\ n_1 D_p t \cdot R^{-2} \text{ or } n_2 \left(D_p t \cdot R^{-2}\right)^{1/2}, & 1 < B_i < 100 \\ \frac{6}{\sqrt{\pi}} \left(D_p t \cdot R^{-2}\right)^{1/2}, & B_i \geq 100 \end{cases} \tag{8}$$

where $a$, $n_1$, and $n_2$ are constants with values equal to the slopes of the linear regression lines for different $B_i$ values shown on Fig. S3. While the fractions of BFRs released from the microplastic pellets over 150 days were in the ranges of $10^{-5.72}$ to $10^{-2.74}$, the model predicts that all the BFRs in the microplastic pellets would have been completely released by 150 days at 30 °C (i.e., $\frac{M_t}{M_0} = 1$) for the cases of $B_i \leq 1$ and $1 < B_i < 100$ (Table S3). Thus, the $B_i$ values for releases of BFRs from the microplastic pellets must be greater than 100. Based on fitting of the experimentally observed $\frac{M_t}{M_0}$ values, $B_i$ ranged from $10^9$ to $10^{15}$ for different BFRs (Table S4).

Figure S4 shows the plots of $\frac{M_t}{M_0}$ versus $(D_p t \cdot R^{-2})^{1/2}$ for the releases of PBDEs and BTBPE from the two types of microplastic pellets. Good linearity is observed in all cases, and the slopes of the fitted lines for the releases of BFRs from the pellets (30−40 mesh) of plastics A ($3.31 \pm 0.54$) and B ($3.38 \pm 0.29$) are all reasonably close to the value of $\frac{6}{\sqrt{\pi}}$ (i.e., 3.38). These results consistently indicate that the release kinetics of BFRs from the microplastic pellets could be well described by the following equation (for $B_i \geq 100$):

$$\frac{M_t}{M_0} = \frac{6}{\sqrt{\pi}} \left(D_p t \cdot R^{-2}\right)^{1/2} \tag{9}$$

As a result, $D_p$ can be estimated as:

$$D_p = \frac{\pi R^2}{36 t} \left(\frac{M_t}{M_0}\right)^2 \tag{10}$$

The mass transfer Biot number reflects the relative importance of the external mass transfer and the diffusive mass transfer within the solid matrix. It has been reported that external mass transport resistance controls the mass transfer step when $B_i < 1$ for HOC desorption from spherical particles, and diffusion in the plastic is the step controlling mass transfer when $B_i$ is greater than 100, while both mass transfer steps are important when $B_i$ is between 1 and 100 (Cho et al., 2006). For desorption of water from a flat slab, diffusion in the matrix has been shown to control the overall mass transfer when $B_i$ is above 30 (Cdrdova-Quiroz et al., 1996). Based on the typical values of the related parameters, the values of $B_i$ for diffusion of BFRs from the plastic matrix to the aqueous phase are much greater than 100 ($10^9$-$10^{16}$) and are orders of magnitude higher than the corresponding ones for their transport from the aqueous phase onto the LDPE film (Table S4). That is, diffusion of BFRs within the matrix of microplastics is the overall rate-limiting step in the leaching system (Fig. 1), which is also consistent with the previous findings that the diffusion rates of BFRs within the microplastic pellets were far smaller than those within the aqueous phase and the LDPE film (Mato et al., 2001; Narváez Valderrama et al., 2016). As a result, it is reasonable to assume that the overall leaching of BFRs, which are initially distributed homogeneously in the matrix of microplastic pellets, is controlled solely by their diffusion within the plastic matrix. Accordingly, the fraction of BFRs leached ($\frac{M_t}{M_0}$) from the microplastic pellets at a given time, $t$, can be estimated as (Crank, 1975):

$$\frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_p n^2 \pi^2 t}{R^2}\right) \tag{11}$$

Based on the Poisson's equation, the above equation can be transformed and re-arranged as (Reichenberg, 1953):

$$\frac{M_t}{M_0} = \frac{6}{\pi^{3/2}} \sqrt{Bt} - \frac{3}{\pi^2}(Bt) + \frac{6}{\pi^{\frac{3}{2}}} \int_0^{Bt} \frac{\sum_{n=1}^{\infty} e^{-\frac{n^2 \pi^2}{Bt}}}{\sqrt{Bt}} d(Bt) \tag{12}$$

where $B = D_p \pi^2 / R^2$. Because only the first two terms of equation (12) are significant (Reichenberg, 1953), it can be reduced to:

$$\frac{M_t}{M_0} = \frac{6}{\pi^{3/2}} \sqrt{Bt} - \frac{3}{\pi^2}(Bt) \tag{13}$$

As the fractions of BFRs that leached out of the microplastic pellets were only in the range of $10^{-5.72}$ to $10^{-2.74}$ over the experimental period, equation (13) can be further simplified as:

$$\frac{M_t}{M_0} = \frac{6}{\pi^{3/2}} \sqrt{Bt} = \frac{6}{\pi^{3/2}} \sqrt{D_p \pi^2 t / R^2} = \frac{6}{\sqrt{\pi}} \left(D_p t \cdot R^{-2}\right)^{1/2} \tag{14}$$

Equations (9) and (14) are identical. That is, after incorporation of the partition constants of BFRs between plastic pellets and the surrounding water at the interface, the model is the same for the specific set of conditions in this study as that derived based on the assumption that the external resistance in the plastic-water boundary layer is negligible compared to that of mass transfer within the plastic matrix.

