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Leaching of microplastic-associated additives in a quatic environments: A critical review $\overset{\bigstar}{}$



Anh T.Ngoc Do, Yeonjeong Ha, Jung-Hwan Kwon

Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea

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ABSTRACT

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Microplastic pollution has attracted significant attention as an emerging global environmental problem. One of the most important issues with microplastics is the leaching of harmful additives. This review summarizes the recent advances in the understanding of the leaching phenomena in the context of the phase equilibrium between microplastics and water, and the release kinetics. Organic additives, which are widely used in plastic products, have been introduced because they have diverse physicochemical properties and mass fractions in plastics. Many theoretical and empirical models have been utilized in laboratory and field studies. However, the partition or distribution constant between microplastics and water (K_p) and the diffusivity of an additive in microplastics (D) are the two key properties explaining the leaching equilibrium and kinetics of hydrophobic organic additives. Because microplastics in aquatic environments undergo dynamic weathering, leaching of organic additives with high K_p and/or low D cannot be described by a leaching model that only considers microplastic and water phases with a fixed boundary. Surface modifications of microplastics as well as biofilms colonizing microplastic surfaces can alter the leaching equilibrium and kinetics and transform additives. Further studies on the release of hydrophobic organic additives and their transformation products under various conditions are required to extend our understanding of the environmental fate and transport of these additives in aquatic environments.

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1. Introduction

Plastic pollution poses a global environmental threat to aquatic ecosystems (Barnes et al., 2009). From the mid-1950s, plastic production increased exponentially (Rebelein et al., 2021) and massive amounts of plastic waste ultimately entered in the oceans, accounting for approximately 10% of the global total plastic waste (Andrady, 2011). Once in the aquatic environment, plastic debris undergoes degradation, producing smaller pieces (<5 mm) called microplastics (MPs) (Galloway

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* Corresponding author.

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and Lewis, 2016). The environmental half-lives of thermoplastics were estimated to be years to thousand years depending on type of plastic as well as the surrounding environment (Chamas et al., 2020). Although plastic degradation is an extremely slow process, approximately 90% of plastic debris becomes MPs in the aquatic environment (Barnes et al., 2009; Paluselli et al., 2018; Suaria et al., 2016). As aquatic organisms are exposed to MPs, they may accumulate in the body (da Silva et al., 2022; Li et al., 2021; Zhang et al., 2020); hence, microplastic pollution in aquatic environments is an important concern.

Plastic products usually contain additives such as plasticizers, flame retardants, photostabilizers, antioxidants, and pigments (Stevens, 1990). These additives are intentionally added into polymers at different concentrations during production (0.1–70 wt%) to maintain or enhance their properties (Hahladakis et al., 2018). Many additives are included in diverse plastic products; consequently, the production of plastic additives increases with increasing plastic production (Aurisano et al., 2021; Pfaendner, 2006). Many of these organic additives are hazardous and have been documented as being carcinogenic, mutagenic, or endocrine disruptors to aquatic organisms (Groh et al., 2019). Some of them are listed as substances of very high concern by the European

E-mail address: junghwankwon@korea.ac.kr (J.-H. Kwon).

Abbreviations		LDPE – POM –	low-density polyethylene
MPs –	microplastics	PDMS –	polydimethylsiloxane
ECHA –	European Chemical Agency	HDPE –	high-density PE
HOCs –	hydrophobic organic chemicals	pp-LFER	 poly parameter linear free energy relationships
PHs –	petroleum hydrocarbons	D-R mod	el – Dubinin–Radushkevich model
PBDEs -	polybrominated diphenyl ethers	PAHs –	polycyclic aromatic hydrocarbons
DEHP –	di-2-ethylhexyl phthalate	DHM –	dissolved humic matter
PVC –	polyvinyl chloride	BFRs –	brominated flame retardants
DEP –	diethyl phthalate	ABS –	acrylonitrile-butadiene-styrene copolymer
DBP –	di-n-butyl phthalate	BHT –	2,6-di- <i>tert</i> -butyl-p-cresol
PET –	polyethylene terephthalate	IPD	intra-particle diffusion model
PA –	polyamides	BLD	boundary layer diffusion model
PE –	polyethylene	PCBs	polychlorinated biphenyls
PP –	polypropylene	EPS	extracellular polymeric substances

Chemical Agency (ECHA) or persistent organic pollutants under the Stockholm Convention (Gunaalan et al., 2020; Wagner and Schlummer, 2020). Because plastic additives are not covalently bonded to the polymer matrix, they can leach out into the surrounding media (Kwan and Takada, 2016; Teuten et al., 2009). Although many studies have reported the occurrence of plastic additives in aquatic systems (Gunaalan et al., 2020; Luo et al., 2019; Zeng et al., 2008) and the environmental load of widely used additives was assessed (De Frond et al., 2019), the processes involved in the liberation of additives from the plastic matrix and their distribution in the environmental media are not clearly understood yet.

If there is no transformation of additives and plastics do not degrade, the release of plastic additives into the aquatic environment is interpreted using phase equilibrium and transfer kinetics. Three key processes are diffusion within the plastic phase, partitioning at the plasticadjacent medium interface, and diffusion in the aqueous boundary layer (Fig. 1) (Cheng et al., 2020; Kwon et al., 2017). Indeed, the equilibrium distribution of hydrophobic organic chemicals (HOCs) between various plastic materials and water has been evaluated using several sorption isotherms (e.g., linear, Langmuir, and Freundlich equations), mostly focusing on the sorption/desorption of chemical contaminants from the environment to MPs. For instance, the sorption of triclosan (Tong et al., 2021), several pharmaceuticals (Razanajatovo et al., 2018), petroleum hydrocarbons (PHs) (Hüffer and Hofmann, 2016; Song et al., 2021), and brominated organic compounds, such as polybrominated diphenyl ethers (PBDEs) (Xu et al., 2019) on MPs have been reported. It is also important to understand the mass transfer kinetics of chemical contaminants between plastics and water. Empirical equations have been utilized, such as pseudo-first order and pseudo-second order equations, assuming the sorption on the active sites in MPs as the controlling step of



Fig. 1. Schematic illustration of the leaching of plastic additives in the aquatic environment.

the overall process (Liu et al., 2018; Razanajatovo et al., 2018; Song et al., 2021; Tong et al., 2021; Wang and Wang, 2018). In contrast, more theoretical diffusion models for the transfer considering both intraparticle and external diffusion of HOCs have also been employed to explain the release of HOCs from MPs (Blanco et al., 2017; Endo et al., 2013; Guo et al., 2020; Lee et al., 2018; Seidensticker et al., 2017).

Because the values of the chemical properties of organic additives, such as molar liquid volume and 1-octanol-water partition constant (Kow), have wide ranges, the applicability of empirical and diffusionbased theoretical models has not been rigorously evaluated, especially for emerging additives such as photostabilizers and antioxidants. If the leaching time scale of these additives is very long, it is necessary to consider the complex interactions of MP surfaces with biota and organic matter (Hartmann et al., 2017; Koelmans et al., 2016). This adds an additional layer that may accelerate or retard the release of additives from MPs. Another important factor that should be considered is the degradation or weathering of MPs. Plastic surfaces become more hydrophilic as they undergo weathering, and the surface modification changes the distribution of HOCs between MPs and water at the interface, affecting the overall leaching rate (Gewert et al., 2015; Liu et al., 2020; Sun et al., 2020). Breakage of (micro)plastics to smaller particles would accelerate the leaching of extremely hydrophobic additives, for which the leaching half-life is estimated to be very long (Gewert et al., 2015; Sun et al., 2019, 2020).

