

Accumulation of HOCs via Precontaminated Microplastics by Earthworm *Eisenia fetida* in Soil

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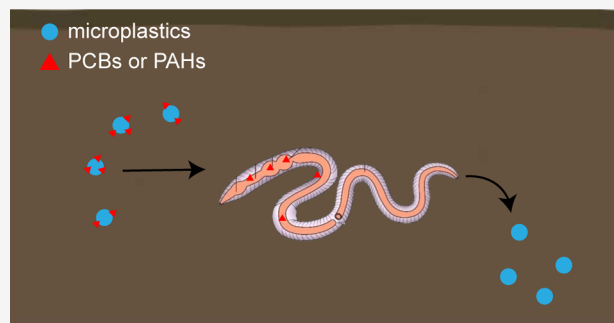


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Supporting Information

ABSTRACT: Soil is a primary sink for plastics, but the influence of microplastics as carriers on terrestrial cycling of persistent contaminants is poorly understood as compared to aquatic systems. Studies to date have disregarded the potential fact that microplastics are generally contaminated before their entry into soil. In this study, earthworm *Eisenia fetida* was incubated for 28 d in a soil amended with five common types of microplastics precontaminated with polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) to elucidate contaminant transfer. Accumulation of HOCs in *E. fetida* varied greatly among different plastic types and HOCs. The freely dissolved concentration (C_{free}) of HOCs showed that desorption of HOCs from microplastics into soil was closely related to plastic types and HOC hydrophobicity and was much slower for polystyrene or polypropylene than polyethylene. Biodynamic model analysis suggested that ingestion of microplastics could act as a significant pathway for some microplastics, likely due to HOCs on the plastics being in an “over-equilibrium” state. This was in contrast with mixing clean microplastics into HOC-contaminated soil, where the microplastics decreased bioaccumulation. Therefore, whether microplastics serve as facilitators or inhibitors of HOC bioaccumulation depends on the fugacity gradient of HOCs between microplastics and soil, which highlights the importance of considering the sequence of contamination between the plastics and soil. These findings also question the validity of short-term experiments because of the generally very slow partition kinetics of HOCs on plastics.



INTRODUCTION

The widespread contamination of microplastics (i.e., plastic particles ranging from 0.1 μm to 5 mm) has raised significant concerns due to their adverse ecological effects.^{1–6} Deleterious physiological and biochemical effects from direct ingestion of microplastics have been well documented for aquatic organisms, including marine mammals,⁷ seabirds,⁸ fish,^{9,10} turtles,¹¹ and aquatic invertebrate.^{12,13} Recent studies also demonstrated that microplastic contamination may be harmful to terrestrial faunas.^{14–17} Furthermore, due to their hydrophobicity and large specific surface areas, microplastic particles have been shown to sorb various hydrophobic organic contaminants (HOCs).^{18–20} Therefore, in addition to their direct effects, microplastics may act as carriers for transferring HOCs into organisms.²¹

A number of experimental and mathematical modeling studies have considered the potential for microplastics acting as HOC carriers in aquatic environments.^{22–26} Even though terrestrial environments are the direct and primary sink of plastics,^{27–29} our understanding of microplastics as a HOC carrier for soil-dwelling organisms is relatively limited. Microplastics may enter soil through a range of routes, i.e., application of sewage sludge, disposal of wastewater effluent, and use and disposal of plastic mulch and greenhouses in agricultural production.^{30,31} Because of the general affinity of

HOCs for plastics and the environmental stability of both HOCs and plastics, previous studies have shown contamination of various HOCs (e.g., PAHs, PCBs, PBDEs) on microplastics collected from the environment.^{25,32} Hence, a more realistic scenario is that these contaminants are already present on microplastics before their entry into soil. This is in contrast to studies to date (e.g., Besseling et al., 2013; 2017; Wang et al., 2019) where the influence of microplastics on HOCs bioaccumulation was evaluated by adding contaminant-free plastics.^{23,33,34}

