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ARTICLE

Relative Importance of Microplastics as Vectors of Hydrophobic Organic Chemicals to Marine Fish and Seabirds

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Abstract
Microplastics are suspected to deliver hydrophobic organic chemicals (HOCs) to marine organisms as it has high sorption capacity towards HOCs. In this study, the roles of microplastics ingestion in the overall uptake of HOCs by fish and seabird were evaluated quantitatively using mass-balance models including their biological features and possible HOCs intake routes (i.e., air, seawater, food, and microplastics). HOCs having wide range of partitioning properties ($n = 203$) were chosen and the contribution of microplastics was compared with other intake routes and further visualized using 2-dimensional contour diagrams. For most of the non-additives ($n = 170$), the contribution of microplastics was observed to be negligible (< 5%), as compared to the other intake routes. On the other hand, plastic-bound intake can be important for plastic additives ($n = 33$) with high log octanol–water partition constant (log K_{ow}) when the fugacity in microplastics is significantly greater than in other media, indicating the importance of further studies on leaching of hydrophobic additives under various conditions.

Keywords Bio-transfer · Equilibrium partitioning · Fugacity · Microplastics · Plastic additives

1 Introduction

Plastic production has been increasing at a rate of approximately 9% every year; it has increased from 1.5 million tons in the 1950s to 350 million tons in 2018 (PlasticsEurope 2019). Increasing production of plastics and their indiscreet use led to the accumulation of large amounts of "microplastics", plastic particles smaller than 5 mm (Auta et al. 2017). These microplastics are misconceived as prey and ingested by marine organisms (Cole et al. 2013; Desforges et al. 2015; Hipfner et al. 2018). Plastic ingestion by fish and seabirds was first noted in the 1960s (Kenyon and Kridler 1969). Later, for example, Nelms et al. (2018) observed 1–4 microplastics in one-third of the wild-caught Atlantic mackerel (*Scomber scombrus*). Microplastics have high sorption capacity for hydrophobic organic chemicals (HOCs) (Lee et al. 2014); hence, upon the ingestion of microplastics the HOCs can be transferred to the organisms with micropastics acting as the vectors (González-Soto et al. 2019; O'Donovan et al. 2018). Marine microplastics can get enriched with HOCs from the surrounding environmental media via (ad) sorption (Bakir et al. 2012; Lee et al. 2014; Rochman et al. 2013) or they inherently contain high concentrations of HOCs as additives during the production of plastic products (Jang et al. 2016; Rani et al. 2015). As the ingestion of plastic debris by marine organisms has been recorded for decades and given that plastics may transfer HOCs to the biota, there is a need to understand whether microplastics are a substantial source of uptake and accumulation of HOCs in marine organisms.

Laboratory- and field-scale experimental studies along with mass balance modeling studies have been conducted to verify the role of microplastics as transport vectors for HOCs. However, the results between the experimental and mass balance modeling studies have been inconsistent. For examples, Gassel et al. (2013) showed that nonylphenol from plastic debris was detected in the tissues of wild-caught juvenile yellowtail (*Seriola lalandi*) and polybrominated diphenyl ethers (PBDEs) from microplastics were transferred to the tissues of the marine amphipod (*Allorchestes compressa*) (Chua et al. 2014). However, the debate has raised questions regarding the contribution of microplastics

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to the bio-transfer of HOCs as the experiments did not reflect the real environmental conditions. In many studies, the number of plastic debris and the concentration of the HOCs in the debris were much higher than the reported concentrations in the environment; moreover, the contribution from the other environmental phases (i.e., air, water, and food) were neglected and not compared with microplastic-bound intake (Koelmans 2015). In contrast, several mass balance modeling studies with the hypothesis that fugacity, a tendency of a molecule to escape from its confined medium, of HOCs in microplastics are the same (i.e., at equilibrium) or lower than that in the aquatic environment showed that the contribution of microplastics to the overall bio-transfer and bioaccumulation of HOCs to marine organisms is relatively small compared to that of other media (Gouin et al. 2011; Koelmans et al. 2013, 2016; Lee et al. 2019).

Inconsistencies among studies occur under different initial experimental conditions. While studies that used highly contaminated plastics stated that they could act as "sources", studies that used plastics that were relatively clean compared to the organism suggested that plastics could act as "sinks" (Nor and Koelmans 2019). Depending on their origin, HOCs can be divided into plastic additives and non-additives. Non-additives (ad)sorb to plastics from nearby environmental media; thus, the fugacity of non-additives in plastic is more likely to be equal to or smaller than that in the surrounding medium. On the other hand, additives are added during plastic production and are present in plastics at very high concentrations, leading to a great fugacity gradient between microplastics and water (Kwon et al. 2017). Thus, studies need to quantitatively compare additives and non-additives with diverse physicochemical properties to demonstrate the role of plastics as a transport vector of HOCs to marine organisms.

