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Estimating microplastic-bound intake of hydrophobic organic chemicals by fish using measured desorption rates to artificial gut fluid

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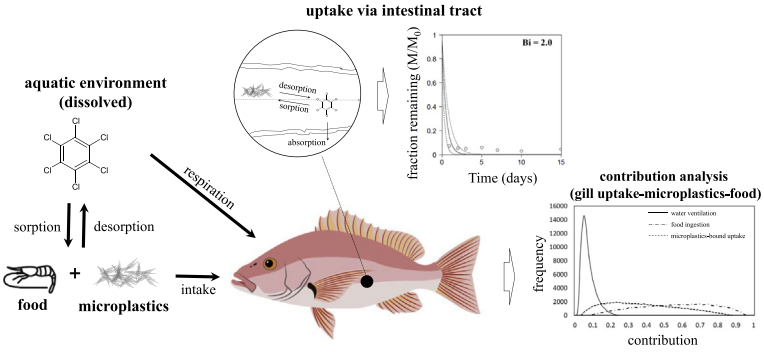
HIGHLIGHTS

- The contribution from ingested MPs to overall uptake of HOCs by fish was evaluated.
- $K_{MP/SIF}$ and $K_{om/SIF}$ were determined for HOCs using a tree-phase partitioning method.
- HOCs leaching from MPs in artificial gut fluid was compared with model predictions.
- The contribution of plastic-bound intake was assessed using a fish bioaccumulation model.
- The results suggest that the role of ingested MPs may play as "dilution" for HOCs.

GRAPHICAL ABSTRACT



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ABSTRACT

One of the most important concerns about marine microplastics is their role in delivery of chemical contaminants to biota. The contribution of microplastic ingestion to the overall uptake of five hydrophobic organic chemicals (HOCs) [α-, β-, and γ-hexachlorocyclohexanes (HCHs), pentachlorobenzene (PeCB), and hexachlorobenzene (HeCB)] by fish is evaluated in this study. Partition coefficients of all five HOCs between surfactant micelles and simulated intestinal fluid (SIF), as well as between protein and SIF, were experimentally determined. Desorption of model HOCs from a polyethylene film into an artificial gut solution was measured to estimate the fraction of HOCs that can be absorbed from microplastics during their gut retention time. Monte-Carlo simulation (n = 100,000) showed that the uptake via microplastic ingestion will be negligible for HCHs as compared to uptake via other exposure routes, water ventilation and food ingestion. On the other hand, microplastic ingestion might increase the total uptake rate of PeCB and HeCB due to their accelerated desorption from microplastics into the artificial gut solution under the model scenario, assuming an extremely high intake of microplastics. However, the steady-state bioaccumulation factor was predicted to decrease with increasing ingestion of microplastics, showing a dilution effect by microplastic ingestion. Results indicate that HOCs that are close to be at phase equilibrium between microplastics and environmental media are not likely to be further accumulated via ingestion of microplastics; this is true even for cases, where ingestion of microplastics contributes significantly to the total uptake of HOCs. Therefore, future studies need to focus on hydrophobic plastic additives that may exist in microplastics at a concentration higher than their equilibrium concentration with water.

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1. Introduction

Accumulation of microplastics in marine environments is one of the most serious environmental problems in this century. Many researchers have studied the potential adverse and long-term environmental effects of microplastics (Andrady, 2011; Engler, 2012; Faggio et al., 2018; Moore, 2008). One of the central hypotheses about the adverse effects of microplastics is their role in the delivery of harmful chemicals to biota (Avio et al., 2015; Browne et al., 2013; Koelmans et al., 2013; Rochman et al., 2013a; Teuten et al., 2009). Marine microplastics may contain high concentrations of hydrophobic organic chemicals (HOCs) because they are often intentionally added to enhance the properties of plastic products (Kwon et al., 2017); alternatively, microplastics may gain HOCs from polluted environments due to their high sorption capacity for HOCs (Bakir et al., 2012; Lee et al., 2014; Liu et al., 2016; Rochman et al., 2013b; Velzeboer et al., 2014). Since the ingestion of plastic particles by marine organisms has been well-documented for decades (e.g., Choy and Drazen, 2013; Davison and Asch, 2011; Foekema et al., 2013; Jang et al., 2016; Kühn et al., 2015; Laist, 1997; Provencher et al., 2010; Remy et al., 2015; Rummel et al., 2016, Tanaka and Takada, 2016), it has created an important question of whether microplastics significantly contribute to the uptake and accumulation of HOCs through the marine food-web.