When microplastics are present in a soil, they act as another sorbent phase, in addition to soil, for HOCs. Therefore, in a soil containing microplastics, HOCs are physically present in three forms, i.e., sorbed to the soil solid phase, dissolved in soil porewater, and sorbed to plastic particles. From voluminous literature, HOC sorption to and desorption from plastics are kinetically slow, ranging from weeks to even years under static

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conditions, especially for strongly hydrophobic HOCs.^{35,36} Such time scales are likely orders of magnitude longer than the equilibria for the same HOCs between soil and water, or between biological tissues and a gut fluid.^{37–39} Therefore, central to the influence of microplastics on HOC bioaccumulation is the slow sorption/desorption kinetics of HOCs on plastic particles, which, as a rate limiting step, may be expected to play a pivotal role in influencing bioaccumulation of HOCs by soil-dwelling organisms. To date, only a few modeling studies have addressed the role of the reversible sorption on HOC accumulation in aquatic organisms.^{22,23,26} Knowledge gaps still surround the extent to which microplastics affect bioaccumulation of HOCs.

In this study, we characterized bioaccumulation of HOCs in soil by the earthworm *Eisenia fetida* after introduction of precontaminated microplastics and further compared the results with that after the addition of clean microplastics to a contaminated soil. We hypothesized that (i) HOCs sorbed to microplastics can be assimilated by earthworm *E. fetida*, (ii) the efficiency in transfer of HOCs differs between the two scenarios due to constraints originated from the slow sorption kinetics, and (iii) the difference further depends on the types of plastics and HOCs.

METHODS AND MATERIALS

Materials. High-density polyethylene (HDPE), low-density polyethylene (LDPE), polystyrene (PS), polypropylene (PP), and polyvinyl chloride (PVC) particles were chosen as the typical microplastics due to their frequent detection in the environment.^{2,3} The particles were sieved to the size range of 250–300 μm to be representative of microplastics in soil.⁴¹ The particles were then cleaned with methanol to remove the adsorbed chemicals, dried at 40 $^{\circ}\text{C}$, and stored at 4 $^{\circ}\text{C}$ before use. Standards of three PCB congeners, including PCB52, PCB70, and PCB153 and three PAHs, including fluoranthene (FLA), pyrene (PYR), and benzo[α]pyrene (BaP) were chosen as the model HOCs. Thin polydimethylsiloxane fiber (430 μm diameter, 35 μm thickness) was used for the solid phase microextraction (SPME) to detect the freely dissolved concentration (C_{free}) of HOCs in the soil porewater. A sandy loam soil was collected from the Agricultural Experiment Station at University of California, Riverside. Adult *E. fetida* with well-developed clitellum were purchased from Uncle Jim's Worm Farm (Spring Grove, PA). More details on these materials are given in Supporting Information (SI).

Preloading of HOCs onto Microplastics. The microplastics were preloaded with HOCs through sorption in deionized water. Briefly, 10 g of each type of microplastic particles and 200 mL of deionized water were added into a 500 mL glass jar. A stock solution in acetone (100 μL) containing all six HOCs was added. The jars were sealed and horizontally shaken at 120 rpm at room temperature for 30 d. The microplastics particles were collected by filtering the solution through a glass fiber filter paper, rinsed with deionized water, air-dried, and stored at 4 $^{\circ}\text{C}$ before use. The initial chemical concentrations on microplastic particles were determined by GC/MS. The analytical details and the total concentrations on microplastics are given in SI.

