

Modeling Releases of Polymer Additives from Microplastics into the Aqueous
Environment
by

Siyuan Feng

Department of Civil and Environmental Engineering
Duke University

Date: _____

Approved:

Mark Wiesner, Advisor

P. Lee Ferguson

Marc Deshusses

Thesis submitted in partial fulfillment of
the requirements for the degree of
Master of Science in Department of Civil and Environmental Engineering
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ABSTRACT

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Abstract

Microplastics (MPs) are becoming an emerging problem due to increased consumption of plastic. Despite research on MPs acting as sinks of contaminants, the potential of leaching additives out of MPs has been given little attention. Given challenges like the slow release rates of additives and the variety of physical chemical properties of MPs, mathematical models are great tools to explore this problem. In this study, the internal controlled diffusion model was used to describe release behaviors of additives from MPs into aqueous environments. This model was then applied to study Bisphenol A (BPA) and 4-t-butylphenol (TBP) leaching from epoxy MPs. Simulations on the influence of properties of microplastics and various temperatures were completed. Calculated diffusion coefficients of BPA and TBP based on leaching experiments data range from $10^{-13.3}$ cm²/s to $10^{-14.3}$ cm²/s and $10^{-12.1}$ cm²/s to $10^{-12.7}$ cm²/s, respectively. Though at low release rates, the release process was accelerated significantly by smaller sizes and irregular shapes of MPs. With a particle radius reduced from 1mm to 100 nm, the half-life of BPA changes from 3000 years to several minutes, and from 30 years to several seconds for TBP. Also, temperature dependence of migration obeys the Arrhenius equation and activated energies for BPA and TBP are 48.9 kJ/mol and 27.0 kJ/mol, respectively. To sum up, simpler plastic structures, smaller sizes, rough surfaces, smaller additive molecules, and the higher temperature facilitate the release process. This model contributes to the risk assessment of additives releasing from MPs. Yet the real problem might be far more complex considering special properties of plastics materials and

environmental conditions. Thus, more research is required for a deeper understanding of this problem.

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1. Introduction

Since the beginning of commercial production in the 1950s, plastic has exponentially increased in demand. In 2005, the amount increased to 322 million tons from 225 million tons produced in 2004. The global consumption of plastics has a growth rate of 4% per year (PlasticsEurope, 2016). By 2025, the amount of plastics that exist in the ocean will exceed 250 million tons. Among the estimation of 270,000 tons of floating marine plastics, there are 51 trillion pieces of microplastic debris (Van Sebille et al., 2015). Furthermore, according to Rochman et al. (2015), 8 trillion pieces of microplastics are discharged into the surface waters per day in America. Though accurate environmental loads of microplastics are hard to be quantified, these tiny chemical complexes are supposed to be everywhere due to the massive use of plastic materials. Upon Thompson's study (2004) published in Science, this largely overlooked problem started to obtain growing attention as the global ubiquity of microplastics and their potential harm to the environment as well as human health.

1.1 Microplastics and relevant risks

The definition of microplastics (MPs) given by the National Oceanic and Atmospheric Administration (NOAA) is plastic particles with diameters from 100 nm to 5mm. Based on sources, they are divided into two types: primary MPs and secondary MPs. The former are produced intentionally with microscales and used in personal care products as friction agents. Secondary MPs are generated from larger plastics breakdown

by weathering process including ultraviolet light, oxidation, mechanical abrasion, hydrolysis and biodegradation (Olubukola, 2018).

1.1.1 MPs as sink of pollutants

With large rough or porous surface and high specific surface area, MPs are regarded as the “PM 2.5 in the aqueous environment” and are an emerging pollution problem. It has been widely accepted that MPs have a high potential to adsorb hydrophobic organic compounds (HOCs) due to their hydrophobicity property. Most concern is in the ability for these chemicals to be transported to new locations and then diffuse into the new aqueous environment. Thus, the MPs become a vector of transport for potentially hazardous organic pollutants. Typical HOCs that can be adsorbed by MPs include polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), DDT and other persistent organic pollutants (POPs). Both experimental research and theoretical research have been widely studied, which includes modeling the kinetic release behavior of HOCs from MPs particles into the aqueous environment and organisms (Karapanagioti et al., 2011; Bakir et al., 2012; Endo et al., 2013; Vandermeersch et al., 2015).

1.1.2 MPs as source of contaminants

Because plastic materials can contain up to hundreds of different chemical additives and most of them are hazardous, MPs provide another avenue for contaminants migration into the aqueous environment. However, less research has been done on releasing polymer additives from MPs to the aqueous environment. As Engler (2012)

mentioned, additives are mixed into polymers rather than chemically bonded so they have the ability to leach out of polymers into surroundings. These leached chemicals include alkylphenolics, phthalates, brominated flame retardants (BFRs) and so on. Hirai et al. (2011) and Rochman et al. (2014) found BPA, PBDEs, and nonylphenol in field MPs; Fries et al. (2013) measured various antioxidants including 2,4-di-tert-butylphenol (2,4-DTBP) from MPs in Norderney Island; Hermabessiere et al. (2017) detected BPA, phthalates and 2,4-DTBP in marine plastic debris. All of these reveal the risk of hazardous additives leaching out of MPs. Furthermore, small size determines that MPs might be ingested by aqueous organisms creating the potential for the accumulation of persistent chemicals within the marine food chain. In addition, another ecosystem risk of MPs is that the ingestion of them lead to mechanical damage to organisms (Gall and Thompson, 2015).

Table 1: Commonly produced polymers and associated additives in EU, 2015.

(Hansen et al., 2013).

Polymer	Consumption (Mt)	Additive types	Additives amount (% w/w)	Additive substances
PP*	9	Flame retardants;	12-18	BFRs;
		Antioxidants	0.05-3	BPA, OP, NP
HDPE*	8	Flame retardants;	12-18	BFRs;
		Antioxidants	0.05-3	BPA, OP, NP
LDPE*	6	Flame retardants;	12-18	BFRs;
		Antioxidants	0.05-3	BPA, OP, NP

PVC*	5	Plasticizer	10-70	Phthalate;
		Stabilizers	0.5-3	BPA, NP

*: PP: Polypropylene; HDPE: High Density Polyethylene; LDPE: Low Density

Polyethylene; PVC: Polyvinyl Chloride.

1.2 Polymer additives

Additives are have a variety of functions and are added into the polymer in to enhance or protect the structure.

1.2.1 Common additives in polymers

According to Hunt (2000), fillers and reinforcements, such as carbon fibers, glass fibers and fibrous, are used to increase the stiffness of resins and to reduce shrinkage. Flame retardants are commonly added in electrical applications and furniture to prevent them from combusting. Lubricants including fine fluoropolymers powders are used both inside and outside of polymers to prevent blockages. Impact modifiers, or tougheners, can modify plastics' impact strength so that they have sufficient resistance under various situations like low- and high-temperature environment. Plasticizers used to increase or maintain the plastics' flexibility mainly contain phthalates. Colorants include inorganic and organic pigments and dyes to make plastics commercially attractive. While pigments particles are mixed physically with initial products, dyes often chemically bonded to polymers. The exposure to the sunlight usually results in significant deterioration on most polymers caused by the ultraviolet light. Therefore, UV stabilizers or antioxidants such as 2,4-di-tert-butylphenol and 4-tert-butylphenol are necessary for plastics to avoid UV

degradation. These non-chemical-bonded substances have been detected migration into food from plastics packaging (Lau and Wong, 2000) and smaller molecules leach out of the plastic matrix easily into the surrounding environment and they have been found ubiquitously (Net et al., 2015).

Table 2: Common additives and their octanol-water partition coefficients.