The hypothesis that microplastics play an important role as a transport vector of HOCs has been tested in two-ways: laboratory- and field-scale experimental studies and mathematical modeling studies. A few laboratory experiments indicated that plastic-bound HOCs are either transferred to test organisms (e.g., Chua et al., 2014) or substantially leached under simulated physiological conditions (Bakir et al., 2014). Chua et al. (2014) showed that polybrominated diphenyl ethers from microplastic debris can significantly assimilate in the tissues of the marine amphipod, *Allorchestes compressa*. Bakir et al. (2014) showed that the desorption rates of model HOCs (phenanthrene, di-2-ethylhexyl phthalate, perfluorooctanoic acid, and dichloro-diphenyl-trichloroethane) were faster under physiological conditions than in water without organic matter. However, these experimental studies did not reflect the actual marine environmental conditions because the number and mass concentration of plastic particles used in the experiments and the concentration of HOCs in the plastic phase were much higher than the concentrations reported for marine environments. In addition, the roles of other exposure routes (i.e., respiratory uptake and assimilation from prey) and loss processes (e.g., metabolic transformation and fecal egestion) were not quantified or compared to the contribution of microplastic-bound intake. In contrast to experimental studies, mathematical modeling studies (e.g., Gouin et al., 2011; Herzke et al., 2016; Koelmans et al., 2013) have suggested a limited role of microplastics as transport vectors for HOCs. When the distribution of HOCs between environmental media and microplastics is assumed to be in equilibrium, the fugacity of HOCs in microplastic phase is expected to be close to or lower than that in aquatic organisms at higher trophic levels. The ingestion of relatively "cleaner" microplastics may decrease the overall bioaccumulation of HOCs in piscivorous fish (Gouin et al., 2011) and in lugworm, *Arenicola marina* (Koelmans et al., 2013). Even for avians, the contribution of leachable persistent organic pollutants (POPs) from ingested microplastics to the overall bioaccumulation in northern fulmar (*Fulmarus glacialis*) was reported to be limited; ingested microplastics may act as a "passive sampler" for selected POPs in the body (Herzke et al., 2016).

The discrepancy between laboratory experimental and modeling studies is attributable to the different initial equilibrium conditions and kinetic rates. For non-additives, such as polychlorinated biphenyls, the acquired concentration in microplastic-phase from the environmental media is close to or lower than the concentration at phase equilibrium. However, chemical concentration of hydrophobic additives in microplastics could be higher than the equilibrium concentration by a few orders of magnitude. In addition, the desorption rates in the digestive tracts, where organic matter facilitates transfer of HOCs, are also much enhanced (Bakir et al., 2014). Thus, it needs to be further studied whether microplastics contribute to the bioaccumulation of plastic additives or not (Kwon et al., 2017).

The release of HOCs from microplastics has been studied and models describing the phenomenon have been developed for the cases of desorption into seawater (Endo et al., 2013; Lee et al., 2018a, 2018b) and into wastewater containing organic matter (Seidensticker et al., 2017). Studies are required on the equilibrium distribution of HOCs in digestive fluid that contains non-lipid organic matter, such as proteins and surfactants, and on the quantitative evaluation of desorption rates of HOCs to provide refined parameters for estimation of the transfer of HOCs from microplastics to organisms.

In this study, we evaluated the contribution of ingested microplastics to the overall transfer of HOCs into fish with experimentally determined parameters. Polyethylene (PE) was chosen as a model plastic material because it is most frequently used and identified as a type of microplastic (Hidalgo-Ruz et al., 2012). Five model HOCs, including three isomers of hexachlorocyclohexanes (HCHs) and two chlorinated benzenes (CBs), were chosen as model HOCs because their physico-chemical properties required for the estimation of desorption have been intensively studied in our earlier works (Lee et al., 2014, 2018a). The equilibrium partition coefficients between microplastics and simulated intestinal fluid (SIF) and also between organic matter components (surfactant and digestive enzymes) and SIF were experimentally determined. The leaching of HOCs from plastic phase into the artificial gut fluid, SIF dissolving organic matter components, were measured in a batch test; the results were compared with predictions made using a convection-diffusion model for desorption (Lee et al., 2018a). Finally, the contribution of plastic-bound intake was assessed using a one-compartment fish bioaccumulation model with an uncertainty analysis using Monte-Carlo simulation.

2. Material and methods

2.1. Materials and chemicals

High purity α- (99.8%), β- (99.5%), and γ-HCH (99.8%), pentachlorobenzene (PeCB) (98%), and hexachlorobenzene (HeCB) (99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), or Fluka (Buch, Switzerland). All partitioning and leaching experiments were conducted using two mixtures of chemicals with similar hydrophobicity: HCHs and CBs mixtures. Simulated intestinal fluid (SIF) was prepared by dissolving 500 mM potassium dihydrogen phosphate (KH_2PO_4) and 224 mM sodium hydroxide (NaOH) in deionized water (pH 6.8).

Medical-grade polydimethylsiloxane (PDMS) sheets (thickness = 1 mm, density = 1170 kg m^{-3}) were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA). The PDMS sheet was cut into disks of 6-mm diameter for partition coefficient experiments and into rectangular sheets (10 mm × 50 mm) for leaching experiments. The custom-cut PDMS disks and sheets were cleaned using *n*-hexane followed by methanol for 2 h each and stored in methanol until use.

Polyethylene (PE) films with a thickness of 75 μm and density of 940 kg m^{-3} were purchased from Goodfellow Cambridge Ltd. (Huntingdon, UK). The PE film was cut into 10 mm × 10 mm square sheets, which were cleaned using *n*-hexane followed by methanol for 2 h each and stored in methanol until use.

2.2. Determination of partition coefficients between PDMS and simulated intestinal fluid (SIF) ($K_{PDMS/SIF}$) and between polyethylene microplastics and SIF ($K_{MP/SIF}$)

Due to the low solubilities of model HOCs in the aqueous solutions, partition coefficients between microplastics and SIF ($K_{MP/SIF}$) were determined using a three-phase partitioning method (Kim et al., 2014;