Bioaccumulation Experiments. A similar protocol to Wang et al. (2019) was followed, with the exception that HOCs were introduced into soil via the means of precontamination of microplastics.³⁴ Briefly, adult *E. fetida* with similar sizes were removed from the culture, rinsed in

water, and kept on damp filter paper in the dark for 48 h to void their gut content. The worms were then exposed in three different treatments: noncontaminated soil only (unamended control), noncontaminated soil amended with 0.1% (w/w) HOC-contaminated spiked microplastics (0.1% MP), and noncontaminated soil amended with 1% HOC-contaminated microplastics (1% MP). These amendment rates of microplastics were likely well above environmentally relevant levels and were selected to facilitate quantitative evaluation of HOC transfer processes.⁴⁰ Five earthworms and 200 g of the treated soil (dry weight) were introduced into glass beakers, and deionized water was added to keep the soil moisture content constant ($20.0 \pm 1.0\%$). Three replicates were employed for all treatments. After exposure for 28 d, the worms were retrieved and the tissue concentrations of PAHs and PCBs were analyzed following a previously published method, and the details are given in SI.³³

Measurement of C_{free} in Soil Porewater. A previously established SPME method was used to measure the freely dissolved concentration C_{free} of HOCs in soil porewater to understand the influence of treatments on contaminant bioavailability.⁴¹ Briefly, a 1 cm PDMS fiber was placed into 5.0 g of the soil, followed by the addition of 200 mg/L sodium azide solution. The sample vials were gently mixed on a horizontal shaker at 120 rpm for 28 d at room temperature. The fibers were retrieved and the HOC concentrations on the fibers were analyzed by GC/MS. Details on extraction and instrumental analysis are given in SI. The C_{free} was derived by dividing the concentration in the PDMS fiber (C_{PDMS}) over the PDMS-water partition coefficients K_{PDMS} ⁴¹

$$C_{\text{free}} = \frac{C_{\text{PDMS}}}{K_{\text{PDMS}}} \quad (1)$$

Biodynamic Modeling of HOC Accumulation in *E. fetida*. To compare the relative contributions of the different routes of exposure, i.e., microplastic ingestion, soil particle ingestion and dermal uptake, to the HOC accumulation in *E. fetida*, a modified biodynamic model based on steady-state conditions was parametrized to describe the mass balance of chemical uptake and loss processes^{23,26,34}

$$\frac{dC_{\text{B},t}}{dt} = k_{\text{derm}} \times C_{\text{W}} + IR \times S_{\text{soil}} \times a_{\text{soil}} \times C_{\text{soil}} + IR \times S_{\text{PL}} \times C_{\text{PLR},t} - k_{\text{loss}} \times C_{\text{B},t} \quad (2)$$

where $dC_{\text{B},t}/dt$ ($\mu\text{g}/(\text{g} \times \text{d})$) is the total accumulation of HOCs in the earthworm; $k_{\text{derm}} \times C_{\text{free}}$ is the uptake from dermal sorption via porewater, which is the product of C_{free} in the porewater ($\mu\text{g}/\text{L}$) and the dermal uptake rate constant k_{derm} ($(\text{L} \times \mu\text{g})/\text{d}$); $IR \times S_{\text{soil}} \times a_{\text{soil}} \times C_{\text{soil}}$ represents the accumulation through soil ingestion, with IR as the soil ingestion rate ($\text{g}/(\text{g} \times \text{d})$), a_{soil} the absorption efficiency from the ingested soil, S_{soil} the mass fraction of soil in the diet, and C_{soil} the HOC concentration in the soil; and $IR \times S_{\text{PL}} \times C_{\text{PLR},t}$ equals the accumulation through plastic particle ingestion, with S_{PL} as the mass fraction of plastics in the diet and $C_{\text{PLR},t}$ ($\mu\text{g}/\text{g}$) the net concentration transferred from plastic during gut passage at time t . The sum of mass fractions of soil and plastic particles in the diet is assumed to be 1, i.e., $S_{\text{soil}} + S_{\text{PL}} = 1$. The overall loss through elimination and egestion is given by $k_{\text{loss}} \times C_{\text{B},t}$ where k_{loss} (d^{-1}) is the first-order rate constant for the loss. Additional details on the parameters and the model are shown in the SI.