The aims of this review are (1) to summarize recent experimental and theoretical studies on the distribution of HOCs between MPs and water and the leaching kinetics of additives from MPs, (2) to compare existing models used for distribution equilibrium and release kinetics, and (3) to propose future research prospects for the leaching of hydrophobic plastic additives for which simple diffusion models are not appropriate. Specifically, recent experimental studies on equilibrium sorption, desorption, and partitioning of diverse HOCs were reviewed with models explaining the phenomena. Empirical and diffusion-based theoretical models employed for plastic additives are summarized and compared. The review also discusses how the release of additives is affected by the association of MPs with organic biofilm and plastic weathering. Finally, directions for future research to elucidate the environmental fate of hydrophobic plastic additives are proposed.

2. Organic plastic additives

Many organic additives are intentionally mixed with polymers during the manufacturing process to maintain or enhance the physical and chemical properties of plastics. The major families of organic plastic additives are plasticizers, flame retardants, photostabilizers, antioxidants, and pigments. The total amount of global plastic additive production was approximately 20 Mt in 2019, and the projected production volume will reach 2000 Mt by the end of 2050 (Aurisano et al., 2021; Gever et al., 2017). The purposes and properties of typical organic additives are presented in Table S1, Supplementary Material. The weight fraction of plastic additives may vary from up to 70% for plasticizers, up to 25% for flame retardants, and 0.1-3% for antioxidants and photostabilizers (Hahladakis et al., 2018). The type of additive depends on the plastic material and the performance of the products (Hahladakis et al., 2018; Hermabessiere et al., 2017). For instance, plasticizers such as di-2-ethylhexyl phthalate (DEHP) are the most commonly used in polyvinyl chloride (PVC) to improve flexibility. Plasticizers, including di-n-propyl phthalate, diethyl phthalate (DEP), and di-n-butyl phthalate (DBP) are also added in polyethylene terephthalate (PET). Flame-retarded polyamides (PA) and polyesters are used in electronic applications and insulation foams, while photostabilizers and antioxidants are employed in many synthetic polymers, including polyolefins (polyethylene (PE) and polypropylene (PP)). In addition, pigments are used in a wide range of plastics, while most slip agents are used in polyolefins, and antimicrobial substances are added to PVC, polyurethane, PE, or polyester. Because most organic plastic additives are lipophilic with a wide range of log K_{ow} values, they can penetrate cell membranes and induce toxic effects in aqueous organisms (Table S1, Supplementary Material). Although many highly hydrophobic and low-solubility plastic additives have been reported in the literature (Kwon et al., 2017), experimental data are lacking in their environmental partitioning, metabolic transformation, and biodegradation.

3. Leaching equilibrium

To understand the leaching of plastic additives and chemicals sorbed to MPs, the equilibrium distribution of HOCs between MPs and water has been evaluated under controlled laboratory conditions (Bakir et al., 2012; Chen et al., 2021; Do et al., 2022; Guo et al., 2018; Hüffer and Hofmann, 2016; Liu et al., 2019a; Liu et al., 2018; Razanajatovo et al., 2018; Seidensticker et al., 2019; Song et al., 2021; Teuten et al., 2007; Tong et al., 2021; Wang and Wang, 2018; Wang et al., 2018; Yao et al., 2021; Zhan et al., 2016), which are described in detail in section 3.1. The distribution of chemicals between solid phase (e.g., plastics) and water is often described by assuming linear partitioning or non-linear sorption isotherms (Schwarzenbach et al., 2016). The distribution constant between plastic and water (K_p), defined as the ratio of the concentration in the plastic phase (C_p) to that in water (C_w) at equilibrium, obtained in those studies explained the strong sorption capacity of MPs toward HOCs and can also be used to determine the rate of chemical migration from (micro)plastics to the surrounding medium. If (micro)plastics are regarded as a homogeneous medium solubilizing small solute molecules, C_p should increase with increasing C_w, leading to K_p being independent of the concentration. Low-density polyethylene (LDPE) and other plastic materials have been used for the passive sampling of HOCs for decades (Lohmann, 2012) and their distribution between passive samplers and water is regarded as linear partitioning. However, non-linear behavior between C_p and C_w could be expected when the plastic medium is not homogeneous, as they may contain glassy or rubbery parts with potential modification at the plastic surfaces (Velez et al., 2018) (Fig. 1).

3.1. Laboratory sorption/desorption studies

In the last decade, the sorption equilibrium of the HOCs between MPs and water has been extensively documented (Velez et al., 2018). In the linear sorption isotherm, K_p is a constant over the entire range of concentrations, whereas in nonlinear isotherms such as the Langmuir, Freundlich, and Temkin models, $K_{\rm p}$ depends on the concentration. For example, multiple studies have presented the linear sorption isotherms of tylosin on four different plastics (PE, PP, PS, and PVC) (Guo et al., 2018), DEP and DBP on PVC, PE, and PS (Liu et al., 2019a), sulfamethoxazole, propranolol, and sertraline on PE (Razanajatovo et al., 2018), PHs on PA, PE, PS, PLA, and PVC (Song et al., 2021), aliphatic and aromatic hydrocarbons on PE (Hüffer and Hofmann, 2016), triclosan (TCS) on polyhydroxybutyrate, and PE (Tong et al., 2021). These findings indicate that the sorption of these compounds was governed by partitioning between plastic material and water, dominated by hydrophobic sorption of HOCs. Absorption into the bulk polymer (e.g., the rubbery domain of PE) would explain the observed linear distribution of HOCs between MPs and water (Hüffer and Hofmann, 2016).

Non-linear sorption isotherms of HOCs onto MPs have also been documented in the literature (Tourinho et al., 2019). HOCs may sorb with different free energies of transfer to domains with different physicochemical properties. Thus, several nonlinear sorption isotherms were used to describe the observed results. The Langmuir (Liu et al., 2018; Wang and Wang, 2018; Wang et al., 2018; Zhan et al., 2016) and Freundlich isotherms (Bakir et al., 2012; Fan et al., 2021; Guo et al., 2018; Hüffer and Hofmann, 2016; Razanajatovo et al., 2018; Seidensticker et al., 2019; Song et al., 2021; Teuten et al., 2007; Tong et al., 2021; Zuo et al., 2019) were the most frequently applied. More complicated models based on different thermodynamic assumptions, such as Temkin (Chen et al., 2021; Wang and Wang, 2018; Wu et al., A.T.Ngoc Do et al.

2020), Polanly-Manes (Seidensticker et al., 2019), Dubinin-Radushkevich (Ma et al., 2019; Song et al., 2021; Wu et al., 2020), and Redlich-Petersen isotherm (Wang and Wang, 2018) have also been applied, and these mechanisms are discussed in Section 3.2.