Additive and abbreviation	Octanol-water partition coefficients (Log K_{ow})
Bisphenol A (BPA)	3.32
Polybrominated diphenyl ethers (PBDEs)	5.52-11.22*
Butyl benzyl phthalate (BBP)	4.73
Di(2-ethylexyl) phthalate (DEHP)	7.60
Hexabromocyclododecane (HBCD)	5.07-5.47*
Nonylphenol (NP)	4.48-4.80*
4-Tert-Butylphenol (TBP)	3.33

*: Hermabessiere et al. (2017)

1.2.2 BPA and TBP

Endocrine disrupting compounds (EDCs) are exogenous chemicals that can affect the endocrine system by mimicking endogenous estrogens and typical EDCs include BPA and alkylphenols. These chemicals might affect estrogenic activity and cause the proliferation of estrogen target cells. Even low concentration exposure of EDCs can lead to ecological problems, such as changing reproductive parameters in rodents, feminization of aqueous organisms (Metzler, 2001).

With production of over 3 million tons annually, Bisphenol A (BPA) is the most ubiquitous chemical among Bisphenols, which are widely used additives (Laing et al., 2016). BPA is not only the monomer of epoxy resins and polycarbonates (PC), but also a common plasticizer or UV stabilizer of many plastics (PP, PE and PVC) (Rani et al., 2015). Back to 1993, Krishnan et al. (1993) have found released BPA from laboratory PC flasks at high temperatures. The mainly human exposure is leached BPA out of plastics packaging into food and drinking water (Sajiki and Yonekubo, 2003; Vandermeersch et al., 2015). Besides, it has been reported that BPA existed globally in the surface waters in Europe, Asia and North America (Vethaak et al., 2005; Fu et al., 2007; Basheer et al., 2004).

4-tert-Butylphenol (TBP) is one of alkylphenols that can affect the endocrine system. It is widely used to produce plastic materials such as epoxy resins and PC as plasticizers and antioxidants. In 2001, the production of TBP in Europe was 25 kilotons (European Chemicals Bureau, 2008). The detection of TBP has been found in a wide range of aqueous environments, including surface water and wastewater treatment plant sewage (Heemken et al., 2001; Inoue et al., 2002). It has been demonstrated that TBP has high estrogenic effects along with acute and chronic toxicity to aqueous organisms, and due to poor biodegradability, TBP is persistent in the environment (Makhatova, 2019).

Epoxy resins, also called polyepoxides, have extensive applications, including coating, painting, adhesives and industrial composites as their excellent adhesion, chemical stability, heat resistance and capability to prevent corrosion (May, 1988). Food- and water- contact epoxy resins commonly exist inside metal food containers and cans;

the interior of water towers, drinking water pipes and wine storage vats (Lambert and Larroque, 1997). BPA and TBP are two widely used additives in epoxy resins production and manufacture.

1.3 Migration of additives release from MPs

The comprehensive problem including exponential production and disposal of plastic, hundreds of polymer additives incorporated into these materials, and the potential of these potentially hazardous chemicals to be released into aqueous environments from MPs highlights the significance of studying the transport and fate of polymer additives leaching from MPs.

1.3.1 Challenges of research on additives migration

Despite the high potential, there are lots of challenges for experimental studies on additives leaching out of plastics. First, the rate of additives migration is quite low even at high temperatures (Mercea et al., 2018) so the leaching experiment itself is time-consuming. Furthermore, the released additives are usually at trace levels so the expensive instrumentation or extensive method preparation is required. Additionally, the release behavior of polymer additives highly depends on several factors simultaneously: properties of plastic particles, which include chemical composition, density, size and shape; water chemistry including pH, temperature and ionic strength; the systematic factors such as hydrodynamic conditions, weathered degree and so on. Under this situation, a theoretical model, specifically, a mathematical model can be a useful tool to predict polymer additives migration behavior from microplastics.

1.3.2 Model transport of polymer additives

Since the migration of penetrant molecules is evidently a critical problem in polymer industries, enormous scientific publications have attempted to describe this transport phenomenon (Calvert and Billingham, 1979; Lee, 1980; Norbert et al., 1999; Teuten et al., 2009). While the mass transfer of penetrants through plastics membranes usually goes to steady-state in a short time, the diffusion of additives adsorption and desorption could cost much longer time and thus undergoes the unsteady-state circumstance (Karimi, 2011). The driving forces of the above situations are the concentration gradients between different phases. Therefore, both situations follow the mass transfer mechanism. The Fick's first law was used to describe the former system and the second law for the latter, which is the scenario discussed in this study. Release of additives starts at the parties' surface. After additives located at the surface have depleted, inner layer chemicals will diffuse to the surface and continue this leaching process until the equilibrium with the surrounding environment has been reached.

1.4 Scope of this study

The object of this study is to model the migration of polymer additives and monomers BPA and TBP from microplastics into aqueous environment via analytical solving Fick's second law with experimental data. The parameter half-life used to quantify the effect of plastic particle size, specific surface area, and temperature. Besides, release behaviors under various situations would be simulated based on theoretical and experimental data to evaluate the risk of leached additives from microplastics into

surroundings. The influence of weathering process would be attempted to explore as a moving boundary problem.

2. Materials and Methods

2.1 Experimental work

2.1.1 Materials

The plastic material epoxy composites were formed by commercial sales Araldite LY 8601 resin and Aradur 8602 hardener (Durham, NC, USA). High purity (99% or higher) chemicals were purchased: sodium bicarbonate and potassium chloride (EMD Millipore Sigma, USA); magnesium sulfate and calcium sulfate (Fisher Scientific, USA). Deionized water (18.2 mΩ) used to rinsing and made solvent was provided by Millipore Milli-Q®. Analytical grade standards were used to analyze chemicals, which include BPA, TBP (Sigma Aldrich, USA) and the internal standard BPA-d8 (Toronto Research Chemicals, Canada).

2.1.2 Production of epoxy microplastics and synthesis water

Compositions of the epoxy system are Araldite LY 8601 Resin and Aradur 8602 Hardener. The resin and hardener (w/w is 5:1) were added into a centrifuge tube. After stirred by a glass stir rod for three minutes, the mixture was poured into aluminum pins evenly and next, they were put into a desiccator to remove gas bubbles under vacuum for one hour. These primary polymer plates were heated for an hour in a furnace to cut into small pieces and kept heating for another 8 hours until they were hard enough. Final products were then cryomilled by a FreezerMill with liquid nitrogen as a coolant to keep the temperature under the melting temperature of epoxy. The size distribution of

microplastics was determined by the mastercizer and the average diameter was 150 μm (75 μm for radius).

EPA moderately-hard water (MHW) was used as the leachate solution in order to mimic the surface water. Preparation of MHW followed Marking and Dawson (1973), and the composition is NaHCO_3 96.0 mg/L, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 60.0 mg/L, MgSO_4 60 mg/L, KCL 4.0 mg/L. After 24 hours of aeration, the approximate water quality is: pH 7.4-7.8, hardness 80-100 mg CaCO_3/L and alkalinity 57-64 mg CaCO_3/L .

2.1.3 BPA and TBP leaching experiments

Releases of BPA and TBP from epoxy microplastics were investigated in a covered glass vessel. 30mL MHW was added into vessels with 1.00g microplastics and then vessels were covered to set in a dark temperature-constant incubator (at 25 °C, 45°C and 65°C, respectively). No mechanical mixing of samples to maintain the stagnant environment. At time points 0, 0.5h, 1h, 2h, 4h, 8h, 24h, 48h, 72h, 96h, 120h, 1mL leachate was sampled by a glass syringe and filtered into a chromatography vial with 0.2 mL internal standard until the total volume reached 1mL. Chromatographic grade acetonitrile was used to rinse the syringe three times after each sampling. Triplications were conducted to improve reproducibility. To reduce the evaporation interference, the mass of water was recorded before sampling and a constant water volume was maintained after every sampling. All samples were stored in a -20 °C freezer until analyzed by LC/MS-MS.