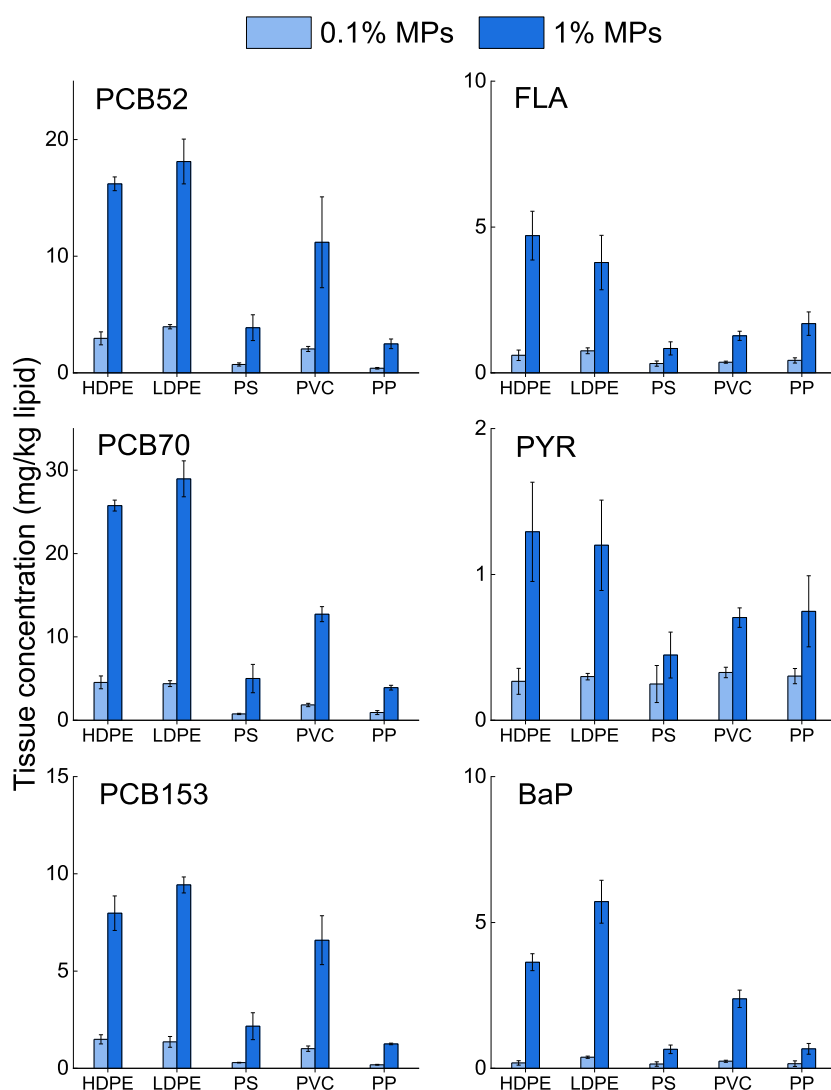


Figure 1. Concentrations of HOCs in earthworm tissues after exposure to soil amended with 0.1% or 1% contaminated microplastics. HDPE = high-density polyethylene; LDPE = low-density polyethylene; PS = polystyrene; PP = polypropylene; PVC = polyvinyl chloride. Data are described as mean \pm SD ($n = 3$).

Quality Control and Statistical Analysis. All measurements were conducted in triplicates, and the results were expressed as mean \pm standard deviation. External surrogates and internal standards were used in all samples to monitor the extraction efficiency and calibrate for potential instrument drift. A known amount of HOCs was spiked into clean plastics or earthworms to measure the method recovery, which ranged from $82.7 \pm 4.5\%$ to $112.5 \pm 3.2\%$. The limits of instrumental detection of the six HOCs were 0.05–0.1 ng/mL. An eight-point calibration curve ranging from 1 to 500 ng/mL was used for instrumental calibration, and the regression coefficient was ≥ 0.99 . Statistical differences (one-way analysis of variance, ANOVA) between different groups were performed with the SPSS 19.0 software package. All of the plots were created using Origin 2019b. Differences were considered statistically significant at $p < 0.05$.