## 3. Results

### 3.1. Leaching rates of BFRs

As shown on Table S1, BDE-209, which was present at $63.00 \pm 1.26$ and $910.9 \pm 19.5$ μg/g in plastics A and B, respectively, accounted for >85% of the total PBDEs in both plastics, while di-BDEs to hexa-BDEs occurred at μg/g levels. BTBPE, a replacement for octa-BDE, was also detected at rather high levels in them (A: $6.06 \pm 0.10$ mg/g; B: $660.00 \pm 2.98$ μg/g). The leaching behaviors of PBDEs and BTBPE from the microplastic pellets (30−40 mesh) in water are shown on Fig. S5. The masses of BFRs leached (quantified from those accumulated on the LDPE strips) increased linearly over time, which indicates that the uptake capacities of the LDPE stripes for the BFRs were not saturated (i.e., they functioned as an "infinite sink") during the experimental period (Table S5). The leaching fluxes of BFRs from microplastics A and B were 0.28-38.90 and 0.16−7.43 ng m$^{-2}\cdot$d$^{-1}$ at 10 °C, and 2.24-116.31 and 0.86−38.16 ng m$^{-2}\cdot$d$^{-1}$ at 30 °C, respectively.

As expected, the most abundant BFRs in the microplastic pellets, BDE-209 and BTBPE, also had the highest leaching fluxes. Based on the data reported by Tanaka et al. (2015), the flux of BDE-209

leaching from HDPE plate (2 mm × 3 mm × 3 mm) in aqueous media (distilled water, seawater, and pepsin solution) at 20 °C was up to $2.10 \times 10^5$ ng m$^{-2}$·d$^{-1}$ (Tanaka et al., 2015), which is 3—4 orders of magnitude higher than those observed for BDE-209 leaching from the microplastic pellets here. This may be due to the much lower $T_g$ of HDPE compared to that of ABS plastics evaluated in this study, as discussed later. According to the results of field sorption experiment conducted by Mato and co-workers, the combined sorption rate of polychlorinated biphenyls (PCBs) onto polypropylene (PP, 0.1—0.5 cm pellets in seawater) was approximately 0.1 ng g$^{-1}$·d$^{-1}$ at 12 °C (Mato et al., 2001). This translates to an area-specific sorption rate of up to 45.5 ng m$^{-2}$·d$^{-1}$, which is comparable to the leaching fluxes of BFRs ($\Sigma_9$PBDEs + BTBPE) from the microplastic pellets of 30—40 mesh at 10 °C observed in this study (Table S6).

### 3.2. Diffusion coefficients of BFRs in plastic matrices

Table 1 summarizes the estimated values for diffusion coefficients ($D$) of PBDEs and BTBPE in the matrices of plastics A and B at 10 and 30 °C. The values of Log$D$ (m$^2$·s$^{-1}$) for PBDEs and BTBPE ranged from −28.30 to −22.06, and from −26.80 to −21.04 at 10 and 30 °C in the matrix of plastic A, respectively, while the corresponding values were −25.71 to −21.93 at 10 °C, and −24.42 to −20.84 at 30 °C in the matrix of plastic B. Although both materials were made primarily of ABS, the manufacturing processes and the types and amounts of additives (e.g., plasticizers and flame retardants) added to the polymers probably changed over the years. Compared to plastic B (manufactured in 2005), plastic A (manufactured in 1994) had been subjected to aging for a much longer time, while its polymer structure was probably more compact and thus had greater steric hindrance for the diffusing BFR molecules. Besides increasing the surface area of microplastics, weathering introduces a variety of oxygen-containing functional groups to the polymers, which can slow down the diffusion rates of hydrophobic molecules within the plastic matrix due to the increased intermolecular forces (Satoto et al., 1997). On the other hand, rearrangement of the amorphous part caused by weathering of polymers can contribute to a slight increase in their crystallinity (Satoto et al., 1997), which also reduces the diffusion rates of hydrophobic molecules within the plastic matrix.

Polymers with low $T_g$ values have greater chain segmental mobility, allowing diffusant molecules to move more easily (George and Thomas, 2001). The diffusion coefficient of benzene in various polymers at 25 °C has been shown to increase with decreases in the polymer's $T_g$ (Brown and Park, 1970). The diffusant's diffusion coefficient in plastic matrix can be predicted from the $T_g$ of the plastic based on the following relationship (Brown and Park, 1970):

$$\ln D = C - \frac{B}{f_v} \tag{16}$$

where $C$ is an empirical constant, $B$ is a constant that depends on the critical local free volume needed for diffusion and its value increases with the molecular size of the diffusant, and $f_v$ is the fractional free volume of the diffusant at temperature $T$. $f_v$ can be estimated as:

$$f_v = f_g + (a_1 - a_2)(T - T_g) \tag{17}$$

where $a_1$ and $a_2$ are the expansion coefficients in the glassy state and at the transition to the rubbery state, respectively, and $f_g$ is the fraction of free space in the polymer at $T_g$.