The objective of this study was to investigate the role of microplastics as a transport vector of HOCs in the bioaccumulation process using the chemical properties of the latter, especially for marine fish and seabird. Pacific saury (*Cololabis saira*) (body weight = 100 g and lipid content = 5%) and black-tailed gull (*Larus crassirostris*) (body weight = 500 g and lipid content = 10%), common residential organisms along Korean coastline (Kwon et al. 2013), were chosen as model marine fish and seabird, respectively. Polyethylene (PE) was chosen as the representative plastic material because partitioning to PE has been studied for many HOCs and its light density allows it to be consumed by organisms. HOCs included 33 plastic additives and 170 non-additives. In the model, two settings were applied to differentiate between the initial conditions of additives and non-additives. The uptake of HOCs from seawater, air, food, and plastic were considered; moreover, the contribution of each route was estimated considering a wide range of chemical properties of HOCs (i.e., logarithmic octanol–water partition constant (log K_{ow}), logarithmic octanol–air partition constant (log K_{oa}), and logarithmic plastic–water partition constant (log K_{pw})). Finally, the contribution of microplastics was visualized through a contour graph for four different scenarios (i.e., non-additives and additives in fish and seabird model) with respect to the chemical properties.

2 Methods

2.1 Chemicals and Domain of Applicability of the Models

A total of 203 HOCs were selected to cover both non-additives as well as additives. Non-additives included 21 polycyclic aromatic hydrocarbons (PAHs), 33 alkylated-PAHs, 63 polychlorinated biphenyls (PCBs), 24 organochlorine pesticides (OCPs), 11 alkyl benzenes, five alkyl phenols, nine aliphatic hydrocarbons, and four other compounds. Additives included 16 polybrominated diphenyl ethers (PBDEs), five ultraviolet (UV) stabilizers, and 12 antioxidants.

As equilibrium partitioning properties determine the bio-transfer of HOCs to fish and seabird, data on log K_{ow}, log K_{oa}, and log K_{pw} were collected from literature or estimated using EPISuite™ program (USEPA 2012). When multiple values were available in the literature, median values were chosen. The ranges of log K_{ow}, log K_{oa}, and log K_{pw} were 2.69–18.08, 1.96–30.33, and 2.0–18.85, respectively. All the values are shown in Table S1 (Supplementary Material). When log K_{pw} was not available in the literature, it was estimated using an empirical linear relationship between log K_{pw} and log K_{ow} obtained for 167 HOCs (Figure S1, Supplementary Material).

$$\log K_{pw} = 1.13 \log K_{ow} - 1.07 \quad r^2 = 0.82 \tag{1}$$

2.2 Initial Environmental Distribution of HOCs

For non-additives that are not intentionally added to plastics, it was assumed that these HOCs are distributed in different environmental media at phase equilibrium (i.e., the same fugacity in air, water, and microplastics). On the other hand, the fugacity of plastic additives in microplastics was assumed to be much greater than that in the environmental media. To cover a wide range of fugacity differences, the fugacity ratio (fugacity in microplastics to that in environmental media; R_f) was assumed to be between 10^0 and 10^5. Indeed, the fugacity analysis of polycyclic aromatic hydrocarbons (PAHs) in the previous study (Lee et al. 2017) reported that the R_f values of PAHs between polyethylene

(PE) and seawater were ranged from 10^{-2} to 10^{3}, and plastic additives should have greater R_f values than PAHs.

2.3 Fish Model

Chemical uptake and elimination processes in fish are described by a series of following processes mentioned in Eq. 2: uptake from seawater, consumption of foods and microplastics, and the overall elimination, including growth dilution, reproduction process, fecal egestion, and biotransformation as follows:

$$\frac{dC_{fish}}{dt} = k_w C_{sw} + IR_{food} C_{food} \alpha_{food} + IR_{MP} C_{MP} \alpha_{MP} - k_{loss} C_{fish}, \quad (2)$$

where k_w is the gill uptake rate constant (L kg^{-1} day^{-1}); C_{sw} is the total concentration of the chemical in seawater (ng L^{-1}, assumed as 1 for all HOCs); IR_{food} and IR_{MP} are the intake rates of the prey (kg kg^{-1} d^{-1}) and microplastic (kg kg^{-1} d^{-1}), respectively; C_{food}, C_{MP}, and C_{fish} are the concentrations of chemical in prey (ng kg^{-1}), microplastic (ng kg^{-1}), and fish (ng kg^{-1}), respectively; α_{food} and α_{MP} are the absorbed fraction of chemical (unitless) from prey and microplastic, respectively; k_{loss} is the overall elimination rate constant (day^{-1}).