A sequentially repeated bath sonication and soxhlet extraction was applied to obtain the accurate amount of additives that can leach out of microplastics M_{∞} . The 24 hours soxhlet extractions used 0.25 grams of epoxy microplastics and 250 mL methanol with three replicates. Sonication used 0.25 grams plastic and was sequentially extracted using 2 mLs of methanol every 15 minutes. The results of these two ways are similar to each other for BPA and different for TBP. Soxhlet results were chosen for later analysis.

2.1.4 Chemicals analysis

LC/MS-MS was used to qualify and quantify leached additives. All extracts and water leachates were analyzed using an Ultimate 3100 Series LC coupled with an Altis triple quadrupole MS detector, equipped with the Xcalibur Quan browser to analyze spectral data. A Hypersil Gold aQ Polar Endcapped C18 columns (100 x 2.1 mm; 1.9 μm) was used for chromatographic separation and the sample of 10 μL was injected at 35 $^{\circ}\text{C}$. The mobile phase has the composition of water for solvent 'A' and acetonitrile 'B' with the flow rate of 300 $\mu\text{L}/\text{min}$. The total gradient elution time is 14 minutes: the gradient started at 20% B and ended at 99% B with a constant increase rate over the first 8 minutes; it maintained at this gradient for 2 minutes and then went back to 20% B over 2 minutes; this gradient last for 2 minutes to re-equilibration. The Electrospray Ionization (ESI) mass spectrometry operated in positive and negative ionization mode with parameters of ion source are spray voltages - 2.5 kV, vaporizer temperature 300 $^{\circ}\text{C}$, capillary temperature 360 $^{\circ}\text{C}$, sheath gas 40 psi and auxiliary gas 12 psi. The parent ion of 277 and product ion 212 were used to quantification BPA while ion 133 was to

confirmation; as for TBP, the parent ion is 149, quantification product ion is 133 and confirmation ion of 144.9. The internal standard method was applied in order to reduce matrix interference and 0.2 μL BPA-d8 as the internal standard was added into all samples with a volume of 0.8 μL to maintain a concentration of 200 ng/mL. A seven point calibration curve of 1 to 500 ng/mL was used to quantify all compounds.

2.2 Modeling release of polymer additives from microplastics

2.2.1 Model description

The transport of additives from polymer into water is a two-step process. The first step is additives diffuse from the plastic matrix into the plastic-water boundary layer, which is also called the internal diffusion; the second step is that release from the boundary layer into the aqueous environment, which is the external diffusion. This unsteady-state process is governed by the diffusion mechanism Fick's second law:

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

and

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right) \quad (2)$$

for radial diffusion, where C is the local concentration of additives, D is the diffusion coefficient of additives transport inside the plastic matrix, and x or r is the distance leave from the center of plastic particles. Figure 1 schematically illustrates this migration process.

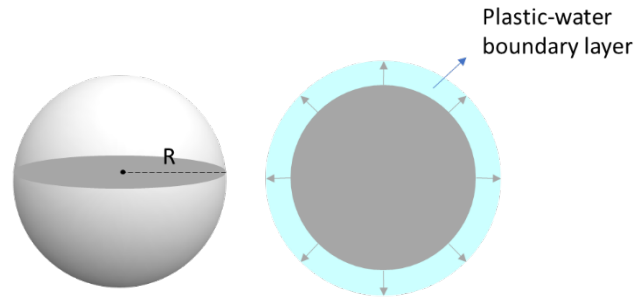


Figure 1: Schematic illustration of the migration process.

2.2.1.1 Assumptions

Appropriate assumptions can simplify the problem and useful for the analytical solution. Assumptions of the model are listed as follow:

1. The plastic particle has a regular shape and the surface remains intact;
2. The plastic composition is homogeneous and isotropic;
3. Polymer additive is uniformly distributed inside the plastic and has the initial concentration of C_0 ;
4. Water is regarded as an “infinite sink”, the volume of water is constant so the diffusion coefficient is a constant D ;
5. The concentration at the particle surface is at equilibrium with the aqueous environment and constant at C_s ;
6. The aqueous environment is stagnant, so the influence of turbulence is neglect.

By applying the assumptions, the specific initial condition and boundary conditions have been set to:

1. $C = C_0, 0 < x < l, t = 0$;
2. $C = C_0, x = 0, t \geq 0$;
3. $-D \frac{\partial C}{\partial x} = k(C_0 - C_s), x = l, t \geq 0$,

where l is half of the thickness of the plastic and k is the mass transfer coefficient.

2.1.1.2 Analytical method and solution

There are two analytical methods, separation of variables and Laplace transformation, to solve the diffusion equation. The former assumes that the concentration can be expressed in terms of the product of a space function and a time function: $C(x,t) = X(x)T(t)$, so the partial differential equation (PDE) tends to the ordinary differential equation (ODE). The application of the latter transforms the time domain into the complex domain so that removes the time variable to solve PDE.

Via applying the Laplace transformation, the analytical solution of C analogized from Carslaw and Jaeger (1959) as Eq. (3)

$$\frac{C - C_0}{C_s - C_0} = 1 - \sum_{n=1}^{\infty} \frac{2Bi \cos \frac{\beta_n x}{l} \exp\left(-\beta_n^2 \frac{Dt}{l^2}\right)}{(\beta_n^2 + Bi^2 + Bi) \cos \beta_n} \quad (3)$$

In order to trace the migration of additives more conveniently, the ratio of the amount of additives remained inside plastics matrix to the total amount that can release from plastics into the aqueous environment is

$$\frac{M}{M_{\infty}} = \sum_{n=1}^{\infty} \frac{2Bi^2 \exp\left(-\beta_n^2 \frac{Dt}{l^2}\right)}{\beta_n^2 (\beta_n^2 + Bi^2 + Bi)} \quad (4)$$

For the sphere,

$$\frac{M}{M_{\infty}} = \sum_{n=1}^{\infty} \frac{6Bi^2 \exp\left(-\beta_n^2 \frac{Dt}{R^2}\right)}{\beta_n^2 (\beta_n^2 + Bi^2 - Bi)} \quad (5)$$

where $\beta_n \cot \beta_n + Bi - 1 = 0$ and $Bi = \frac{kR}{D}$

2.2.2 Biot number

When both the internal diffusion and external diffusion is significant, Eq. (4) and (5) can well describe the diffusion process. The Biot Number Bi , which is the ratio of the external diffusion rate to the internal diffusion rate, is used to evaluate the significance of the two diffusion steps.

$$Bi = \frac{kL}{D_p} \quad (6)$$

$$k = \frac{D_w}{K_{pw}\delta} \quad (7)$$

$$Bi = \frac{D_w}{D_p} \frac{1}{K_{pw}} \frac{L}{\delta} \quad (8)$$

where k is the mass transfer coefficient in boundary layer, D_p is the diffusion coefficient within the plastic matrix, D_w is the diffusion coefficient in water, K_{pw} is the plastic-water partition coefficient, and δ is the thickness of the plastic-water layer ($R=\delta$ for stagnant aqueous environment).

Thus, the external diffusion dominates the desorption process if $Bi \gg 1$ and the rate-limiting step is internal diffusion. This internal-controlled condition is called Case I. Case II happens when Bi around 1, which means rates of two steps are almost equal so we should take account of both transport from plastics to the boundary layer and that from the surface to the water. When $Bi \ll 1$, the situation is the opposite of Case I and such an external-controlled condition is called Case III.

2.2.3 Case I: Internal-controlled

According to Crank (1975), the following initial condition and boundary conditions could be applied under Case I:

$$C = C_0, 0 < x < l, t = 0;$$

$$C = C_0, x = 0, t \geq 0;$$

$$C = C_s, x = l, t \geq 0;$$

Eq. (1) could be solved as

$$C(x, t) = \frac{4C_0}{\pi} \sum_{n=0}^{\infty} \frac{1}{2n+1} \sin \left[\frac{(2n+1)\pi x}{l} \right] e^{-\frac{(2n+1)^2 \pi^2 D}{l^2} t} \quad (9)$$

The remaining mass fraction is

$$\frac{M}{M_{\infty}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-(2n+1)^2 \pi^2 \frac{Dt}{l^2} \right] \quad (10)$$

For spheres, the result turns into

$$\frac{M}{M_{\infty}} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-n^2 \pi^2 \frac{Dt}{R^2} \right) \quad (11)$$

2.2.4 Case III: External-controlled

Under this condition, the rate-limiting step could be expressed as follows:

$$V \frac{\partial C}{\partial t} = A k (C_s - C_0) \quad (12)$$

And the result is

$$\frac{M}{M_{\infty}} = \exp\left(-\frac{D_w}{K_{pw}\delta L_c} t\right) \quad (13)$$

where V, A and L_c are the volume, surface area and characteristic length of the plastic particle, respectively.