Reduction in the diffusivity of diffusant in polymers with increasing glass transition temperatures has long been documented (Van Amerongen, 1950). For example, the diffusion coefficients of polycyclic aromatic hydrocarbons (PAHs) and PCBs permeating through silicone rubbers, which have some of the lowest $T_g$ values of plastics, were much higher than those in LDPE (Rusina et al., 2007, 2010a). Based on the molecular volumes (0.18—0.34 nm$^3$) (Xu et al., 2007), the mean molecular diameter ($d$) of PBDEs are estimated to be in the range of 0.55—0.70 nm (Table S7). As shown on Fig. 2, the Log$_{10}D$ values of PBDEs in the matrices of microplastics A and B depend linearly on their molecular diameters and apparently follow the linear line established by Berens and Hopfenberg (1982). According to the fitting method reported by Brown and Park (1970), it is reasonable to expect that the diffusion coefficients of PBDEs in ABS are close to those in polystyrene (PS) because they have comparable $T_g$ values ($\cong 100$ °C). Based on the linear relationship between log$_{10}D$ and the molecular diameter of diffusant in PS at 30 °C, the values of log$_{10}D$ (m$^2$·s$^{-1}$) for PBDEs in ABS are about −19 (BDE-1) to −23 (BDE-209), which are higher than those of BDE-209 in the matrices of plastic B (−23.99) and plastic A (−26.38). It is obvious that the measured diffusion coefficients of PBDEs are much lower than those estimated from the linear relationship, which was established from anisometric molecules (e.g., normal alkanes). Compared with the anisometric molecules, PBDEs molecules have rigid symmetric spherical structures, thus they diffuse more slowly than the more elongated molecules of same molecular masses, which have greater conformational freedom (Berens and Hopfenberg, 1982; Rusina et al., 2010b). Although the BFR molecules are additives and only interact with the plastic matrix through Van der Waals force and hydrogen bonding, the rather low diffusion coefficients probably arise from the significant steric hindrance due to the need for constant bending of certain chemical bonds during their diffusion through the tight polymer brushes.

### 3.3. Leaching half-lives of BFRs from microplastics

Table 1 also summarizes the activation energies ($E_a$) for diffusion coefficients of the BFRs estimated from their temperature dependence based on the Arrhenius equation. The $E_a$ values ranged from 64.1 to 131.8 and 75.3 to 120.8 kJ mol$^{-1}$ in the matrices of plastics A and B, respectively. Fig. 3 plots the activation energies for diffusion coefficients of BFRs in the plastic matrices as a function of their molecular diameters. The $E_a$ values for diffusion of PBDEs in the ABS plastics roughly observe the linear trend-line between $E_a$ and the molecular diameter of diffusant observed in PS plastic reported by

**Table 1**
Summary of the diffusion coefficients ($D$) and apparent activation energies ($E_a$) of diffusion for BFRs in the matrices of two types of microplastic pellets determined based on leaching experiments conducted at 10 and 30 °C.

| BFR | Plastic A | | | Plastic B | | |
|---|---|---|---|---|---|---|
| | Log$_{10}D$, m$^2$·s$^{-1}$ | | $E_a$[a], kJ·mol$^{-1}$ | Log$_{10}D$, m$^2$·s$^{-1}$ | | $E_a$[a], kJ·mol$^{-1}$ |
| | 10 °C | 30 °C | | 10 °C | 30 °C | |
| BDE-7 | −22.06 | −21.04 | 83.6 | −21.93 | −21.01 | 75.3 |
| BDE-15 | −22.76 | −21.98 | 64.1 | −21.79 | −20.84 | 78.6 |
| BDE-118 | −23.73 | −22.48 | 102.7 | −22.61 | −21.54 | 88.0 |
| BDE-138 | −23.71 | −22.44 | 104.1 | −22.57 | −21.41 | 94.5 |
| BDE-153 | −24.06 | −22.65 | 115.3 | −22.48 | −21.39 | 89.6 |
| BDE-206 | −28.30 | −26.80 | 123.4 | −25.71 | −24.42 | 106.1 |
| BDE-207 | −27.06 | −25.48 | 129.4 | −24.31 | −23.20 | 90.9 |
| BDE-208 | −27.95 | −26.50 | 119.4 | −24.54 | −23.28 | 103.3 |
| BDE-209 | −27.98 | −26.38 | 131.8 | −25.46 | −23.99 | 120.8 |
| BTBPE | −25.98 | −24.52 | 119.5 | −24.66 | −23.38 | 104.7 |

Note.
[a] — Apparent activation energy for diffusion coefficient is determined based on its temperature dependence using the Arrhenius equation.
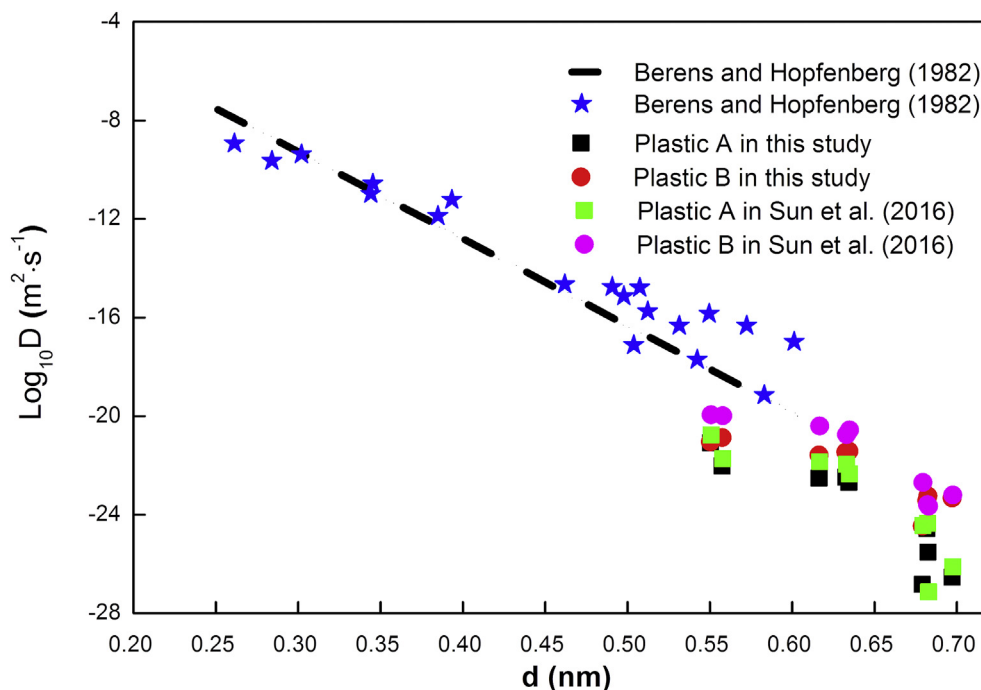
**Fig. 2.** Empirical relationship between the logarithms of diffusion coefficients ($Log_{10}D$) of PBDEs in the microplastic pellets processed from two model waste plastics determined in this study and their molecular diameters ($d$), along with literature data reported in Berens and Hopfenberg (1982) and Sun et al. (2016).