Numerous simple relationships were acquired from the literature to describe the parameters for the uptake processes. Arnot and Gobas (2006) demonstrated the rate of chemical absorption from water via gill uptake, k_w, as a function K_{ow} of the chemical and the weight of the organism BW (kg) as follows:

$$k_w = \left(1.85 + {}^{155}/_{K_{ow}}\right)^{-1} \left({}^{980BW_{fish}^{0.65}}/_{7.1}\right) BW_{fish}^{-1}, \quad (3)$$

where BW_{fish} is the wet weight of the fish (0.1 kg was used in this study).

IR_{food} was assumed to be 1.5% of their weight as fish are known to consume food which is approximately 1–5% of their body weight (Craig et al. 2017). IR_{MP} was assumed to be 0.1% of their daily food consumption to maximize the plastic contribution in the worst-case scenario. According to Baak et al. (2020), the maximum mass of microplastic found in the seabirds is 0.1 g. To make the worst-case scenario, if we assumed that 0.1 g microplastics was ingested per day, the ratio between microplastic ingestion rate (0.1 g day^{-1}) to daily food assumption (138.4 g day^{-1}, calculated using Eq. 16) is approximately 0.001 supporting that 0.1% was chosen to maximize the plastic contribution. IR_{food} and IR_{MP} were expressed in Eqs. 4 and 5, respectively.

$$IR_{food} = 0.015 \quad (4)$$

$$IR_{MP} = 0.001\ IR_{food} \quad (5)$$

C_{food} was calculated from the Eq. (6) as follows:

$$C_{food} = C_{sw} f_{lipid} K_{ow} / \rho_{lipid}, \quad (6)$$

where the prey species was assumed to be a phytoplankton (Odate 1994) with a lipid fraction (f_{lipid}) of 10% (Rossi et al. 2006), and ρ_{lipid} is density of lipid (kg L^{-1}) which was assumed to be 1 kg L^{-1}. C_{MP} was calculated using Eq. 7 as follows:

$$C_{MP} = R_{fug} C_{sw} K_{pw}, \quad (7)$$

where R_{fug} is the fugacity ratio of the HOC between the plastic and water phases. α_{food} was assumed to be 1 as fish have high lipid digestibility of up to 97% (Olsen and Ringø 1997). α_{MP} was assumed to be 1 for non-additives as they are (ad)sorbed to the plastic phase from the environmental phase and are likely to be found primarily in the outer layer of the plastic. For additives, it was assumed that they are equally distributed inside the (micro)plastic. Two different absorbed fraction values, 0.01 and 0.1, were used because only those at the outer layer of the plastic can leach out to the gut fluid within the gut retention time (12–14 h) (Magnuson 1969). Although it depends on the partitioning behavior of additives and the size of ingested microplastics, an experimental study in our group showed that approximately 1 to 10% of UV stabilizers leached from plastic fibers to cosolvents (acetonitrile and water mixture) within 10 h (unpublished data). Using the above parameters, the contributions of plastic, seawater, and food were evaluated using the following equation:

$$\text{Plastic contribution}(\%) = \frac{IR_{MP} C_{MP} \alpha_{MP}}{k_1 C_{sw} + IR_{food} C_{food} \alpha_{food} + IR_{MP} C_{MP} \alpha_{MP}} \times 100(\%) \quad (8)$$

$$\text{Seawater contribution}(\%) = \frac{k_1 C_{sw}}{k_1 C_{sw} + IR_{food} C_{food} \alpha_{food} + IR_{MP} C_{MP} \alpha_{MP}} \times 100(\%) \quad (9)$$

$$\text{Food contribution}(\%) = \frac{IR_{food} C_{food} \alpha_{food}}{k_1 C_{sw} + IR_{food} C_{food} \alpha_{food} + IR_{MP} C_{MP} \alpha_{MP}} \times 100(\%) \quad (10)$$