Table 3 summarizes all the expressions of the mass fraction ($F = \frac{M}{M_{\infty}}$) under three cases for plastics of flat shape and spherical shape.

Table 3: Summaries of analytical solutions under three cases.

Mathematical solutions of remaining mass fraction F under Case I, Case II, and Case III.

Case	Expression of F	Parameters			
Case I	$F = \sum_{n=1}^{\infty} B_n \exp(-A_n^2 \cdot Fo)$		A_n	B_n	
		Flat	$(2n+1)\pi$	$2/A_n^2$	
		Cylinder	$R_c \alpha_n$	$4/A_n^2$	
	Sphere	$n\pi$	$6/A_n^2$		
Case II	$F = \sum_{n=1}^{\infty} \frac{A \exp(-\beta_n^2 Fo)}{B_n}$		A_n	B_n	
		Flat	$2Bi^2$	$\beta_n^2(\beta_n^2 + Bi^2 - Bi)$	$\beta_n \tan\beta_n - Bi = 0$
		Cylinder	$4Bi^2$	$\beta_n^2(\beta_n^2 + Bi^2)$	$\beta_n J_1[\beta_n] - Bi J_0[\beta_n] = 0$
	Sphere	$6Bi^2$	$\beta_n^2(\beta_n^2 + Bi^2 + Bi)$	$\beta_n \cot\beta_n + Bi - 1 = 0$	
Case III	$F = \exp(-Bi \cdot Fo)$				

* Fo: Fourier number, which characterizes transient mass transfer, is the ratio of diffusive

transport rate to the storage rate. $Fo = \frac{Dt}{L_c^2}$.

2.2.5 Measurement of diffusion coefficients of BPA and TBP

According to Mercea, et al. (2018), the diffusion coefficients of BPA and TBP in high-density polyethylene (HDPE) are nine to eleven orders of magnitude smaller than

those in water. Besides, Lee's (2014) study on the sorption of plastic for HOCs indicates that the plastic-water partition coefficient K_{pw} is slightly smaller than the octanol-water partition coefficient K_{ow} . This can be explained by the less hydrophobicity of plastics than octanol. Hence, Bi values for additives releasing from plastics into water would be much larger than 100, which means their migration behaviors obey Case I internal diffusion, Eq. (11). Biot numbers of several additives leaching from three plastics were calculated as Table 4.

Table 4: Calculated Biot Number.

Additives	HDPE	PP	PB*
4-Tert-Butylphenol (TBP)	67316	118625	46564
2, 4-Di-Tert-Butylphenol (DTB)	1134	502	2164
Diethyl Phthalate (DEP)	394995	\	\
Dibutyl Phthalate (DBP)	611300	\	\
Bisphenol A (BPA)	5.4E07	\	\
Methyl-3-(3,5-di-tert-butyl-4-Hydroxyphenyl)-Propionate (MHP)	635	377	671

*PB: Polybutylene; Data from Mercea, et al. (2018 & 2019).

coefficient inside plastic matrix. Many simplifications have been conducted on Eq. (11) to obtain measurements of D_p . One of well-known results imported by Boyd et al., (1947) as follows:

$$\frac{M_t}{M_\infty} = \frac{6}{\pi^2} \sqrt{Bt} \quad (14)$$

where M_t is the amount of released additives, B is $\frac{\pi^2 D_p}{R^2}$. Weber and Morris (1963) have plot $\frac{M_t}{M_\infty}$ versus \sqrt{t} based on Eq. (14) to study the adsorption kinetics of carbon from solution, which is also called Weber-Morris intraparticle diffusion model. This simplification works well at the early adsorption stage, for $\frac{M_t}{M_\infty} < 0.3$, or $\frac{M}{M_\infty} < 0.7$ for desorption. By Weber plotting $\frac{M}{M_\infty}$ versus \sqrt{t} , the slope k is $-\frac{6}{R} \sqrt{\frac{D_p}{\pi}}$. In this way, D_p can be determined to be $\frac{\pi R^2}{36} (-k)^2$.

3. Results and Discussions

3.1 Simulation of analytical solutions

The release of polymer additives from spherical microplastics over time with various Biot numbers based on Eq. (5) were simulated as Figure 2 using Python. The effect of Bi value is obvious. With 1 as the demarcation point, the trends of mass fraction curves become extremely distinct. At the region close to 1, a little change of Bi can make a big deviation from the baseline, the curve of Bi=1. Note the D_p is a constant here thus the conclusion that all the external diffusions are much slower than internal diffusion cannot be drawn from this figure and the other reason will be discussed in the following part.

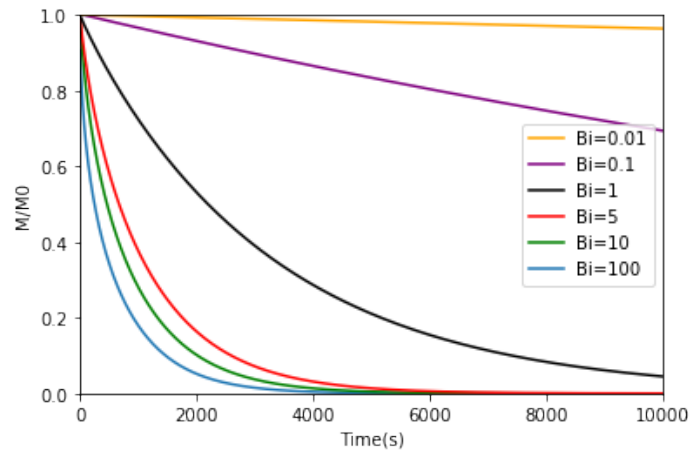


Figure 2: Effect of Bi number.

The remaining mass fraction ($\frac{M}{M_\infty}$) of additives in spherical microplastics with the same diffusion coefficient in plastics D_p and particle radius R for different Biot numbers (after Crank (1975)).

By comparing Case II (Eq. (5)) with various Bi numbers larger than 1 and Case I (Eq. (11)) in the same graph (Figure 3), we can claim that as Bi number increases, the remaining mass fraction curve of Case II approaches to that of Case I. The larger Bi number, the closer Case I curve and Case II curve. For $Bi > 100$, curves of two cases turn to be the same one. Thus, Eq. (11) can be applied for additives with Bi value bigger than 100 approximately.