Berens and Hopfenberg (1982). The activation energies for diffusion of PBDEs are higher than those of anisometric molecules (e.g., normal alkanes) of comparable sizes, probably because of the lower conformational freedom associated with their rigid symmetric structures.

The release rates of BFRs from the two plastic materials in the air were measured in our previous study (Sun et al., 2016), and their values were found to be in the same bulk ranges with the reported rates of PBDE releases from TV plastics and waste TV (Hirai et al., 2006; Kemmlein et al., 2003; Ortuño et al., 2015). As shown in Tables 1 and S8, the diffusion coefficients of BFRs and the corresponding activation energies of diffusion in the two plastic materials determined with the leaching experiment in aqueous medium



**Fig. 3.** Empirical relationship between the activation energies ($E_a$) of diffusion coefficients of PBDEs in the microplastic pellets processed from two model waste plastics determined in this study and their molecular diameters ($d$), along with literature data reported by Berens and Hopfenberg (1982) and Sun et al. (2016).

are comparable to those estimated based on their releases to the air. These results further corroborate that diffusion within the plastic matrix is the rate-controlling step in the releases of BFRs from the ABS microplastic pellets, irrespective of the surrounding medium (e.g., air or water).

Based on the Arrhenius equation, the diffusion coefficients, and thus leaching half-lives (i.e., time for depletion of 50% of the initial masses) of BFRs from microplastic pellets, can be predicted at different ambient temperatures (Table S9). Millions to hundreds of billions of years could be required for half of the BDE-206, -207, −208, −209, and BTBPE to leach out of the microplastic pellets at 10 and 30 °C, if their structures could remain intact. Due to their very slow leaching rates under ambient conditions, the BFRs contained in microplastics could pose very low risk to the marine environment when only diffusion is considered. Nonetheless, in natural environment, a range of processes, such as breakdown of plastic matrix by physical and chemical processes, and alteration of the polymer structure (e.g., by UV exposure and swelling of the plastic matrix brought by the presence of organic phase), can significantly enhance the releases of BFRs from microplastics and thus increase their risk, as discussed later.

The size of the microplastic pellets also plays a key role in controlling the leaching rates of BFRs. Mechanical abrasion and chemical processes can damage the structural integrity of the plastic matrix and increase the specific surface areas of microplastics, accelerating the releases of BFRs (Gaylor et al., 2013). Fig. 4 shows the leaching of PBDEs from microplastics A and B of 10−20 and 50−100 mesh sizes at 10 °C, along with the model predictions. As expected, the leaching rates of BFRs increased significantly with reduction in their particle sizes. These results indicate that further breakdown of microplastics in marine environment would accelerate the leaching of BFRs due to the increase in their surface-area-to-volume ratios. Consequently, the actual times for releases of significant portions of the BFRs out of the microplastics would be greatly reduced.
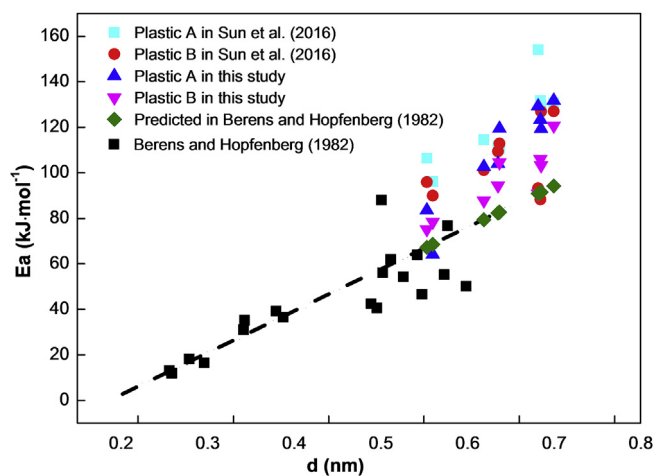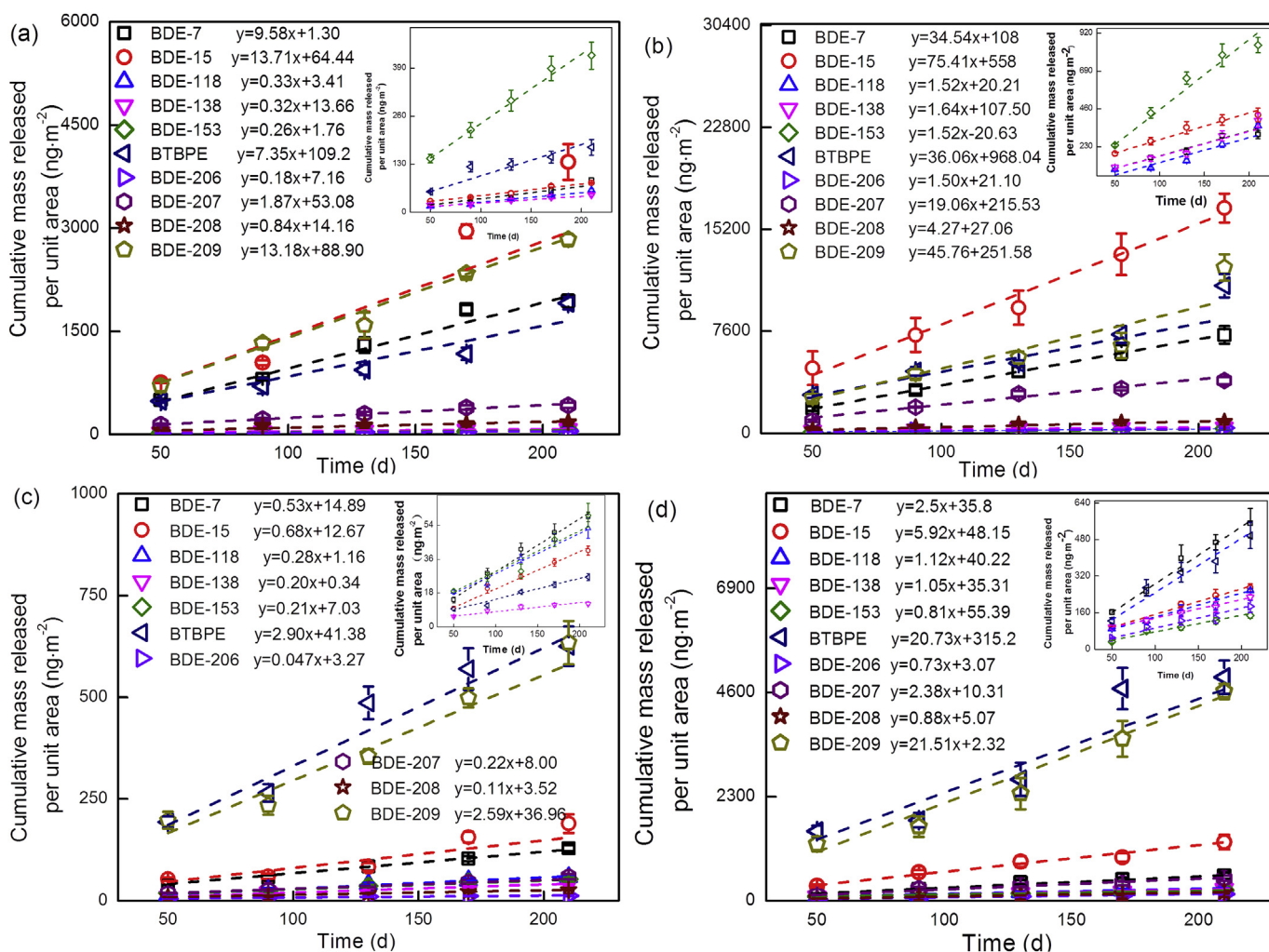
**Fig. 4.** Masses of BFRs leached out of microplastic pellets processed from two model waste plastics (at 10 °C) over time: (a) plastic A of 10—20 mesh, (b) plastic A of 50—100 mesh, (c) plastic B of 10—20 mesh, and (d) plastic B of 50—100 mesh.