The polymer matrix structure and the distance between polymer chains are important parameters that would be expected to directly result in the different sorption behaviors of HOCs to MPs. Polymers often consist of crystalline and amorphous regions. Depending on the glass transition temperature (T_g), amorphous regions can be rubber-like polymers or glass-like polymers (Stevens, 1990). In addition, the greater the distance between polymer chains, the faster the chemicals diffuse through the polymer matrix, resulting in a higher sorption capacity (Hartmann et al., 2017; Lee et al., 2014). The sorption isotherms of rubbery PE in batch sorption studies were generally linear within the

Table 1

Common sorption isotherm models based on microscopic viewpoint applied to evaluate sorption/desorption equilibrium between plastics and organic compounds in several surrounding media.

	Type of model	Equation	Description	Fitting parameters	References	
Sorption isotherm	Linear isotherm (Henry's isotherm)	$q_e = K_p C_e$	At low concentration $(C_e \rightarrow 0)$ Kp: the equilibriumthe sorption isotherm is a straight line, simulating a partitioning process.coefficient [L/g]		Guo et al. (2018); Liu et al. (2019a); Razanajatovo et al. (2018); Song et al. (2021); Tong et al. (2021); Yao et al. (2021); Zuo et al. (2019)	
	Langmuir $q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$ Describes the sorption isotherm process taking plac at specific homogeneous site within the adsorbent and occurs in a monolayer that covers the surface of the material.		Describes the sorption isotherm process taking place at specific homogeneous sites within the adsorbent and occurs in a monolayer that covers the surface of the material.	Q _{max} : maximum capacity [µg/ kg] K _L : Langmuir affinity coefficient [µg/L]	Liu et al. (2018); Wang and Wang (2018); Wang et al. (2018); Zhan et al. (2016)	
	Freundlich	$q_e = K_f C_e^{1/n}$	This empirical equation can be applied to non-ideal sorption on an energetically heterogeneous surface as well as multilayer sorption.	K _f : Freundlich affinity coefficient [(µg/kg)/(µg/L)] ^{1/} ⁿ n: Freundlich exponential coefficient [-]	Bakir et al. (2012); Fan et al. (2021); Guo et al. (2018); Hüffer and Hofmann (2016); Razanajatovo et al. (2018); Teuten et al. (2007); Tong et al. (2021); Zuo et al. (2019)	
	Brunauer-Emmett- Teller (BET)	$q_e = rac{q_{Bet}C_{Bet}C_e}{\left(C_e - C_s ight) + \left(1 + \left(C_{Bet} - 1 ight)rac{C_e}{C_s} ight)}$	The equation was used for submonolayer-to-multilayer vapor adsorption on a solid surface that are not highly heterogeneous.	<pre>q_{Bet}: the monolayer adsorption capacity of the adsorbent [mg/g] C_{Bet}: the energy of interaction with the surface [mL/mg] C_s: the adsorbate monolayer saturation concentration [mg/mL]</pre>	Fan et al. (2021)	
	Polanyi-Manes	$\log q_e = \log Q_m + a \left(rac{arepsilon_{SW}}{V_m} ight)^{ m d}$	Useful for both gas and aqueous adsorption on energetically heterogenous surface and applicable for pore filling and flat surface.	Q _m : maximum capacity [µg/ kg] a: fitting parameter d: fitting parameter	Hüffer and Hofmann (2016)	
	Temkin	$q_e = rac{RT}{b_T} \ln(a_T C)$	Often applied to describe the sorption on solid surfaces, assuming heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmically, with coverage.	b_T : Tempkin isotherm constant [J/mol] a_T : Tempkin isotherm constant [L/g]	Chen et al. (2021); Song et al. (2021); Wang and Wang (2018); Wu et al. (2020)	
	The Dubinin–Radushkevich	$q_e = q_s \exp(-B\epsilon^2)$	Sorption isotherm is related to the adsorption in micropores by pore-filling, rather than layer-by-layer surface coverage.	B: Dubinin–Radushkevich isotherm constant q_s : theoretical isotherm saturation capacity [µg/g]	Ma et al. (2019); Song et al. (2021); Wu et al. (2020)	
	Redlich-Petersen	$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}}$	Hybrid between the Langmuir and Freundlich equation. The equation can be applied for sorption isotherm over wide range.	K_R : Redlich–Peterson isotherm constant [L/g] α_R : Redlich-Petersen isotherm constant [L/µg] β : Redlich-Petersen isotherm exponent	Sørensen et al. (2020); Wang and Wang (2018)	
Desorption isotherm	Desorption hysteresis	$\mathrm{HI}=rac{q_e^t-q_e^s}{q_e^s}\Big _{\mathrm{T,Ce}}$	The desorption hysteresis indicates greater apparent affinity of adsorbate in the desorption than the sorption process.	HI: desorption hysteresis index	Song et al. (2021); Tong et al. (2021); Zuo et al. (2019)	

 q_e : equilibrium concentrations of contaminant(s) sorbed onto plastic [$\mu g/g$]; C_e : equilibrium concentrations of contaminant sorbed in the aqueous phase [$\mu g/L$]; ε_{sw} = RT ln (C_w/C_e) [kJ/mol]: effective sorption potential; V_m : molar volume [cm^3/mol]; R [8.314 × 10⁻³ kJ/molK]: universal gas constant; T [K]: absolute temperature; C_w : aqueous solubility [$\mu g/L$]. C: Proportional to the boundary layer thickness [$\mu g/g$]; ε : Dubinin–Radushkevich isotherm constant, q_e^d and q_e^s : equilibrium concentration of contaminant(s) sorbed onto plastic in the desorption and sorption experiments [$\mu g/g$]. range of aqueous concentrations investigated owing to its lower crystallinity compared to those of other glassy polymers (such as PS, PET, and PVC) (Hüffer and Hofmann, 2016; Liu et al., 2019b; Razanajatovo et al., 2018; Rochman et al., 2013; Seidensticker et al., 2019; Song et al., 2021; Tong et al., 2021; Wang and Wang, 2018). Hence, either the sorption mechanism is dominated by the partitioning of hydrophobic pollutants into a homogeneous polymer phase or the sorbed concentration in PE is sufficiently low and its strongest adsorption sites are far from saturated. A similar principle is applied to most polyethylene devices used as passive samplers (Lohmann, 2012). Single-phase polymeric samplers using LDPE have been widely used to assess trace concentrations of hydrophobic organic contaminants in aquatic and atmospheric environments (Adams et al., 2007; Fries and Zarfl, 2012; Hale et al., 2010; Lampert et al., 2015; Velzeboer et al., 2014). Other popular single-phase polymeric materials such as polyoxymethylene (POM) and silicone rubber, including polydimethylsiloxane (PDMS), have also been used as passive samplers (Cornelissen et al., 2008; Endo et al., 2011b; Lohmann, 2012; Ter Laak et al., 2008) or the passive dosing phase (Birch et al., 2019; Kramer et al., 2010; Kwon and Kwon, 2012; Kwon et al., 2011; Kwon et al., 2009; Mayer and Holmstrup, 2008), owing to the wide linear partitioning range.