RESULTS AND DISCUSSION

Bioaccumulation of HOCs in Earthworm. The accumulation of HOCs in *E. fetida* in soil amended with microplastic particles precontaminated with HOCs was assessed by deriving

lipid normalized HOC concentrations in the earthworm. *E. fetida* was found to accumulate HOCs in all treatments (Figure 1). For example, in the soil with 0.1% LDPE microplastic amendment, the summed concentrations of the three PAHs and three PCBs were 0.29–0.76 and 1.36–4.69 mg/kg, respectively. Amendment of the contaminated microplastics at the higher rate resulted in further increases in the tissue concentration; the lipid content normalized tissue concentrations of three PAHs and three PCBs increased to 1.21–5.71 and 9.43–28.97 mg/kg, respectively, in the soil with 1% LDPE microplastics. The concentrations of individual HOCs in the earthworm further varied with the types of plastics. The tissue HOC concentrations were consistently higher in the soil amended with polyethylene microplastics than with the other plastic types. For instance, in the soil amended with microplastics at 1%, the mean PCB52 concentrations in the earthworm were 18.12 and 16.20 mg/kg for LDPE and HDPE, respectively, which were significantly higher ($P < 0.05$) than those for PVC, PS, or PP (11.19, 3.87, and 2.49 mg/kg, respectively). Similarly, the mean tissue concentrations of FLA in the soil amended with LDPE and HDPE were 3.78 and 4.71 mg/kg, respectively, which were 2.2–5.9 folds that in the PVC,

PS or PP amended soil. In the soil amended with microplastics at 0.1%, a similar pattern was also observed for the three PCB congeners, although statistically significant difference was not always found in the tissue concentrations of the three PAHs between the polyethylene plastics and the other types of plastics, likely due to the lower amendment rate and uncertainties in measurement.

To compare the efficiency in the transfer of HOCs between microplastic and natural soil particles, the unamended (plastic-free) soil was spiked with the six HOCs at concentrations similar to those with 1% precontaminated LDPE. After exposure for 28 d, the lipid normalized levels of HOCs in earthworm in the unamended soil were significantly higher than those in the soil amended with microplastics. For example, the mean tissue concentrations of PCB70, PCB 153, and BaP were 59.04, 29.46, and 16.25 mg/kg lipid, respectively, which were 2.0–3.1 times higher than those in the soil amended with 1% precontaminated LDPE (Figure S1). This finding implied that under the experimental conditions, microplastics not only acted as the source of HOCs but also served as a stronger sorptive sink than soil organic matter, leading to an overall reduced HOC bioavailability. In our previous study (Wang et al., 2019) where clean microplastics were added in HOC-spiked soil, the earthworm tissue concentrations of HOCs in soil without microplastics were 1.9–2.6 fold higher than those in the soil amended with LDPE at 1%.³⁴ The likewise decreases in tissue concentrations caused by microplastics in relation to plastic-free soil suggested that plastic particles can simultaneously serve as both a source and a sink for HOCs. The overall negative influence of microplastics on HOC bioavailability in soil is likely driven by the fact that sorption/desorption kinetics of HOCs for plastics is considerably slower than that for soil or biological tissues. It must be noted that in the real environment, the level of microplastics in soils is likely much lower than those considered in this study; therefore, the role of microplastics acting as a competitive sink for contaminants may be significantly smaller.