## 4. Discussion

Diffusion in the plastic matrix and diffusion in the plastic-water boundary layer are important steps involved in the leaching or desorption of HOCs from plastic materials. Depending on the physiochemical properties of the HOC and the environmental conditions, either diffusion in the plastic matrix or diffusion in the plastic-water boundary layer, or both could control the overall mass transfer rate. Lee et al. (2018) observed that the desorption of HOCs with low ($<10^3$) and high ($>10^4$) plastic-water partition coefficients from polyethylene (PE) and polypropylene (PP) sheets was controlled by diffusion in the plastic film and diffusion in the aqueous boundary layer, respectively. Although diffusion across the plastic-water boundary layer is usually a rate-limiting step for HOCs with $K_{ow}>10^4$ in planar passive samplers (Lohmann, 2012; Rusina et al., 2007), the approximately spherical shape of the microplastic pellets in this study would result in a much steeper concentration gradient across the boundary layer (Schwarzenbach et al., 2003). The extremely high $B_i$ values for the mass transfer of BFRs from the microplastic pellets to aqueous phase indicate that their releases were limited by the diffusion within the plastic matrix, and the leaching process was independent of the boundary conditions.

Endo et al. (2013) investigated the long-term (128 days)

desorption of PCBs from field-collected marine plastic pellets that had relatively high PCB concentrations. The desorption kinetics could not be described by an intra-particle diffusion model, but followed an aqueous boundary layer diffusion model, and the diffusion coefficients of PCB congeners in PE pellets were estimated to be in the range of $10^{-13}$-$10^{-15}$ m$^2$·s$^{-1}$ (Endo et al., 2013). Nonetheless, it should be noted that although PCB congeners were not spiked onto these field-collected PE pellets, they sorbed from the environment onto them, and thus were more enriched near the surface layer of the plastic pellets. Theoretically, the greater abundance of sorbate molecules at the particle surface would render diffusion in the plastic matrix less important (i.e., there are already enough supply of sorbate molecules on the plastic-water boundary layer). In contrast, the additives (e.g., BFRs and plasticizers) were present uniformly in the plastic matrix, and there are no excess additive molecules on the plastic-water boundary layer, thus diffusion in the aqueous boundary layer cannot be a rate-limiting step. In fact, diffusion within polymers has been well argued as the rate-limiting step in the transfers of HOCs from microplastics to sediment-dwelling organisms (Teuten et al., 2007, 2009). In the conceptual model developed to simulate the effect of plastic on bioaccumulation of HOCs, Koelmans et al. (2013) considered that transfer of contaminants from PE plastic into the lugworm *Arenicola marina* is controlled by diffusion in the polymer only. Teuten et al.