Only a few studies have investigated the desorption isotherms of HOCs from MPs. Most of the HOCs investigated are not plastic additives such as triclosan (Chen et al., 2021; Tong et al., 2021), pharmaceuticals (Razanajatovo et al., 2018), phenanthrene (Zuo et al., 2019), and antibiotics (Fan et al., 2021). Although some studies have shown that desorption is not the exact reverse of adsorption (Zhang et al., 2019; Zuo et al., 2019) and desorption hysteresis (HI) was observed (Table 1) (Huang et al., 1997; Tong et al., 2021; Zhang et al., 2019; Zuo et al., 2019), it is unclear whether the initial distribution of these compounds in the MPs before the desorption experiments was homogeneous. Linear, Langmuir, and Freundlich isotherms were used to fit the desorption data of HOCs on MPs, and the values of HI were calculated using the fitting models (Song et al., 2021; Tong et al., 2021; Zuo et al., 2019). The desorption isotherm of HOCs depends on the specific relationship between HOCs and polymers and the properties of HOCs and plastics (Song et al., 2021). The desorption of triclosan, bisphenol A, and phenanthrene on PE was reported to be a reversible process, whereas the desorption of bisphenol A from PVC, PS, and PET was partially reversible (Liu et al., 2019b) and desorption hysteresis was observed for the desorption of phenanthrene from PS (Zuo et al., 2019). The differences among the different polymer materials were likely due to the rubbery and flexible structure of PE and the glassy structure of PVC, PS, and PET. However, Song et al. reported that the desorption isotherm of PHs on PA, PE, PS, PVA, and polylactic acid (PLA) was fully reversible (Song et al., 2021), leaving the question of the irreversibility between sorption and desorption of HOCs in plastics.

Although many desorption studies of HOCs from MPs attempted to assess the roles of MPs as a vector for HOCs, it is noteworthy that the mass distribution of those HOCs in plastics should be much smaller than those of other media (i.e., dissolved organic carbon, organic colloids, black carbon, and biota) (Gouin et al., 2011; Koelmans et al., 2016), limiting the role of MPs in transferring HOCs to the biota after the ingestion of MPs by organisms. In addition, strong sorption of HOCs by MPs would make non-digestible MPs a sink of HOCs, as they would be absorbed from the environment under most conditions (Bang et al., 2021; Koelmans et al., 2016; Liu et al., 2019b). However, the continuous leaching of hydrophobic additives from MPs might be considered an important transfer pathway in aquatic environments because of the strong fugacity gradient between MPs and the surrounding media (Gouin, 2021; Kwon et al., 2017). Therefore, further research on the desorption equilibrium for hydrophobic additives should be conducted rather than the sorption/desorption of HOCs that are not intentionally included in plastic products.

3.2. Mechanistic models for distribution between plastics and water

The equilibrium distribution of HOCs between plastics and water is determined by their chemical activity coefficients in both phases (Schwarzenbach et al., 2016). Traditionally, it has been described using a distribution constant (K_p), assuming that the HOC concentration sorbed to microplastics (C_p) increases linearly with aqueous concentration (C_w), at least within a range of C_w for trace HOCs, even for nonlinear sorption models. Both the experimental and estimated values of K_p have been reported in the literature (Endo and Koelmans, 2016). Although the experimental values of K_p of HOCs for various organic phases have been determined under laboratory and field conditions (Bakir et al., 2012; Lee et al., 2014; Lohmann, 2012; Rochman et al., 2013; Velzeboer et al., 2014), it is still challenging to obtain reliable estimates of K_p because of the low solubility of HOCs in water, resulting in a long experimental time to achieve phase equilibrium (Endo and Koelmans, 2016; Lee et al., 2014).

With limited experimental K_p data, quantitative mathematical models predicting K_p have been developed (Endo et al., 2011a; Endo and Goss, 2014; Lee et al., 2014; Lohmann, 2012). It should be noted that these predictive models assume pristine and pure polymers; thus, their applications to highly weathered microplastics should be limited. The simplest approach to estimate K_p is a simple log-log correlation with the octanol-water partition constant (K_{ow}) (Schwarzenbach et al., 2016):

$$\log K_{\rm p} = \alpha \log K_{\rm ow} + \beta \tag{1}$$

where coefficients α and β are empirically calibrated using the experimental K_p and K_{ow} values. The relationships between log K_p and log K_{ow} were linear for five plastic materials (LDPE, high-density PE (HDPE), PP, PVC, and PET) with polychlorinated biphenyls and polycyclic aromatic hydrocarbons (Rochman et al., 2013), indicating that LDPE and HDPE showed the highest sorption capacity, followed by PP, PET, and PVC. This simple model is very useful for estimating the K_p values for structurally similar HOCs to those used to obtain the regression coefficients.

More sophisticated approaches include multiparameter models such as polyparameter linear free energy relationships (pp-LFER), solvation models (e.g., SPARC), and quantum chemistry models (e.g., COSMOtherm) (Goss, 2011; Hilal et al., 2004). Even though pp-LFERs might become a convenient tool for estimating the log Kp of any neutral chemical irrespective of its chemical class, this method still depends on a limited set of measured (Abraham's) parameters for HOCs of interest (Lohmann, 2012). Both simple log Kp-log Kow correlations and pp-LFERs require empirical description and fitting coefficients, which are often not available for plastic materials frequently found in aquatic environments as MPs. COSMOtherm and SPARC only require the molecular structures of polymers and chemicals as inputs; therefore, these models can be used for any chemicals and sorbing phases. However, empirical models such as simple log Kp-log Kow correlations or pp-LFERs have been suggested for use because their prediction accuracy was better than that of COSMOtherm and SPARC, for chemicals that have similar molecular structures to the chemicals used for the training set in the establishment of log K_p-log K_{ow} or pp-LFERs models (Endo and Koelmans, 2016).

The sorption/desorption process between MPs and organic compounds depends on the properties of MPs, HOCs, and environmental factors (Mosca Angelucci and Tomei, 2020). As discussed in the literature, the interactions of HOCs and MPs are determined by the physicochemical properties of plastics, such as the ratio of crystalline to amorphous regions in the polymer, size and shape of the polymer segment, porosity of plastics, degree of cross-linking, and Tg (Endo and Koelmans, 2016; Fred-Ahmadu et al., 2020; Mei et al., 2020; Velez et al., 2018). For example, five MPs (HDPE, LDPE, PP, PET and PVC) was deployed for 12 months in the ocean water to evaluate sorption of PAHs and PCBs, showing that the sorption capacity of PET and PVC reached to equilibrium faster than HDPE, LDPE and PP due to smaller surface area and higher degree of crystallinity (Rochman et al., 2013). However, the sorbed concentrations of PAHs and PCBs to HDPE, LDPE and PP were higher than those to PET and PVC, owing to the differences in T_g (PE: -120 °C, PP: -10 °C, PET: 70 °C, and PVC: 90 °C) (Hiemenz and Lodge, 2007). The intrinsic characteristics of HOCs are also important in sorption/desorption processes (Fred-Ahmadu et al., 2020). The simplest model (Eq. (1)) indicates that hydrophobicity, as represented by K_{ow}, is often regarded as the driving force for the sorption of many HOCs (Guo et al., 2012; Razanajatovo et al., 2018; Wang et al., 2015). The speciation of an organic chemical should be considered because the pH of the contacting solutions determines the charge state of the weak acid or base substances. Moreover, external factors of the surrounding medium, such as pH, dissolved organic matter, salinity, and temperature may alter the properties of MPs as well as the speciation of the chemicals (Wang et al., 2020).