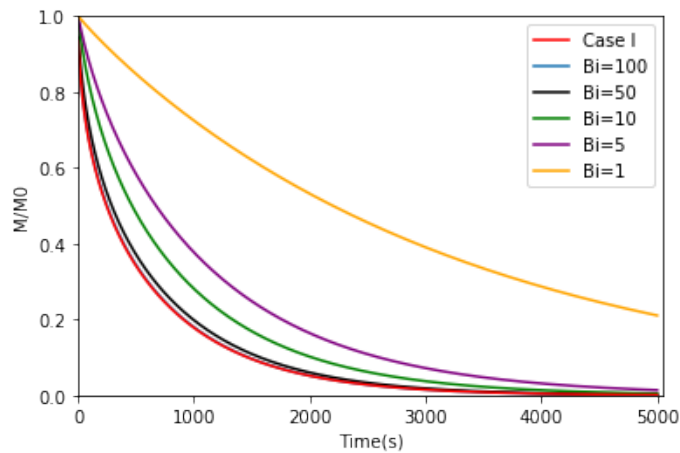


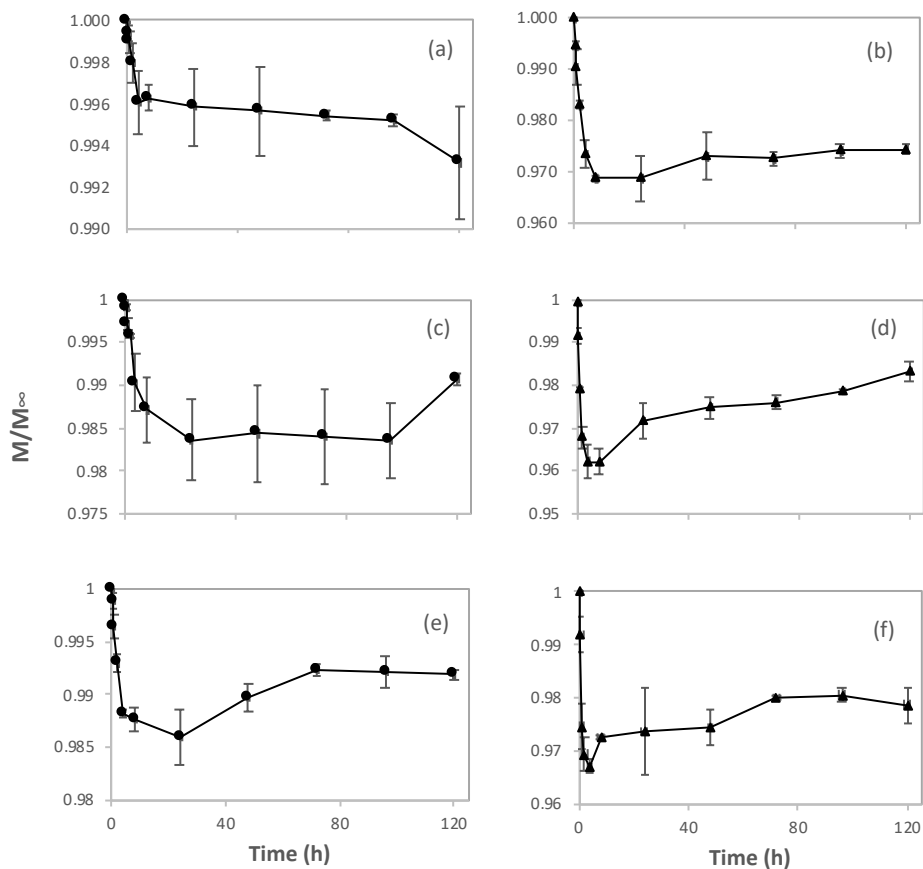
Figure 3: Comparison of Case I and Case II.

Case II with various Bi values and Case I of the same diffusion coefficient in plastics D_p and particle radius R .

3.2 Leaching behaviors of BPA and TBP from epoxy microplastics

Experimental results of remaining mass fraction F over time for BPA and TBP at various temperatures are shown as Figures 4. Comparisons of three figures in each column show the leaching fluxes increase with the surrounding temperature for both two chemicals, which indicates the temperature dependence of the release behavior. Yet the

rise of F after the first few hours was unpredicted. The reason for that might be because of the adsorption by the glass vessels due to the hydrophobicity of BPA and TBP.



Figures 4: BPA and TBP leaching from epoxy microplastics.

Remaining mass fraction profiles of additives leaching from epoxy microplastics with 75 μm radius for (a) BPA at 25°C, (b) TBP at 25°C, (c) BPA at 45°C, (d) TBP at 45°C, (e) BPA at 65°C, (f) TBP at 65°C.

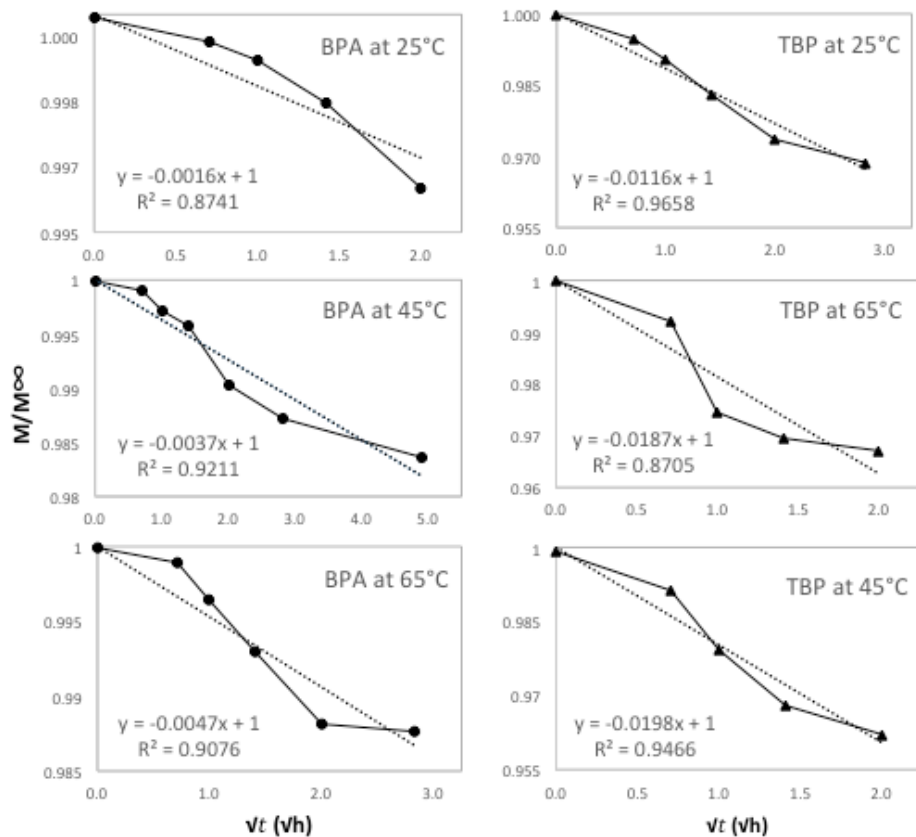
Detections of additives in the methanol solution of glass vessels after leaching experiments confirm it. Therefore, real transport phenomena occur in the experimental system are: (1) desorption of additives from microplastics and (2) the adsorption of

additives on the glass. One of the solutions to control transport phenomena is adding sinks to adsorb model additives. The sink material should have higher affinity and sufficient sorption sites so that it will stay far away from sorption saturation (Endo et al., 2014; Lee et al., 2018). Polyurethane foam (PFU) used in passive sampling with a high adsorption rate is a perfect sink of hydrophobic additives (Sun et al., 2019). The additives quantity on the sink, which is the difference of the extraction values after and before leaching experiments, is the desorption amount of additives from source microplastics. In this way, two predominant transport phenomena of chemicals inside leaching vessels are desorption from the source and adsorption by the sink. This method controls the release behavior of additives without losing via other pathways. Another way is to conduct a series of leaching cells and analysis each cell at designated time until the system at equilibrium. Rinsing cells by organic solvents such as methanol is applied to remove all leaching chemicals. Yet longer time frames needed for the release process to reach equilibrium.

3.2.1 Diffusion coefficients of BPA and TBP in epoxy microplastics

Considering the application scope of Eq. (14) as well as to avoid the error from re-adsorption by the glass, only the first several points were applied to optimize linear fits as Figures 5 shown. The linear relationship of mass fraction and the square root of time confirms the release behaviors of BPA and TBP obey the internal diffusion Case I. Table 4 summarizes calculated diffusion coefficients D_p of BPA and TBP in epoxy microplastics. The diffusion coefficients of BPA and TBP in epoxy range from 10-13.3

cm²/s to 10-14.3 cm²/s and 10-12.1 cm²/s to 10-12.7 cm²/s at temperature 25°C - 65°C, respectively.