2.4 Seabird Model

The uptake and elimination processes for seabird are described by the following mass balance in Eq. 11:

$$\frac{dC_{bird}}{dt} = IR_{air}\left(C_{air}\alpha_{air} + f_{PM}C_{PM}\alpha_{PM}\right) + IR_{food}C_{food}\alpha_{food} + IR_{MP}C_{MP}\alpha_{MP} - k_{loss}C_{bird} \quad (11)$$

where IR_{air} is the breathing rate constant ($m^3\ kg^{-1}\ day^{-1}$). f_{PM} is the amount of particulate matter in the air ($\mu g\ m^{-3}$); C_{air} and C_{PM} are the total concentrations of the chemical in air ($ng\ m^{-3}$) and particulate matter ($ng\ \mu g^{-1}$), respectively; IR_{food} and IR_{MP} are the intake rates of the prey ($kg\ kg^{-1}\ day^{-1}$), and microplastic ($kg\ kg^{-1}\ day^{-1}$), respectively; C_{food}, C_{MP}, and C_{bird} are the concentrations of chemical in prey ($ng\ kg^{-1}$), microplastic ($ng\ kg^{-1}$), and seabird ($ng\ kg^{-1}$), respectively; α_{air}, α_{PM}, α_{food}, and α_{MP} are the absorbed fraction of the chemical (unitless) in air, particulate matter, prey, and microplastic, respectively; k_{loss} is the overall elimination rate constant (day^{-1}).

The uptake rates, IR_{air}, IR_{food}, and IR_{MP} for the seabird model, were estimated considering empirical relationships in the previously reported literature. IR_{air} was calculated using Eq. (14), assuming that their resting hours and flying hours are 22 h and 2 h per day, respectively, using Eqs. 12 and 13 (Morgan et al. 1992) as follows:

$$Ventilation_{resting} = 0.01746BW_{bird}^{0.74}, \quad (12)$$

$$Ventilation_{flying} = 0.3BW_{bird}^{0.74}, \quad (13)$$

$$IR_{air} = 0.984BW_{bird}^{0.74} * BW_{bird}^{-1}, \quad (14)$$

where $ventilation_{resting}$ ($m^3\ h^{-1}$) and $ventilation_{flying}$ ($m^3\ h^{-1}$) are ventilation rates of seabirds during resting and flying, respectively, and BW_{bird} is the wet weight of seabirds (0.5 kg was used in this study).

IR_{food} was calculated based on daily energy expenditure (DEE). The biochemical mean of the energy requirement was used to determine the DEE value using Eq. 15 (Crocker et al. 2002). Then, the IR_{food} was estimated using Eq. 16 as a function of DEE, moisture content of the food, energy content of the food, and assimilation efficiency of the seabirds. Fish was assumed to be the only food type, having an approximate energy content of 20 kJ g^{-1} dry weight and 71.1% moisture content (Penczak et al. 1984). IR_{MP} was assumed to be 0.1% of their daily food consumption to maximize the plastic contribution in the worst-case scenario:

$$\log(DEE) = 1.1482 + 0.6521\left(\log BW_{bird} + 3\right) \quad (15)$$

$$IR_{food} = \frac{DEE}{(\text{Energy in food; kJ } g^{-1}) \times (1 - \text{Moisture}) \times \text{Assimilation Efficiency}} * BW_{bird}^{-1} \quad (16)$$

$$IR_{MP} = 0.001IR_{food} \quad (17)$$

f_{PM} followed the national air quality standard for the annual average PM_{10}, which is 50 $\mu g\ m^{-3}$ (USEPA 2004). C_{air} was calculated as a function of the octanol–air partition constant (K_{oa}), octanol–water partition constant (K_{ow}), and concentration of HOC in the water phase (assumed $C_{sw} = 1$).

$$C_{air} = K_{ow}K_{oa}^{-1}C_{sw} \quad (18)$$

C_{PM} was calculated from the linear regression model developed to estimate the sorption of semi-volatile organic compounds (Finizio et al. 1997) as follows:

$$\log K_p = \log K_{oa} - 12.61, \quad (19)$$

where K_p is the particle–gas partition coefficient ($m^3\ \mu g^{-1}$). The concentration of HOC in the food was estimated based on the maximum bioconcentration factor (BCF) model without considering body metabolism by Dimitrov et al. (2002).

$$\log BCF = 3.93\exp\left(-\frac{\left(\log K_{ow} - 6.61\right)^2}{11.9} + 0.931\right), \quad (20)$$

$$C_{food} = BCF_{max}C_{sw}, \quad (21)$$

C_{MP} was calculated using Eq. 22 and we assume that seabirds ingest solely microplastics floating in seawater.

$$C_{MP} = R_{fug}C_{sw}K_{pw} \quad (22)$$

The fugacity ratio of the HOC between the plastic and the water phase in the seabird model was also assumed to be the same for the non-additives. For additives, two different ratios (i.e., 10^1 and 10^3) were applied to demonstrate the changes in plastic contribution with an increase in the fugacity ratio. α_{air} and α_{PM} were assumed to be 1 because an avian respiratory system has paired lungs, making it more efficient for gas exchange (Duncker 1974). Furthermore, α_{food} was assumed to be 1 because seabirds are highly efficient (efficiency greater than 90%) at assimilating wax esters because of their unique digestive system (Place 1992). α_{MP} was assumed to be 1 for non-additives and for additives; however, the value of 0.01 was applied as explained in the previous section.