To explain the observed distribution of HOCs between MPs and water, different empirical models have been used to describe the sorption of HOCs from the liquid phase to the MP phase (Table 1). The general mechanisms of these models are briefly described below (Alberti et al., 2012; Chiou, 2003; Hu and Zhang et al., 2019; Atkins et al., 2017; Piccin et al., 2011; Salvestrini et al., 2014; Schwarzenbach et al., 2016).

The linear isotherm is the simplest model which considers the ratio between the concentration of the chemical remaining in solution and sorbed to the solid phase as constant at any concentration. It is also known as Henry's equilibrium and presupposes that at low concentrations, the sorption isotherm is a straight line. The parameter K_p derived from the linear model can be used to describe the sorption capacity of MPs, which depends on the interaction of HOCs and MPs, such as the formation of hydrogen bonds between the sorbate and MPs (Song et al., 2021), strong π - π interactions between the benzene rings of HOCs and PS (Liu et al., 2019a; Song et al., 2021), or hydrophobic interactions (Liu et al., 2019a; Razanajatovo et al., 2018). In addition, the degree of crystallinity of plastic also affects the sorption capacity when linear sorption on PE with its low crystallinity was often observed in fitting by the linear isotherm (Guo et al., 2018; Hüffer and Hofmann, 2016; Razanajatovo et al., 2018; Tong et al., 2021). Therefore, the linear sorption isotherm can be used to explain partitioning into a bulk polymer (absorption) or adsorption onto a polymer surface. If the mass fraction of hydrophobic additives is low (Hahladakis et al., 2018; Kwon et al., 2017), this is a good approximation for many additives. As a proof of this principle, Do et al. (2022) showed that chemical activities of selected UV stabilizers in PE, PP, and PET increased linearly with increasing mass fraction in plastics when it is typically lower than a few percent.

The Langmuir isotherm is obtained based on the assumption that sorption cannot proceed beyond monolayer coverage, and all sorption sites on the surface are equivalent. Although the Langmuir model agrees well with some studies on the sorption of 3,3',4,4'-tetrachlorobiphenyl (PCB77) on PP (Zhan et al., 2016), pyrene (Pyr) on PE, PS, and PVC (Wang and Wang, 2018), tris-(2,3-dibromopropyl), and hexabromocyclododecanes on PP (Liu et al., 2018), its applicability to the distribution of HOCs between microplastics and water is doubtful, without proof of the saturation of the sorption sites for HOCs in microplastics. The Brunauer-Emmett-Teller (BET) model, extending the Langmuir isotherm to multiple layers, was applied to the sorption of chlortetracycline and amoxicillin on original and aged tire wear particles (TWP) and PE (Fan et al., 2021). However, this model was not the best fit model in their study, likely due to the high heterogeneity of the MP surface after aging treatment caused the surface of TWP and PE to become rough with numerous tiny and deep holes (Fan et al., 2021).

The Freundlich isotherm can be applied to non-ideal sorption onto heterogeneous surfaces, as well as multilayer sorption. Multiple sorption sites with different free energies of transfer and site abundance acted in parallel. Some sorption isotherms fitted well with the empirical Freundlich model of HOCs listed in Section 3.1, indicating the heterogeneity of the surface and the exponential distribution of the sites and their energies (Guo et al., 2018; Razanajatovo et al., 2018). The Polanyi-Manes model has long been recognized as the most powerful model for dealing with sorption on energetically heterogeneous solids. Theoretically, the model considers that for a molecule located within the attractive force field of a microporous solid, there exists an (attractive) sorption potential (ε) between the molecule and the solid surface. This attraction derives from the induced dipole–induced dipole force (i.e., the London force) of the molecule and the surface atoms. The potential ε at a particular location within the sorption space may be viewed as the energy required to remove the molecule from that location to a point outside the attractive force field of the solid. Thus, the magnitude of ε for an adsorbate depends on its proximity to the solid surface. It is highest in the narrowest pore (or in the narrowest portion of a pore) because the sorbate is close to a more solid material. The model was used to describe the sorption of phenanthrene onto PS and PA because of the increasing presence of pores (Seidensticker et al., 2019).

The Temkin model assumes that the most energetically favorable sites are occupied first. The Temkin isotherm constant a_{τ} and the parameter related to the heat of sorption b_{τ} (J/mol) indicates that the sorption heat of all molecules decreases linearly with an increase in the coverage of the sorbent surface. The Temkin model is a modification of the Langmuir model, assuming that the enthalpy of sorption is independent of surface coverage. The sorption isotherm of TCS onto PE and PS was best fitted with the Temkin model (Chen et al., 2021). The model was also the most applicable for the sorption isotherm of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) onto aged PS under seawater soaking and UV irradiation conditions for 90 days (Wu et al., 2020). However, the Temkin model was not suitable for the sorption of Pyr on PE, PS, and PVC (Wang and Wang, 2018) or PHs onto PLA, PA, PE, PET, PS, and PVC (Song et al., 2021).

The Dubinin–Radushkevich (D-R) model considers the sorbent size as comparable to the micropore size, and the sorption equilibrium relation for a given sorbate-sorbent combination can be expressed independently of temperature using the sorption potential (ε). The D-R model fitted well with the experimental data of the sorption of PHs on PLA, PA, PE, PET, PS, and PVC (Song et al., 2021) and TCS on PVCs (Ma et al., 2019). To differentiate the physical and chemical sorption mechanisms, the mean energy of the sorption values (E) from the D-R model was used (Ma et al., 2019; Song et al., 2021; Wu et al., 2020).

The Redlich-Peterson model incorporates the features of both the Langmuir and Freundlich models, which can be applied in either homogeneous or heterogeneous systems owing to its versatility. It is suitable for both combined bulk partitioning and surface adsorption at low concentrations (Sørensen et al., 2020). The model was generally the most applicable for the sorption of polycyclic aromatic hydrocarbons (PAHs) on PE and PS in small size (10 μ m) at 20 °C (Sørensen et al., 2020), suggesting that the multilayer sorption was dominant at higher PAH concentrations. As the concentrations of PAHs used in the study were much greater than the range of typical environmental concentrations, this could be approximated to the linear sorption isotherm at environmentally relevant PAH concentrations.