(2009) assumed that desorption of HOCs from plastic spheres is limited by diffusion through the polymer matrix, and estimated that the diffusion coefficients of toluene, o-xylene, and tetrachloroethylene in HDPE and polyvinyl chloride (PVC) were in the ranges of $10^{-14}$ m$^2$·s$^{-1}$ and $10^{-17}$-$10^{-18}$ m$^2$·s$^{-1}$, respectively. Narváez Valderrama et al. (2016) also predicted the releases of microplastic additives in aquatic environment based on the assumption that the mass transfer is solely controlled by diffusion within the microplastic sphere.

According to the linear dependence of both Log$_{10}$D and $E_a$ of diffusants in different types of plastics, including PS, polymethyl methacrylate (PMMA), and PVC, on their molecular diameters (Figs. S6 and S7), the diffusion coefficients (at 20 °C) of BDE-7, -15, −118, −138, −153, −154, −206, −207, −208, and −209 in PS, PMMA, and PVC could be estimated (Tables S10 and S11). Based on the diffusion coefficients of PCB-52, -66, −110, −118 in polytetrafluoroethylen (PTFE, $T_g = 129$ °C), polyetheretherketone (PEEK, $T_g = 162$ °C), PP ($T_g = -10$ °C), HDPE ($T_g = -120$ °C), and LDPE ($T_g = -120$ °C) (Liu et al., 2014), the log$_{10}$D data for these diffusants in the matrices of various plastics could be described by the simple linear functions of $T_g$ (Fig. S8). Apparently, log$_{10}$D of PBDEs in plastics can also be described as a linear function of $T_g$ because of the similar molecular structures of PBDEs and PCBs (Fig. 5a). As a result of their larger molecular sizes, the values of Log$_{10}$D for PBDEs decrease faster as the $T_g$ of the plastic increases compared to PCBs (Brown and Park, 1970). Similarly, the predicted log$_{10}$D values of BDE-209 in a range of microplastics that occur commonly in the marine environment also exhibit the trend of linear dependence on the $T_g$ values of plastics (Fig. 5b).

Microplastics could be a source of PBDEs in aquatic environment and pose risk to aquatic organisms. The typical gut retention times of microplastics are 2–5 h and 3–20 days for lugworm and North Sea cod, respectively (Booij et al., 2003; Koelmans et al., 2014; Narváez Valderrama et al., 2016). Figs. 6 and S9 depict the fractions of PBDEs leached out of different types of microplastic pellets as a function of their particle sizes predicted under the assumption that their overall mass transfer is limited by diffusion within the plastic matrix. For a retention time of 0.15 day, only BDE-7 and -15 could leach out of LDPE, PA, PP, and PS pellets of 0.01 mm in diameter or smaller, while no significant BDE-209 leaching could occur within such a short time period (Table S12). In contrast, PBDEs could not leach out from PET, ABS, PMMA, PVC, and CA pellets in the common

size range (0.01–5 mm) of microplastics. It should be noted that the above estimation only holds for an ideal scenario, where the gut of organism is considered as an "infinite sink", similar to that assumed in previous modeling efforts (Koelmans et al., 2013; Narváez Valderrama et al., 2016). The actual leaching rates of BFRs could be reduced due to the decreased fugacity gradient in the organism gut, while the presence of stomach oil and digestive fluid may enhance their leaching through modifying the plastic matrix, as discussed later. Under the "infinite sink" scenario and in the absence of plastic matrix modification, appreciable releases of all the PBDEs from the LDPE microplastic pellets would occur when the gut retention time is increased to 11.5 days (Table S13). BDE-7, and -15 could leach out of PS particles of less than 0.1 mm, and they could also leach out of PET and ABS pellets of less than 0.01 mm in diameter. None of the PBDEs (<1%) could leach out of PMMA and PVC pellets larger than 0.01 mm. Leaching of BDE-209 from all the microplastics under both body retention times is insignificant (Tables S12 and S13), which is consistent with the absence of significant BDE-209 release from LDPE microplastics under gut retention times of 0.25 and 20 d at 20 °C reported in a recent study (Narváez Valderrama et al., 2016). Under the simple model scenario, the leaching of BFRs from microplastics is very slow due to their extremely low diffusion coefficients in the plastic matrices. BFRs contained in the microplastics can also impact seabirds. It has been reported that microplastics could be retained in the ventriculus of seabirds for six months or more, and worn down in the muscular structures (Ryan, 1988; Spear et al., 1995). Once in the bodies of seabirds, BFRs in the plastic matrix could leach out slowly and become bioavailable (Mato et al., 2001). BDE-209 has been detected as the major BFRs in the liver and abdominal adipose of seabirds, with BDE-207 being most abundant among the nona-BDEs (Tanaka et al., 2015). That is, with sufficiently long body retention times, significant leaching of deca- and nona-BDEs from microplastic pellets could occur.