Figures 5: Weber plots of BPA and TBP leach out of microplastics.

Remaining mass fraction versus \sqrt{t} of additives leaching from epoxy microplastics with 75 μm radius for (a) BPA at 25°C, (b) TBP at 25°C, (c) BPA at 45°C, (d) TBP at 45°C, (e) BPA at 65°C, (f) TBP at 65°C.

Table 5: Summaries of calculated diffusion coefficients of BPA and TBP in epoxy.

Leaching experiments for BPA and TBP in epoxy microplastics at three temperatures: 25°C, 45°C, 65°C.

Temperature (°C)	BPA		TBP	
	D_p (m ² /s)	D_p (cm ² /s)	D_p (m ² /s)	D_p (cm ² /s)
25	4.92E-19	4.92E-15	2.00E-17	2.00E-13
45	1.87E-18	1.87E-14	5.56E-17	5.56E-13
65	5.07E-18	5.07E-14	7.15E-17	7.15E-13

3.3 Influencing factors of release behaviors

3.3.1 Influencing factors of D_p

Calculated diffusion coefficients in this study are comparable to results in Mercea et al.'s study (2018) at low temperature but lower than those at high temperature. Different structures of plastics might contribute to this consequence. In their report, diffusion coefficients of HOCs in PP are two orders of magnitudes smaller than in PE. Table 6 illustrated diffusion coefficients of four additives in various plastics. Each chemical gained its largest D_p in HDPE comparing with other plastics. The reductions of D_p from HDPE to PP and PB might because of the increasing degree of branched carbon structures of the latter. In comparison to PE, PP and PB, BPA based epoxy resins own more complex arrangements that lead to less mobility of additives and lower diffusion rates.

Table 6: Diffusion coefficients (cm²/s) of additives in various plastics.

	HDPE*	PP*	PB*	Epoxy
TBP	2.97E-10	8.31E-11	6.13E-11	2.00E-13
BPA	6.47E-11	\	\	4.92E-15
DTB	3.71E-11	3.69E-11	1.32E-11	\
MHP	7.52E-12	6.10E-12	3.73E-12	\

*: Data from Mercea, et al. (2018 & 2019).

According to Table 5, D_p of TBP is 1-2 orders of magnitude less than that of BPA. Considering their similar $\text{Log } K_{ow}$'s (3.32 and 3.31) and D_w 's ($5.89\text{E-}6 \text{ cm}^2/\text{s}$ and $5.31\text{E-}6 \text{ cm}^2/\text{s}$ (Sharma and Kalia, 1977)), the different of BPA and TBP on D_p is unexpected. However, compared to their molecular weights (228.29 g/mol and 150.22 g/mol), the steric hindrance of BPA would much higher than that of TBP, which may lead to the lower diffusion coefficient. Similar results have also been discussed in the study of Sun et al. (2016 and 2018), in which they plotted $\text{Log } D$ values and apparent activated energies versus the molecular diameters of brominated flame retardants, respectively. Sun et al. found that diffusion coefficients decrease linearly with the molecular weights whereas the activated energy has a reverse tendency. There is no denying that diffusion rates in air and water decrease as molecular weights become bigger. However, the reduction of molecular diffusion rate in the solid phase is much more significant than that in the gas and liquid phase. Greater steric hindrance occurs when large additive diffuse inside glassy plastics due to higher crystallinity. For molecules with the same molecular weights, different diffusion rates might be expected if their chemical structures are different. Molecules with softer straight carbon chain

structures like alkanes can transport through glassy plastics faster than those with rigid symmetric aromatic benzenes; even if their mass weights are the same (Berens and Hopfenberg, 1982). This also explains why HOCs like BFRs with such high Log K_{ow} values, whose Bi numbers assumed to be lower than 1, have Bi values much larger than 100 and the release behaviors of them are controlled by the intraparticle mass transfer instead of the external diffusion step.

Additionally, larger amount of BPA in epoxy resins and higher solubility of TBP may contribute to higher D_p of TBP than BPA. The epoxy resin is composed of about 60% Bisphenol A diglycidyl epoxy resin and 7% tert butylphenol glycidyl ether resin, and the fragments of them form free BPA and TBP. The release of chemically bond BPA needs more energy to cleavage covalent bonds (Takada et al., 2019). Also, high solubility of TBP enables them readily release into the aqueous environment. As a result, these factors lead to a lower diffusion rate of BPA than TBP, which has been confirmed by higher apparent activate energy of BPA in the later part.

3.3.2 Effects of microplastics properties

3.3.2.1 Particle sizes

One reason why the additives leaching problem is underestimated is because of the extremely low diffusion rate in bulk plastics. However, as larger plastics are degraded into smaller pieces such as microplastics and nanoplastics, this problem deserves reassessment. Based on Eq. (11), it is obvious that the particle size plays an important role during the leaching process. Figures 6 shows the effect of particle sizes for BPA and

TBP releasing from epoxy microplastics at room temperature using the experimental data calculated in Table 4. The reduction of remaining mass fraction is significant with particle radius decreases from 100 μm to several μm . Although it will take more than three years for all of BPA leaches out of a 20 μm microplastic, only around 300 days are needed for that releases from a 10 μm epoxy particle. Two years required for TBP leaches completely from a 100 μm epoxy microplastic while it only needs tens of days for it releases from smaller particles. As plastic particles become smaller and smaller by weathering or biodegradation, release times for additives decrease dramatically.

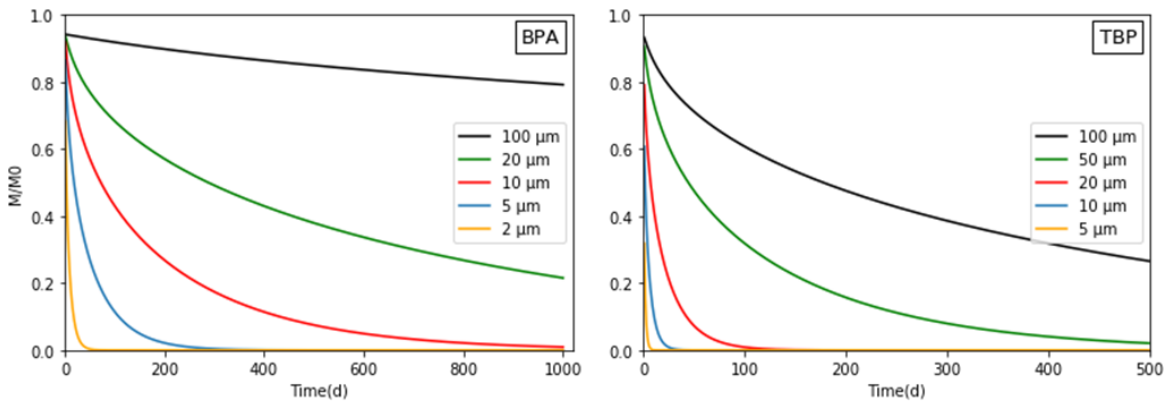
Half-life $t_{\frac{1}{2}}$ is the time required for a quantity release to half of the initial. In this study, $t_{\frac{1}{2}}$ was used to evaluate the release behavior of polymer additives, which is the required time for mass fraction $F = \frac{M}{M_{\infty}} = \frac{1}{2}$.