The nature of microplastic materials, especially after environmental weathering, is not very well understood and may contain highly heterogeneous domains. Nonlinear sorption isotherms can better explain the distribution of HOCs between microplastics and water, especially at high aqueous concentrations, as demonstrated in many studies (Chen et al., 2021; Fan et al., 2021; Ma et al., 2019; Mei et al., 2020; Velez et al., 2018). However, typical environmental concentrations of HOCs are generally much lower than the range of concentrations investigated in laboratory batch sorption experiments (Sørensen et al., 2020; Velez et al., 2018). Therefore, the linear isotherm could be the simplest, but it provides reasonable estimates of K_p . It should be also noted that only limited studies evaluated the equilibrium distribution of plastic additives between microplastics and water (Al-Odaini et al., 2015; Cole et al., 2019; Luo et al., 2019). Because the mass fraction of plastic additives is often very high in plastics, a nonlinear distribution between

microplastics and water may be expected, and further investigations are required on the equilibrium distribution of plastic additives at their typical mass fractions in various plastic products.

4. Kinetic models of leaching

4.1. Empirical kinetic models

Because common plastic additives are not chemically bound to the plastic matrix, they can be freely released from the matrix. Thus, various additives have been found in aquatic environments. Several empirical kinetic models are applied to elucidate the leaching kinetics of chemicals from solid matrices (e.g., zero-order, first-order, second-order, and Weibull equations), and these equations are well summarized in Cheng et al. (2020).

Recent studies have utilized empirical kinetic equations to describe the leaching of additives from plastics to different media such as distilled water, water in the presence of dissolved humic matter (DHM), and gastric and gastrointestinal fluids. Choi et al. (2009) investigated the leaching of PBDEs from pre-molded plastic used for TV covers (black-colored high-impact polystyrene pellets) to both distilled water and DHM solutions. They reported that lower brominated compounds were rarely detected in distilled water even after 20 days; however, octa-, nona-, and deca-BDEs were detected in distilled water and their proportion increased with increasing leaching time. In contrast to distilled water, most compounds leached out into the DHM solution. The plot of leaching concentrations of octa-, nona, and deca-BDEs fit well with the first-order kinetic model (Table 2). The first-order rate constants (k1) of octa-, nona-, and deca-brominated diphenyl ethers in distilled water were not significantly different from those in the DHM solution. However, the maximum concentration of leaching into DHM solution was more than one order of magnitude higher than leaching to distilled water for all three compounds, showing that DHM enhanced the solubility of highly hydrophobic PBDEs.

Guo et al. (2020) investigated the leaching kinetics of brominated flame retardants (BFRs) from acrylonitrile-butadiene-styrene copolymer (ABS) plastics of different sizes ($100 \ \mu m - 2 \ mm$) to gastrointestinal and gastric fluids. They reported that the second-order empirical kinetic

equation is the best fit for the observed leaching kinetics of BFRs, and the second-order rated constants (k_2) are summarized in Table 2. The k_2 values decreased with increasing K_{ow} of BFRs, indicating that more hydrophobic BFRs leach out slower. In addition, k_2 increased with decreasing ABS size because the small plastics have a higher contact area with the medium, which can enhance the leaching of chemicals. There was no significant difference in the leaching rate of BFRs between the gastrointestinal and gastric fluids.

The Weibull model was also applied to describe the leaching of the antioxidant 2,6-di-*tert*-butyl-*p*-cresol (BHT) from HDPEs into lipid food simulants, with different initial concentrations of BHT in the plastics. The experimental data fit well with the Weibull model, with r^2 greater than 0.90, and the kinetic parameter (τ) decreased with increasing initial BHT concentration (Haitao et al., 2015). The Weibull model is considered as an alternative model to the diffusion model, especially for describing the migration of additive compounds from packing materials to foods. However, only a few studies have applied the Weibull model to fit the leaching kinetics of plastic additives (Pocas et al., 2012; Till et al., 1982). Thus, further studies are required to investigate the validity of the Weibull model for swellable microplastics containing various additives.

4.2. Diffusion models

The desorption kinetics of additives from microplastics to environmental media have been traditionally explained by diffusion models based on Fick's second law. Leaching can be divided into two processes: (1) internal diffusion within microplastics and (2) transport from microplastics to environmental media through the medium boundary layer. An instantaneous equilibrium at the MP-water interface is often assumed. Depending on the rate-determining step of the overall process, three models can be used to describe the leaching process: (1) an intraparticle diffusion (IPD) model when internal diffusion is much slower than the diffusion through the boundary layer of the environmental medium, (2) a boundary layer diffusion model (BLD) when internal diffusion is relatively fast and diffusion through the environmental media is much slower, and (3) a model considering both IPD and BLD when both the processes significantly affect the overall diffusion

Table 2

Empirical kinetic models applied for the leaching of additives from microplastics.

Type of model	Equation	Microplastic	Additive	Kinetic parame	eter		Reference
First- order	$C = C_m(1 - e^{-k_1 t})$ C: leaching concentration (µg/L) C _m : the maximum concentration that can be leached out after an infinite time (µg/L) k: rate coefficient (h ⁻¹)	Black-colored high impact polystyrene pellets	Brominated flame retardants	k ₁ (h ⁻¹) 8 BDEs ^a 9 BDEs 10 BDEs	Distilled water 0.0098 0.0054 0.0048	DHM (Dissolved humic matter solution) 0.0038 0.0056 0.0054	Choi et al. (2009)
Second- order	$\begin{split} &1/(C_e-C)=1/C_e+k_2t\\ &C: \text{ leaching concentration }(\mu g/L)\\ &C_{e^{*}}\text{ equilibrium concentration }(\mu g/L) k_2\text{:}\\ &\text{ rate coefficient }((\mu g \ L^{-1})^{-1}h^{-1/2}) \end{split}$	Acrylonitrile- butadiene-styrene copolymer (ABS)	Brominated flame retardants	$\begin{array}{c} k_2 \left((\mu g \\ L^{-1} \right)^{-1} h^{-1/2} \right) \\ BDE153 \\ BDE183 \\ BDE197 \\ BDE207 \\ BDE207 \\ BDE209 \\ BTBPE^b \\ DBDPE^c \\ \end{array}$	Gastrointestinal fluid 0.291-2.502 0.036-0.261 0.088-1.300 0.123-0.320 0.001-0.007 0.012-0.598 0.011-0.024	Gastric fluid 0.006-0.417 0.001-0.323 0.002-2.083 0.004-3.611 0.003-0.004 0.005-0.453 0.004-1.062	Guo et al. (2020)
Weibull	$ \begin{array}{l} \displaystyle \frac{M_{F,t} - M_{F,\infty}}{M_{F,0} - M_{F,\infty}} = \exp \Big[- \left(\frac{t}{\tau} \right)^{\beta} \Big] \\ \displaystyle \mathrm{M}_{\mathrm{F},t}: \text{leaching mass at time t (mg)} \\ \displaystyle \mathrm{M}_{\mathrm{F},\infty}: \text{leaching mass after an infinite time (mg)} \\ \displaystyle \mathrm{M}_{\mathrm{F},0}: \text{leaching mass at initial time (mg)} \\ \displaystyle \mathrm{\tau}: \text{ system parameters (h)} \\ \displaystyle \mathbb{B}: \text{ shape parameters} \end{array} $	High density polyethylene (HDPE)	2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol (BHT)	τ (h) 9.65–21.20		B 0.280–1.040	Haitao et al. (2015)

^a BDEs: Brominated diphenyl ether.