Table 1 Chemical properties for each axis in the scenario

		x axis	*y* axis
Non-additives	Fish	log K_{ow}	log K_{pw}
	Seabird	log K_{oa}	log K_{ow}
Additives	Fish	log K_{ow}	R_{fug}
	Seabird	log K_{oa}	log K_{ow}

Using the above parameters, the contributions of plastic, air, and food were evaluated using Eqs. 23–25:

$$\text{Plastic contribution}(\%) = \frac{\text{IR}_{\text{MP}} C_{\text{MP}} \alpha_{\text{MP}}}{\text{IR}_{\text{air}}\left(C_{\text{air}}\alpha_{\text{air}} + f_{\text{PM}} C_{\text{PM}} \alpha_{\text{PM}}\right) + \text{IR}_{\text{food}} C_{\text{food}} \alpha_{\text{food}} + \text{IR}_{\text{MP}} C_{\text{MP}} \alpha_{\text{MP}}} \times 100(\%) \quad (23)$$

$$\text{Air contribution}(\%) = \frac{\text{IR}_{\text{air}}\left(C_{\text{air}}\alpha_{\text{air}} + f_{\text{PM}} C_{\text{PM}} \alpha_{\text{PM}}\right)}{\text{IR}_{\text{air}}\left(C_{\text{air}}\alpha_{\text{air}} + f_{\text{PM}} C_{\text{PM}} \alpha_{\text{PM}}\right) + \text{IR}_{\text{food}} C_{\text{food}} \alpha_{\text{food}} + \text{IR}_{\text{MP}} C_{\text{MP}} \alpha_{\text{MP}}} \times 100(\%) \quad (24)$$

$$\text{Food contribution}(\%) = \frac{\text{IR}_{\text{food}} C_{\text{food}} \alpha_{\text{food}}}{\text{IR}_{\text{air}}\left(C_{\text{air}}\alpha_{\text{air}} + f_{\text{PM}} C_{\text{PM}} \alpha_{\text{PM}}\right) + \text{IR}_{\text{food}} C_{\text{food}} \alpha_{\text{food}} + \text{IR}_{\text{MP}} C_{\text{MP}} \alpha_{\text{MP}}} \times 100(\%) \quad (25)$$

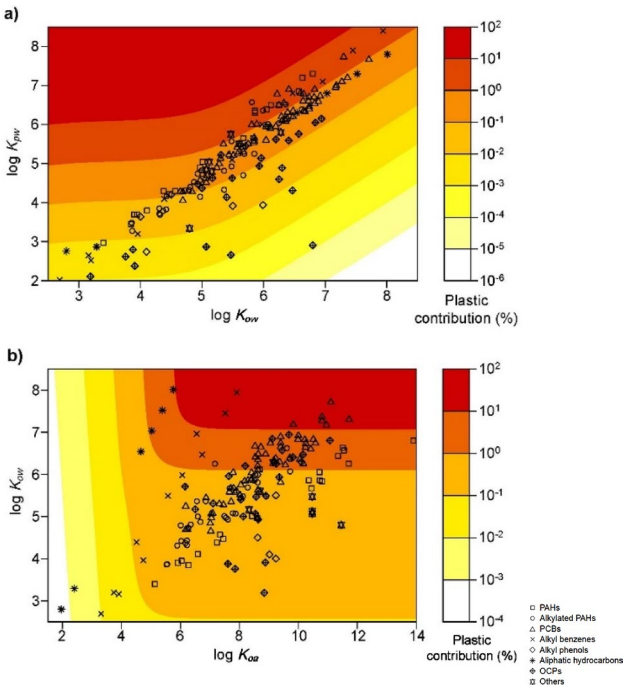

Fig. 1 Contribution of plastics relative to the overall transfer of non-additives in fish (**a**) and seabird (**b**). Both assimilation efficiency via microplastic ingestion (α_{MP}) and the fugacity ratio (R_{fug}) were assumed to be unity

2.5 Visualization of Model Results

The relative contribution of microplastic ingestion to the overall uptake was calculated using Eqs. 8 and 23 for all the selected HOCs. The major variables that determine the contribution of microplastic ingestion are different. The simulations were divided into four cases: non-additives in the fish and seabird models and additives in the fish and seabird models. The results were then visualized in 2-D based on the two most important variables listed in Table 1 for each case using the contour plot of the ggplot2 package in the R software (R Development Core Team 2020). For the additives in the fish model, two different α_{MP} values were selected; for the seabird model, two different R_{fug} values with α_{MP} value of 0.01 were used to represent possible bio-transfer processes.