Previous studies have demonstrated that microplastics could act as a vector for the assimilation of HOCs into marine organisms. Besseling et al. (2012) observed that ingestion of PS microplastics pre-equilibrated with the sediment that was natively contaminated with PCBs at a low PS dose of 0.074% increased the bioaccumulation of PCBs by a factor of 1.1–3.6 in Lugworm *Arenicola marina (L.)*. Chua et al. (2014) observed that the tissue of marine amphipod can assimilate PBDEs derived from PE pellets, with the gut fluids
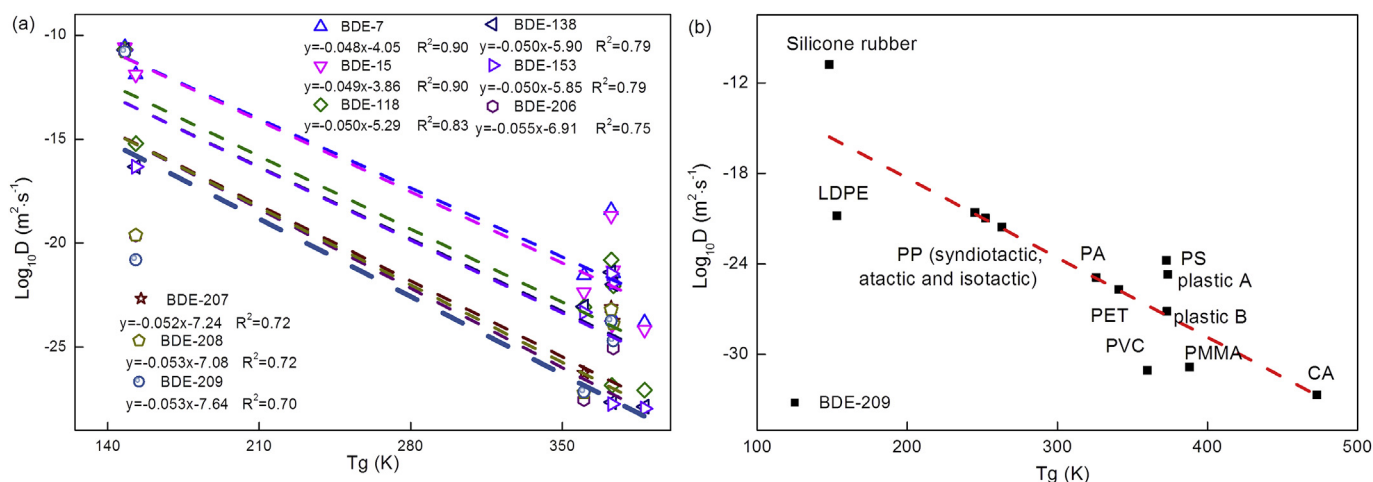


**Fig. 5.** The linear dependence of logarithm of diffusion coefficient (Log$_{10}$D) of diffusant at 20 °C on the glass transition temperature ($T_g$) of plastic material: (a) PBDEs in silicone rubber, LDPE, PVC, PS, and PMMA (estimated in this study), and (b) BDE-209 in silicone rubber, LDPE, PP, PA, PET, PS, PMMA, PVC, CA, and the two ABS materials investigated in this study.
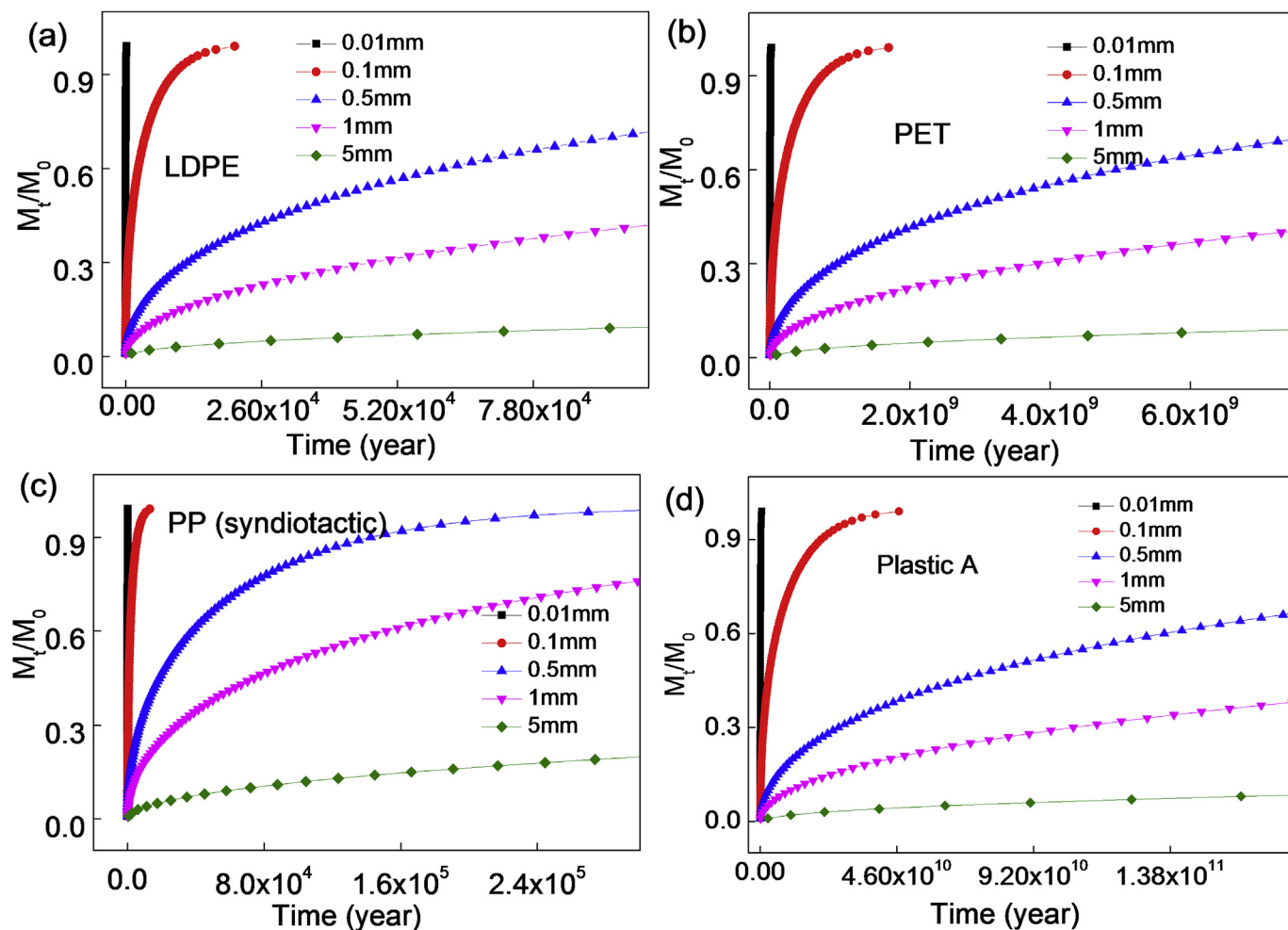
**Fig. 6.** Model predicted fraction of BDE-209 mass leached out of spherical microplastic pellets $(\frac{M_t}{M_0})$ of different sizes made of (a) LDPE, (b) PP (syndiotactic), (c) PET, and (d) plastic A as a function of time under the ideal scenario that their physical and chemical structures would remain intact (at 20 °C).