Eq. (10) and (11) show that mass of additives remained inside plastics decreases exponentially, so the fraction $\frac{M}{M_{\infty}}$ controlled by the first few values of n . According to Crank (1975), Eq. (11) could be approximated to

$$t_{\frac{1}{2}} = -\frac{R^2}{\pi^2 D} \ln \left[\frac{\pi^2}{12} - \frac{1}{9} \left(\frac{\pi^2}{12} \right)^9 \right] = 0.022 \frac{R^2}{D} \quad (15)$$

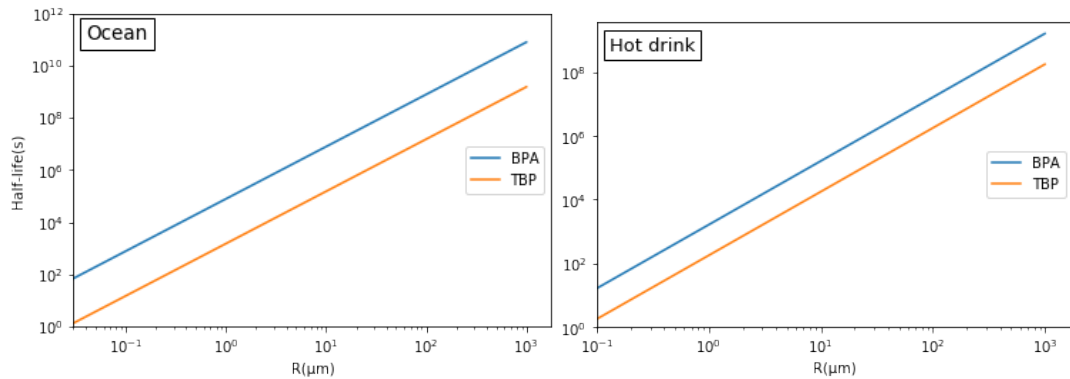
Simulations of release kinetics for BPA and TBP under different scenarios are shown as Figures 7. The temperature of the ocean environment is assumed 17°C and that of hot drinks is 85°C. The required time for half amount of BPA leach out of epoxy

particles in ocean ranges from 3000 years to several minutes and from 30 years to several seconds for TBP as the radius of microplastics reduces from 1mm to 100 nm. These results also indicate that the further degradation of microplastics to nanoplastics will facilitate the release process significantly. In this way, the risk of leaching additives from microplastics is much higher than that of bulk plastics.



Figures 6: Simulations of BPA and TBP leaching from MPs with various sizes.

The remaining mass fraction over time for BPA and TBP leaching from epoxy microplastics at 25°C for various radiuses of plastics



Figures 7: Simulation of particle size affecting leach process in the ocean & hot drinks.

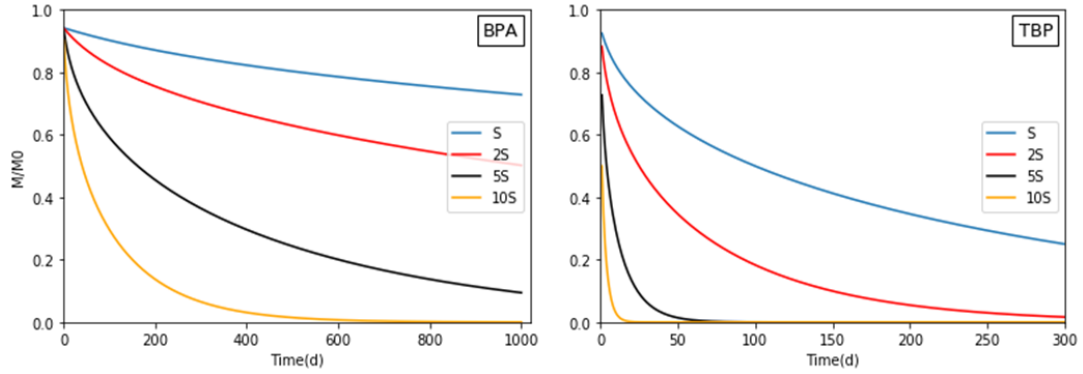
Half-life of BPA and TBP releasing from marine epoxy microplastics with various sizes
(temperature at 17 °C for the ocean, at 85 C° for hot drinks)

3.3.2.2 Particle surface area

As most MPs are secondary products, which are from larger plastics breakdown by various processes, the irregular shape of them can be distinguished from primary MPs. Rough surfaces of microplastics also contribute higher surface area to volume ratios except for their smaller sizes. Quantify the impact of specific surface area on the release half-life of additives from microplastics is helpful when assessing the risk of released additives. Characterization methods such as BET (Brunauer, Emmett and Teller) can provide accurate data of specific surface area to risk assessment. Fourier number was used to derive this problem as below. Therefore, Eq. (17) could be used to simulate the effect of irregular shapes as Figures 8 shown. The exponential rises of release rates for BPA and TBP with larger specific surface areas are evidently. This result combines with the effect of particle size confirm that the breakdown of bulk plastics will significantly accelerate additives' release process so that increase the risk of MPs acting as the source of contaminants.

$$Fo_1 = \frac{Dt_1}{\left(\frac{V}{S_1}\right)^2} = \frac{Dt_1}{\left(\frac{V}{S_2} \cdot \frac{S_2}{S_1}\right)^2} = \frac{Dt_1}{\left(\frac{V}{S_2}\right)^2} \cdot \left(\frac{S_1}{S_2}\right)^2 = Fo_2 = \frac{Dt_2}{\left(\frac{V}{S_2}\right)^2} \quad (16)$$

$$t_2 = t_1 \left(\frac{S_1}{S_2}\right)^2 \quad (17)$$



Figures 8: Simulations of BPA and TBP leaching from MPs with irregular shapes.

BPA and TBP release from epoxy microplastics of 75 μm radius with various specific surface area at room temperature.

3.3.3 Effect of temperature

The Arrhenius equation demonstrated the relationship of reaction rate constants and temperature, it can also be applied to describe the temperature depended diffusion coefficient as Eq. (18) shown.

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (18)$$

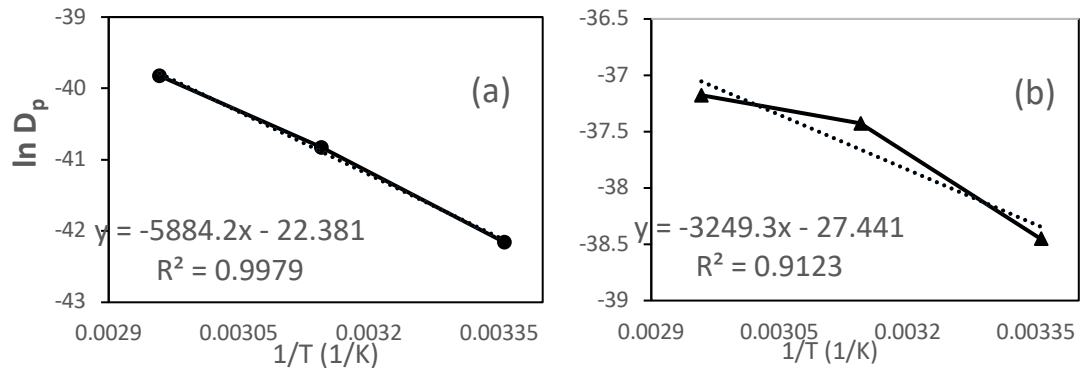
$$\ln \frac{D_{p1}}{D_{p2}} = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (19)$$

Where D_0 is a pre-exponential factor (m^2/s); E_a is the apparent activation energy of the diffusion process (J/mol); R is the ideal gas constant 8.314 ($\text{J}/\text{mol}\cdot\text{K}^{-1}$); T is the absolute temperature (K). Figures 8 show the Arrhenius plot of the diffusion coefficients of BPA and TBP in epoxy microplastics. The great linearity between $\text{Log } D_p$ and $1/T$ reveals that the temperature dependence of diffusion processes of these two chemicals

inside epoxy governed by the Arrhenius equation. Therefore, the apparent activation energy E_a could be deviated based on Eq. (19). By plotting the natural logarithm of D_p and the reciprocal of absolute temperature, the slope would be the quotient of E_a and R . Calculated apparent activation energy of BPA and TBP diffusing in the epoxy matrix are 48.9 kJ/mol and 27.0 kJ/mol, respectively. The lower E_a of TBP than BPA can be explained by Sun et al. (2016)'s conclusion on the molecular size dependence of additives' diffusion and the existence of partial chemically-bound BPA. Yet these results are much lower than that in Mercea's report (2018). The loss of additives might contribute to low apparent activated energies. The other explanation is the different roles of BPA and TBP in epoxy resins. Other than acting as additives, BPA and TBP are the monomers and constituent molecules of epoxy. Free residual monomers might be generated during polymerization and leach out of polymer matrix into the surroundings. Fragmentation processes of plastic particles also include physical ways (mechanically damage, turbulences, etc.), chemically ways (hydrolysis, oxidation, etc.) and biodegradation. The breakdown of polymer long chains generates more monomers leach out easily than additives, and therefore, leads to relatively lower apparent activated energies.