^b BTBPE: 1,2-bts (2,4,6-tribromophenoxy)ethane.

^c DBDPE: Decabromodiphenyl ethane.

process. The equations for each model have been described in previous studies, which are also given below (Endo et al., 2013; Sun et al., 2019) for spherical microplastics.

model:
$$f_{desorbed}(t) = 1 - \frac{M_t}{M_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{\left(-n^2 \pi^2 t D_{MP}/r^2\right)}$$
 (2)

model:
$$f_{desorbed}(t) = 1 - \frac{M_t}{M_0} = 1 - \exp\left(-\frac{D_{Env}S_{MP}t}{\delta V_{MP}K_{MP/Env}}\right)$$
 (3)

where $f_{desorbed}(t)$ is the fraction of an additive leached from the microplastic during time t, M_t and M_0 are the masses of the additive in MPs at time t and zero, respectively; D_{MP} and D_{Env} are the diffusion coefficients of the additive in MPs and environmental media, respectively, r is the radius of the sphere, S_{MP} and V_{MP} are the surface area and volume of MPs, respectively, δ is the thickness of the boundary layer of the environmental media, and $K_{MP/Env}$ is the partitioning constant of the additive between MPs and environmental media.

Model considered both IPD and BLD predicts $f_{desorbed}(t)$ as follows:

$$f_{desorbed}(t) = 1 - \frac{M_t}{M_0} = 1 - \sum_{n=1}^{\infty} \frac{6B_i^2 \exp\left(-\beta_n^2 D_{MP} t r^{-2}\right)}{\beta_n^2 (\beta_n^2 + B_i (B_i - 1))}$$
(4)

where B_i is the mass transfer Biot number, which indicates the ratio of the rate transfer through the environmental media and molecular diffusion inside plastic, and β_n are the roots of

$$\beta_n \cot \beta_n + \beta_i - 1 = 0 \tag{5}$$

Equation (5) depends on the mass transfer Biot number (Bi) and can be simplified as a function of D_{MP} , r and t (the complete equations are summarized in Sun et al., 2019).

The rate-determining step of the overall diffusion process depends on the environmental media, type of plastic, and chemical properties of the additives. Endo et al. (2013) showed that the BLD model with a water boundary layer thickness of 30 µm fits well with leaching experiments of polychlorinated biphenyls (PCBs) from PE pellets to distilled water, whereas the IPD model fails to explain the observed leaching kinetics. This indicates that diffusion across the aqueous boundary layer controls the overall diffusion for highly HOCs, and the desorption half-lives of PCBs are estimated from 14 d to 210 years depending on the PCB congeners. Karapanagioti and Klontza (2008) also suggested that the apparent diffusion of phenanthrene from plastic pellets strongly depends on its K_p values, indicating that the transport from plastic to water is the rate-determining step (Karapanagioti and Klontza, 2008). However, Sun et al. (2019) reported that due to the slow diffusion coefficients (D) of BFRs in the microplastics $(10^{-28.30} \text{ m}^2 \text{s}^{-1} < \text{D} < 10^{-20.84} \text{ m}^2 \text{s}^{-1})$, IPD controls the overall transfer of BFRs from ABS MP pellets to water and the process is independent of the aqueous boundary layer. Furthermore, leaching of hydrophobic plastic additives can differ between various exposed media (Hartmann et al., 2017). For highly hydrophobic chemicals, diffusion via aqueous boundary layer (ABL) is expected to be rate-determining step (Endo et al., 2013). However, the leaching of plastic additives to aquatic environment could be accelerated by the enhanced solubility in ABL, lowering the mass transfer resistance (Kwon et al., 2009). These have been observed in the aqueous media containing dissolved organic matter, digestive fluids or stomach oil (Endo et al., 2013; Lee et al., 2019; Sun et al., 2021; Tanaka et al., 2015; Ter Laak et al., 2009; Teuten et al., 2009).

The diffusion models described in equations (2)–(4) assume a fixed boundary. However, the fixed boundary condition would not be satisfied when the leaching time scale is long, as was the case in Sun et al. (2019). The application of these theoretical diffusion models would be limited to the cases in which the diffusional release of additives is unaffected by (1) the development of biofilm on the MP-medium interface causing an additional mass transfer barrier, (2) the transformation reaction of additives, including conjugation, occurring at the MP surfaces, and (3) the weathering of MP surfaces due to physical, chemical, and biological stresses. However, these models are still useful for estimating the characteristic leaching time of hydrophobic additives. In the following section, we emphasize the potential roles of MP weathering on the release equilibrium and kinetics of plastic additives. However, it is noteworthy that the time scale of the leaching test in Sun et al. (2019) ranged from 50 to 200 d, which is longer than the time scale used by Endo et al. (2013) (1–128 days) and Karapanagioti and Klontza (2008) (1–164 days). Considering that ABS undergoes oxidation and chemical degradation faster than other plastic materials under environmental conditions (Kim et al., 2021; Ramani and Ranganathaiah, 2000), the leaching of BFRs from ABS may result not only from molecular diffusion, but also from ABS degradation. Thus, further studies on the effects of ABS degradation on leaching additives are required.

5. Weathering processes in the leaching kinetics of plastic additives

5.1. Role of biofilm formation on the leaching kinetics of plastic additives

Biofilms are layers of bacterial colonies that are wrapped by a matrix of extracellular polymeric substances (EPS), secreted by microorganisms that are irreversibly attached to the material surfaces (Luo et al., 2021). Microplastics are exposed to environmental conditions for a very long time and are generated from the breakage of larger plastic particles. Biofilms are prone to form on the surface of microplastics. In the early 2000s, many studies emphasized that the corona formation of nanoparticles via environmental factors such as microorganisms, proteins, and humic acid, significantly changed the surface properties of nanoparticles, resulting in reduced accessibility and toxicity of nanoparticles towards living organisms (Guarnieri et al., 2011; Ha et al., 2016; Lesniak et al., 2012). As an extension of those studies, recent studies have reported that the biofilm formation alters properties of nano/micro plastics especially surface properties such as surface charge, roughness and morphology (Johansen et al., 2019; Sun et al., 2020; Tarafdar et al., 2021). These changes inevitably alter the adsorption capacity of microplastics for HOCs and the leaching kinetics of plastic additives (Mosca Angelucci and Tomei, 2020; Rodrigues et al., 2019). However, to the best of our knowledge, there have been no experimental studies on the effects of biofilms on the leaching kinetics of plastic additives. Thus, here, we introduced plausible biofilm effects on the release of additives from microplastics.

First, biofilm formation can act as an additional mass transfer resistance, which slows down the leaching process of additives from microplastics. Wicke et al. (2008) showed that supported biofilms act as a barrier for chemical transport from or to MPs because the biofilm coverage slows down the mass transfer of hydrophobic organic chemicals and effective diffusion coefficients of PAHs in biofilms were estimated to be about 10^{-10} cm²s⁻¹, which was approximately four orders of magnitude lower than those in aqueous solution (~ 10^{-6} cm²s⁻¹) via sorption experiments using glass beads (Wicke et al., 2008).