playing an important role of preferentially removing certain adsorbed PBDEs. A recent study found that the microplastics ingested by European seabass could affect the liver detoxification and lipid distribution of some PCBs and PBDEs (sorbed to microplastics), and thus exacerbate their toxic effects (Granby et al., 2018). Bakir et al. (2014a,b) observed that salinity exhibited no significant effect on the kinetics of sorption and desorption of phenanthrene, dichlorodiphenyltrichloroethane (DDT), perfluorooctanoic acid (PFOA), and di-2-ethylhexyl phthalate (DEHP) on PVC or PE microplastics, while their desorption rates were faster in the presence of a gut surfactant than in seawater alone. It should be noted that the HOCs investigated in the above studies were sorbed to the microplastics, instead of distributed uniformly within the plastic matrices. With diffusion of BFRs within the microplastic matrix controlling their overall release rates, it is unlikely that the presence of organic constituents in the leaching medium could significantly accelerate their leaching when the structure of the plastic matrix is not affected.

Overall, leaching of BFRs from microplastics is very slow due to their extremely low diffusion coefficients in the plastic matrices, thus they could only pose relatively low risk to marine organisms. Based on the empirical relationships between $Log_{10}D$ and the $T_g$ of plastics, as well as the size of microplastics, releases of BFRs from microplastic ingested by marine organisms can be estimated. However, it should be noted that the above analysis holds only

when the physical and chemical structures of the microplastic pieces remain intact. The gradual breakdown of micrplastics in the digestive systems of organisms could reduce their particle sizes and thus significantly enhance the releases of BFRs from their matrices. Furthermore, the swelling of plastic matrix could loosen the polymer chains and facilitate diffusion of BFRs. Narváez Valderrama et al. (2016) observed that swelling of LDPE caused by spiking with *n*-hexane resulted in more homogenous distribution of PBDE congeners in LDPE compared to spiking with methanol/water. In the study of Lee et al. (2018), HOCs were loaded onto the plastic sheets by soaking them in *n*-hexane containing these chemicals for 24 h, and "good swelling" of the plastic sheets was noted. The diffusion coefficients of hexachlorocyclohexanes and chlorinated benzenes in the PE and PP sheets (after swelling by *n*-hexane) were on the orders of $10^{-14}$ and $10^{-16} \, m^2 \cdot s^{-1}$, respectively (Lee et al., 2018), which are several orders of magnitude higher than those of BFRs in the matrices of ABS microplastics determined in this study. This could be caused by the facts that the steric hindrance for diffusion of hexachlorocyclohexanes and chlorinated benzenes in the swollen PE and PP matrices was significantly reduced, and these molecules are much less bulky compared to BFRs. Tanaka et al. (2015) observed that only trace amounts of BDE-209 could be leached out of HDPE plates containing BDE-209 when soaked in distilled water, seawater, and acidic pepsin solution. In contrast, the amounts of BDE-209 leached over 15 days increased by more than

20 and 50 times when the plates were soaked in the stomach oil of seabird and fish oil (Tanaka et al., 2015). Such drastic enhancement in BDE-209 leaching probably resulted from significant reduction in the steric hindrance of the LDPE matrix on diffusion of BFRs with loosening of the polymer chains after penetration of the oil components. Therefore, the magnitude of BFR releases would be underestimated based on their diffusion coefficients in the unaltered plastic matrices. Future study should focus on quantifying the impact of digestive fluids and lipids on the diffusion of BFRs in plastic matrices to better evaluate the bio-accessibility of BFRs in microplastics ingested by marine organisms.

## 5. Conclusions

The leaching of BFRs from microplastic pellets processed from two model waste plastics in water at environmentally relevant temperatures was investigated in this study. The experimental data consistently support that the release rates of BFRs from the ABS microplastics evaluated in this study were limited solely by their diffusion within the plastic matrix. The leaching kinetics of BFRs could be described by the Fick's second law, and their diffusion coefficients and the apparent activation energies were found to be in the ranges of $10^{-28.30}$-$10^{-20.84}$ m$^2$ s$^{-1}$, and 64.1 to 131.8 kJ mol$^{-1}$, respectively. Based on the empirical relationships between $\text{Log}_{10}D$ and the $T_g$ of plastics and molecular size of diffusant, the diffusion coefficients of PBDEs in the matrices of microplastics that appear commonly in the marine environment, including LDPE, HDPE, PS, PA, PET, CA, were also predicted. As a result of their extremely slow diffusion within the matrices of microplastics, the half-lives for releases of BFRs could range from tens of thousands to hundreds of billions of years if their physical and chemical structures could remain intact. On the other hand, the leaching rates of BFRs could increase greatly with further breakdown of microplastics in aquatic environment and alteration of their polymer structures under the actions of digestive fluids once ingested by organisms. Therefore, understanding the physical and chemical weathering processes that can cause the breakdown of microplastics in the natural environment, and the interactions of digestive fluids and lipids with the plastic matrices in organism bodies is critical for more accurate prediction of the releases of BFRs from the microplastics and assessment of their risk.

## Acknowledgement

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2018.12.017.

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