3 Results and Discussion

3.1 Contribution of Microplastics toward the Bio-Transfer of Non-Additives

Figure 1a shows the contour diagram of the contribution of plastic ingestion by fish toward the overall uptake of 170 non-additives having a wide range of log K_{ow} and log K_{pw}. The maximum microplastic contribution was 4.7% for trimethyldibenzothiophene (log $K_{ow} = 5.81$ and log $K_{pw} = 6.57$). All values are shown in Table S2 (Supplementary Material). Generally, the contribution of microplastics increases with increasing ratio of K_{pw} to K_{ow}. Food bound uptake is more important for chemicals that are more hydrophobic (log $K_{ow} > 4.5$), while water ventilation is more important for less hydrophobic chemicals (log $K_{ow} < 4.5$). Even though the model set a harsh condition ($\alpha_{MP} = 1$) to avoid underestimation of microplastic contribution, uptake via microplastic ingestion was estimated to be almost negligible compared to other intake routes.

Figure 1b shows the assessment of microplastic contribution for non-additives in the seabird model. Of the 170 non-additives, 157 showed a microplastic contribution below 10%. Contribution from microplastic being negligible, air and food were the two major uptake routes of HOCs. Microplastic contribution increased with increasing K_{ow} and K_{oa} values. K_{pw} values were not used in the diagram because they were strongly correlated with K_{ow} (Figure S1). Inhalation of air was the dominant intake route for chemicals with low K_{ow} and K_{oa} regions (log $K_{ow} < 4.5$ and log $K_{oa} < 4.5$), whereas food intake was the dominant intake route for chemical with high K_{ow} and low K_{oa} region (log $K_{ow} > 4.5$ and log $K_{oa} < 4.5$). Although α_{PM} was assumed to be 1, contribution of particle-bound uptake during inhalation was almost

negligible for all chemicals. All the values are shown in Table S2 (Supplementary Material).

Even though the role of microplastic as a transport vector was limited for most of the HOCs, 13 HOCs showed a microplastic contribution of over 10%. They are *n*-dodecylbenzene, benzo[*ghi*]perylene, dibenz[*a*,*h*]anthracene, *n*-decylbenzene, *n*-undecylbenzene, PCB-137, -155, -156, -170, -180, -187, -204, and -208. The maximum microplastic contribution was 91%, which was from *n*-dodecylbenzene (log K_{ow} = 7.94, log K_{oa} = 7.91, and log K_{pw} = 8.40). These non-additives are highly hydrophobic (high log K_{ow} and log K_{oa}) belonging to the log K_{ow} > 7 and log K_{oa} > 6 regions. Higher contribution of plastic intake in the seabird model than in the fish model could be explained by Dimitrov's bioaccumulation model (Eq. 18), in which the maximum BCF occurs at log K_{ow} = 6.61. Thus, the concentration in food does not increase linearly with increasing log K_{ow} in the model. In contrast, log K_{pw} is assumed to increase with increasing log K_{ow} (Eq. 1). Higher fugacity in microplastics than in food results in a higher contribution of microplastic ingestion.

Although the relative importance of microplastics was overestimated for non-additives with high log K_{ow} and high log K_{oa} in the seabird model, the assumption of phase equilibrium between microplastics and seawater can be challenged. For highly hydrophobic chemicals, longer equilibration time is expected with increasing log K_{ow} or log K_{pw} (Lee et al. 2017). In addition, larger molar volume of HOCs, especially with higher K_{ow}, prevents HOC partition inside the inner layer of microplastics and the diffusive transfer of those chemicals from seawater to microplastics should be slow (Zhang and Gobas 1995). Thus, the fugacity of non-additives in microplastics may be lower than in seawater under ambient environmental conditions.