On the other hand, biofilms can serve as reactive barriers that can accelerate leaching by increasing the polarity of additives. Microorganisms in biofilms degrade hydrophobic organic chemicals and produce metabolic biochemical substances (Mosca Angelucci and Tomei, 2020; Sun et al., 2020). For example, Cerniglia (1984) indicated that microorganisms have the ability to hydroxylate PAHs ranging from naphthalene to benzo [*a*]pyrene (Cerniglia, 1984). In addition, microbial degradation of PAHs can increase their bioavailability by increasing the hydrophilicity of the chemicals (Johnsen et al., 2005). The release of additives from microplastics can enhance microbial growth, because the additives can serve as a nutrient source. Thus, leaching additives can increase microbial activity and synthesize more metabolites of additives.

5.2. Effects of weathering processes on the leaching kinetics of plastic additives

Once in the aquatic environment, plastics break down and degrade from the exposed surfaces owing to external stresses such as UV light, mechanical forces, heat, chemical oxidation, or enzymatic attack by microbes (Andrady, 2011; Arp et al., 2021; Liu et al., 2020; Stanica-Ezeanu and Matei, 2021; Ward et al., 2019), which result in changes in the physical and chemical properties of MPs (Gewert et al., 2015; Sait et al., 2021). The degree of weathering can be observed by visual changes in color and crazing of the surfaces and later, the interiors. Degradation leads to a reduction in the molecular weight of the polymer segment and the formation of more polar functional groups (e.g., carbonyl and hydroperoxides) (Oelschlägel et al., 2018; Sun et al., 2020). Therefore, the leaching kinetics of organic additives from plastics is expected to be enhanced as the environmental degradation processes cause embrittlement and disintegration of plastics (Luo et al., 2020; Luo et al., 2021). The environmental stability of polymers depends on the polymer type (e.g., plastics with a carbon-carbon backbone, including PE, PP, PS, and PVC or plastics with heteroatoms in the main chain, such as PET and PU) and the presence of additives (Gewert et al., 2015). Although plastic degradation occurs via highly diverse pathways, either simultaneously or sequentially (Gewert et al., 2015), most studies on plastic aging and weathering have explored a few of these processes in isolation (Luo et al., 2021).

It should be noted that plastic additives may be transformed under dynamic weathering conditions as plastic additives are released from the confined matrices. For example, Sørensen et al. (2021) showed that benzophenone and benzotriazole UV stabilizers were rapidly degraded in seawater after leaching under UV irradiation, whereas organophosphorus compounds, phthalide, and phthalimide were more resistant to UV exposure. Microbial degradation processes might also play an important role in the transformation of additives leaching from polymers (Carmen, 2021). Further studies are needed to identify transformation products of plastic additives formed during dynamic leaching conditions in the aquatic environment.

Recently, Chamas et al. (2020) investigated the estimation of the first half-life, which is defined as the time at which the material loses 50% of its original mass, for a variety of common household plastic items to degrade in the environment. Interestingly, the half-life of plastic items in the marine environment is generally shorter than that in land-fill/compost/soil conditions. In particular, LDPE plastic bags (typical thickness $\mu = 100 \ \mu\text{m}$), HDPE milk bottles ($\mu = 500 \ \mu\text{m}$) and laundry

detergent containers ($\mu = 10,000 \ \mu m$), PP food storage containers ($\mu =$ 800 μ m), PET single-use water bottles ($\mu = 500 \ \mu$ m), and biodegradable plastic bags ($\mu = 100 \,\mu\text{m}$) have been estimated to have half-lives of 5, 26, 530, 87, 2.3, and 0.29 years, respectively, in the marine environment (Chamas et al., 2020). The data to estimate the half-life was collected during the degradation process, which was accelerated by UV and thermal treatments. Compared to the desorption of plastic additives in laboratory experiments, the desorption half-life of 38 PCB congeners from PE pellets (r = 2 mm) ranged from 240 days to 3500 years for PCB-8 up to PCB-209 (Endo et al., 2013). Furthermore, Sun et al. (2019) reported that the half-life of BFRs from ABS ranges from tens of thousands to hundreds of billions of years. Fig. 2 illustrates the reported ranges of plastic degradation under different conditions and the leaching half-lives of hydrophobic organic additives from MPs. As shown in Fig. 2, although the ranges span several orders of magnitude depending on the environmental conditions and the size of MPs, the release of organic plastic additives with very high partition coefficients and low diffusion coefficients under environmental conditions is likely to be much slower than the rate of physical and chemical abrasion processes, which also leads to the release of additives into the environment (Lee et al., 2018). Furthermore, the half-life time to reach equilibrium for PCB153 sorption on PE pellets in the field was estimated to be 3-7 months (Rochman et al., 2013), which is much faster than the laboratory results obtained by Endo et al. (2013). This supports the hypothesis that the desorption of plastic additives in the natural marine environment, which is affected by external factors such as sunlight, microorganisms, mechanical forces, or temperature, might be faster than that under controlled laboratory conditions. Thus, clarifying the effects of weathering processes on the release of plastic additives is essential for evaluating the fate and transport of HOCs in the aquatic environment. To date, very few studies have investigated the effect of degradation on the extent of additive leaching under environmentally relevant conditions, warranting further investigation (Brandon et al., 2016; Chen et al., 2020; Fan et al., 2021; Liu et al., 2020; Paluselli et al., 2018; Song et al., 2017; Sørensen et al., 2021; Suhrhoff and Scholz-Böttcher, 2016; Vroom et al., 2017; Zhu et al., 2020).

6. Conclusion and future perspectives

The main insights into the leaching of hydrophobic organic additives from MPs in aquatic environments were comprehensively reviewed. The equilibrium distribution of HOCs between MPs and water has been extensively studied with various sorption isotherms, especially for



Fig. 2. Reported time scale of plastic degradation under various environmental conditions, with leaching half-lives of representative hydrophobic plastic additives.

conventional hydrophobic organic contaminants, to assess their transfer to biota after ingesting microplastic particles. Because the environmental levels of these trace contaminants are typically very low, the linear sorption model is sufficient to describe their distribution between MPs and water. However, further studies on the equilibrium distribution of plastic additives between MPs and the surrounding aqueous media are required because their mass fraction in plastic products is high and nonlinear behavior is expected. The leaching kinetics of plastic additives strongly depend on the physicochemical properties of both microplastics and additives, with the two most important parameters being K_p and D. However, leaching models are limited to cases with a fixed boundary between microplastics and the surrounding media, although the weathering of microplastics is a highly dynamic process affected by physical, chemical, and biological factors. Therefore, further studies should focus on the release of plastic additives from (micro)plastics under environmentally relevant conditions, including the interactions of microplastics with biofilms, to better understand the fate and transport of these plastic additives in the aquatic environment.

CRediT statement

Anh Thi Ngoc Do: Methodology, Investigation, Writing- Original draft preparation. Yeonjeong Ha: Conceptualization, Methodology, Writing - Original draft preparation. Jung-Hwan Kwon: Conceptualization, Supervision, Writing - Review & Editing.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119258.

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