Figures 10 show simulations of release processes of BPA and TBP from epoxy microplastics with a radius of 75 μm at various temperatures based on the calculation of experimental data. Evidently, high-temperature environment facilitates additives' release from plastic debris. Yet the increase of release rate in the region from 65°C to 45°C is less than that from 25°C to 45°C. Except loss of adsorbed additives, the approaching to

glass transition temperature T_g of epoxy might also be the reason. The latter leads to changes in plastics' properties and the affinity of additives, which result in a change of Biot number. Besides, higher temperature facilitates the hydrolysis of additives, which causes more mass loss than cooler aqueous environment.

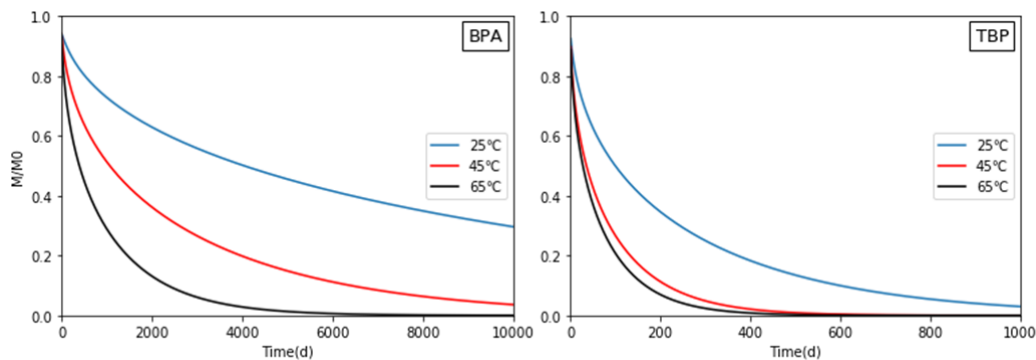


Figures 9: Temperature dependence of release behaviors.

Arrhenius plots the natural logarithm of diffusion coefficients ($\ln D_p$) and the reciprocal of temperature ($1/T$) for (a) BPA and (b) TBP leaching from epoxy microplastics.

As the temperature dependence of release behaviors of additives from microplastics governed by the Arrhenius equation, the half-life could be derivate from Eq. (18) as follows:

$$t_{\frac{1}{2}} = 0.022 \frac{DR^2}{\exp\left[\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]} \quad (20)$$



Figures 10: Simulations of BPA and TBP leaching from MPs at various temperature.

Leaching of BPA and TBP from epoxy microplastics with radius of 75 μm at 25 $^{\circ}\text{C}$, 45 $^{\circ}\text{C}$ and 65 $^{\circ}\text{C}$.

In this way, approximate simulations of the change of half-life with aqueous environmental temperature for BPA and TBP releasing from epoxy microplastics with a radius of 75 μm with the assumption of internal-controlled diffusion was draw by Python. According to Figure 11, it would take around 15 years for half amount of BPA leach out of epoxy microplastics in the ocean, 2.5 to 11 years in the tap water and 100 to 200 days in the hot drinks. Despite the long time of BPA requires to leach out, BPA-contained epoxy resins are widely used and the amount of BPA in epoxy resins is large. The risk of BPA exposure is high taking into account the fact that it has a reverse effect even at trace levels. Due to the high D_p , half-life for TBP is short. It ranges from 100 days in the ocean to only ten days in hot water. Since the persistence of TBP, even a small amount of it will accumulate along the food chain and might reach the peak in the human body. However,

such high-risk problem has not obtained enough focus and little research has conducted on TBP exposure.

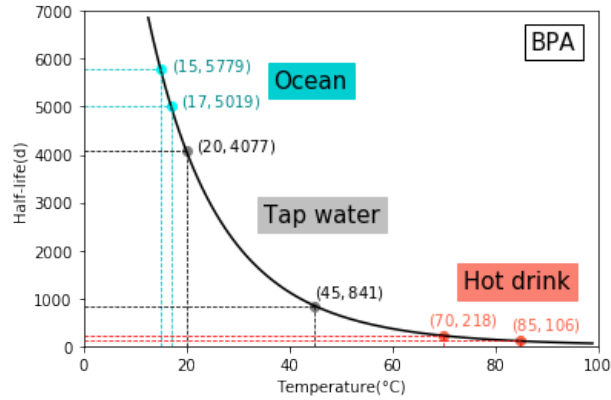


Figure 11: Simulation of the effect of temperatures on BPA release.

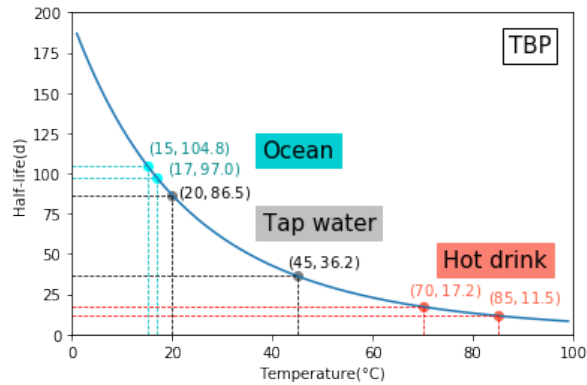


Figure 12: Simulation of the effect of temperatures on TBP release.

Despite the diffusion process obeys the Arrhenius equation, the impact of temperature is far more complicated. Glass transition temperature T_g is a critical feature for polymers. Polymers change from hard, glassy state to the softer, rubbery state at this temperature and the force for additive molecules to migrate gradually decreases as the temperature increases above the glass transition temperature. Rubbery polymers (PE and

PP) whose T_g s are lower than the room temperature (25 °C) are expected to have lower diffusion resistance than those glassy polymers (PVC and PET), which exist as solid-state. The affinity of polymers for additives also changes with the temperature. Hu et al. (2017), Crawford and Quinn (2017) found that the increased sorption of PAH and lubricating oil on polyethylene MPs with temperature, whereas Zhan et al. (2016) claimed the opposite trend of PCBs on polypropylene MPs. Besides, the temperature not only influence the properties of polymer materials, but also impact that of chemical additives. The above influence leads to the change in the Biot number and even the mechanism of release behaviors.

4. Conclusion

This study used diffusion mechanisms to model the migration of additives leach out of microplastics into the aqueous environment. It also summarized analytical solutions under three cases based on the ratio of internal to external mass transfer rate, Biot number. The internal diffusion model was applied to study releases of additives from epoxy microplastics. Leaching experiments were conducted to obtain essential parameter

diffusion coefficients of BPA and TBP, and D_p ranges from $10^{-13.3}$ to $10^{-14.3}$ cm^2/s and $10^{-12.1}$ to $10^{-12.7}$ cm^2/s at 25°C to 65°C , respectively. Considering the fact that MPs have various particle characteristics and they exist in different aqueous environments, the effects of factors have been simulated via applying leaching half-life of additives. Results revealed significant impacts of particle size and specific surface area on additives' release and relative half-life reduced remarkably. The temperature dependence of leaching behavior obeys the Arrhenius equation. Simulations confirmed a higher risk of additives releasing from microplastics than bulk plastics and further breakdown will facilitate this process. In addition, the weathering process and excessive temperature over T_g can make the problem extremely complex. The former might be regarded as a moving boundary problem, while the latter situation may be considered as a series of diffusion problems including concentration-dependent diffusion, non-Fickian transport and so on. Therefore, comprehensive studies are needed to deepen the understanding of this problem.

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