The assimilation efficiency in the gastrointestinal tract (GIT) of organisms should depend on the size of the microplastics ingested. Desorption process in the GIT fluid can be divided into a fast desorption process occurring on the outer layer of the microplastic and a slow desorption process occurring from the internal layer of the microplastic. As the retention time of microplastics in GIT is limited to several hours (Lee et al. 2019), the surface area of microplastics that governs the fast desorption process is important. Thus, larger microplastics with smaller surface-to-volume ratios should have smaller assimilation efficiency. Considering the non-equilibrium phase in real environmental conditions and a

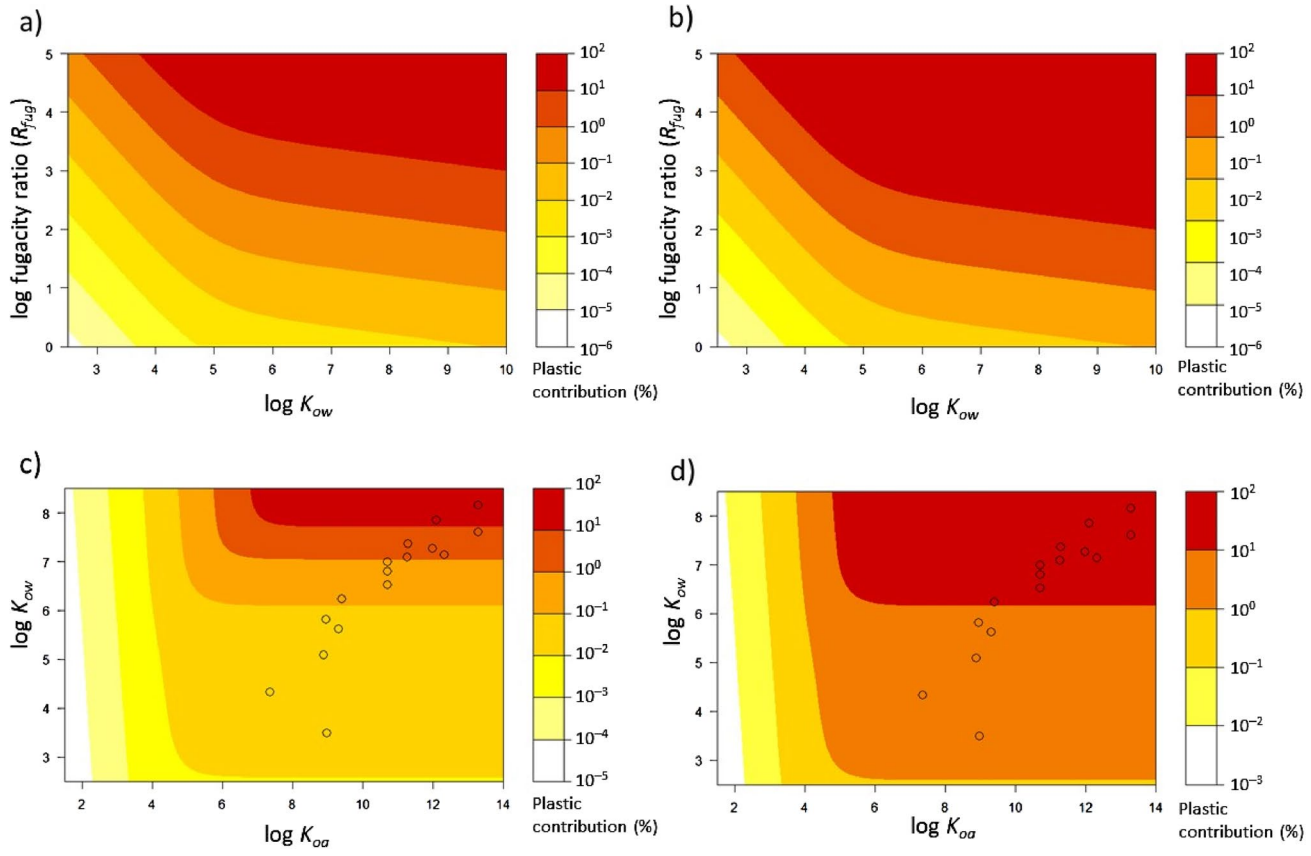

Fig. 2 Contribution of plastic relative to overall transfer of additives in fish with **a** a_{MP} = 1%, and **b** a_{MP} = 10% and in seabird with **c** $R_{fug} = 10^1$ and **d** $R_{fug} = 10^3$ at the same a_{MP} = 1%. Open circles denote the additives chosen in this study and are not shown outside the range

wide range of microplastic sizes for non-additives in fish and seabird models, microplastics play a limited role as transport vectors for bioaccumulation, compared to seawater/air and food. This is true even when the condition of relatively high plastic consumption and leaching of the HOC from the plastic is set.

3.2 Contribution of Microplastics for the Bio-Transfer of Hydrophobic Plastic Additives

Figure 2a and b show the assessment of microplastic contribution for plastic additives for the fish model. Assessment of microplastic contribution using Eq. 8, assuming α_{MP} to be 0.01 and 0.1, is presented in Fig. 2a and b. As shown, the contribution of microplastics increased with increasing log K_{ow} and log R_{fug}. In addition, the increase of α_{MP} from 0.01 to 0.1 increased the contribution of microplastics by one order of magnitude. The role of microplastics as transport vectors depends strongly on log K_{ow}, α_{MP}, and R_{fug}. The bio-transfer of additives from microplastic is almost negligible when log K_{ow}, α_{MP}, and R_{fug} are small. However, the role of microplastics becomes more significant with increasing values of K_{ow}, α_{MP}, and R_{fug}. Many additives (e.g., UV stabilizers, PBDEs, and antioxidants) are added to plastics at a high level of 10–70% by weight for plasticizers, and 0.05–3% by weight for antioxidants and UV stabilizers (Hahladakis et al. 2018). According to Echols et al. (2009), plastic products may contain 5–25% PBDEs by weight; the reported range of PBDEs in seawater is 0.03–0.64 pg L^{-1} (Möller et al. 2011; Xie et al. 2011). Based on their log K_{ow} range between 5 and 10 (Wang et al. 2017), we can estimate that R_{fug} for those additives is in the range of 10^2–10^5. Microplastics may contribute significantly to the transfer of those BFRs at α_{MP} of 0.1 (Fig. 2b). For dimethyl phthalate (log $K_{ow} = 1.61$) (Hermabessiere et al. 2017), the reported range of dimethyl phthalate is 0.02–0.10 µg L^{-1} (Heo et al. 2020). Based on the amount added during production process, R_{fug} is estimated to be in the range of 10^2–10^5. Nevertheless, the contribution of MP intake to overall intake of dimethyl phthalate is negligible. Thus, the role of microplastics as transport vectors is likely negligible for the additives that are less hydrophobic (log $K_{ow} < 3$) (Fig. 2b).

Figure 2c and d reveals the assessment of the microplastic contribution for additives in the seabird model using Eq. 21 at R_{fug} of 10^1 and 10^3, respectively. The contribution of microplastics was found to increase with increasing log K_{ow} and log K_{oa}. In addition, an increase in log R_{fug} resulted in a higher contribution of microplastics by two orders of magnitude. As explained in the fish model, microplastics are likely to act as relatively important transport vectors of additives for seabirds as most of the additives in plastics have R_{fug} higher than 10^3, even when α_{MP} is assumed to be 0.01.

3.3 Implications of Microplastic-Related Chemical Exposure in Aquatic Environments

As demonstrated in this study, uptake of non-additives from the ingestion of microplastics at phase equilibrium between microplastics and seawater is not likely to be the primary uptake route. However, uptake of HOCs from microplastics could become more important when a marine organism living in a relatively clean environment ingests highly polluted microplastics from nearby polluted areas.

On the other hand, hydrophobic additives can be taken up by marine organisms via microplastic ingestion. The partition constants and fugacity ratio are found to be critical parameters that determine the availability of these additives from plastics. Although it was not rigorously assessed in this study, the rate of desorption in the digestive system and the gut retention time are also important. Leaching of plastic additives could be a slow process because the diffusivity of these additives in plastic could be very low (e.g., Sun et al. 2019). When diffusion in the plastic phase is rate-limiting, concentration gradient develops within the plastic phase, slowing down the leaching rate compared to that assuming a homogeneous distribution of additives. If the time scale of leaching is comparable to physical abrasion or (bio) chemical weathering of plastic particles, the concentration near the plastic–water interface can be renewed, leading to the potential transformation of additives with the occurrence of plastic weathering. Given that biofilms develop on microplastic surfaces (e.g., Miao et al. 2019; Michels et al. 2018; Tarafdar et al. 2021), additional mass transfer barrier of biofilm should be considered in many cases and the transformation in this layer could alter the fugacity gradient, affecting the overall availability of hydrophobic additives from microplastics.

4 Conclusion

The contribution of microplastic ingestion toward the overall uptake of HOCs in two representative marine organisms was quantitatively evaluated for 203 HOCs covering a wide range of partitioning properties. For most non-additives ($n = 170$), which are likely at phase equilibrium between microplastics and seawater, microplastic ingestion is not an important route of HOCs exposure. On the other hand, it can be important for plastic additives ($n = 33$) with a high log octanol–water partition constant (log K_{ow}) because the fugacity of additives in microplastics can be much greater than those in other media. Although the importance of microplastic ingestion can be site-specific, other parameters should be considered in detailed analyses. The model

evaluations in this study show a general tendency considering the partitioning properties of HOCs.

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