In Wang et al. (2019), the same soil as in the present study was first treated with the same suite of HOCs, and contaminant-free microplastics were then amended at 0.1% or 1%, followed by a 28 d bioaccumulation assay using *E. fetida*.³⁴ Given that the two studies were conducted under essentially the same conditions, with the exception that HOCs entered the soil differently, i.e., via contaminated soil or contaminated microplastics, biota-soil accumulation factor (BSAF) was calculated for both studies using the total soil concentration as the denominator (Figure 2). BSAFs for the treatments with precontaminated microplastics in this study were smaller than those in the previous study. For example, BSAFs for PCB52, PCB153, and BaP were 223.3, 103.6, and 18.8, respectively, in this study, which were smaller than those in the previous study (302.1, 154.3, and 108.9, respectively). Even greater differences were observed for the treatments with 1% PS microplastics. The BSAFs of PCB52, PCB153, and BaP in the precontaminated soil amended with clean PS were 364.8, 180.5, and 204.5, respectively, which were 6.81–32.6 times greater than those in the clean soil amended with 1% precontaminated PS particles. The relative decreases in bioaccumulation by the earthworm when contaminated microplastics were introduced into a plastic-free soil suggested that the bioavailability of HOCs under the simulated conditions was inhibited, likely due to slow desorption of

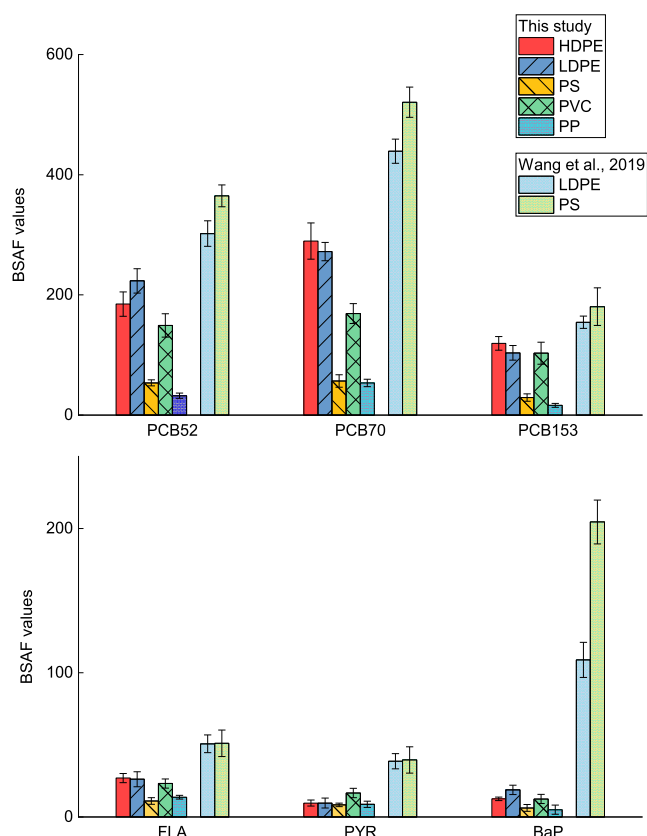


Figure 2. Comparison of biota-soil accumulation factors (BSAFs) in the current study with a previous study where clean plastics were amended in HOC-contaminated soils ($n = 6$). HDPE = high-density polyethylene; LDPE = low-density polyethylene; PS = polystyrene; PP = polypropylene; PVC = polyvinyl chloride.

HOCs from the microplastics into the soil, leading to lower HOC levels in the soil porewater (C_{free}) and on the soil particles (C_{soil}), as compared to the contaminated soil treatments. This effect was more pronounced for microplastics such as PS, suggesting that desorption of HOCs from PS particles was comparatively slower than that for PE particles.

C_{free} of HOCs in Soil Porewater. When precontaminated microplastics enter soil, HOCs are desorbed from microplastics into soil porewater, and a fraction of the desorbed HOC is subsequently adsorbed onto soil particles. Therefore, HOCs may be assimilated by earthworm via two general routes: dermal absorption via soil porewater and ingestion of contaminated soil and plastic particles.^{42,43} To evaluate the relative contribution of dermal uptake, C_{free} in soil porewater was measured by a previously reported passive sampling method.⁴⁰ The C_{free} values of all HOCs were significantly greater in the soils amended with 1% microplastics than those with microplastics at 0.1% (Table S2). For instance, the C_{free} values of PCB52 in soils amended with 1% microplastics ranged from 13.7–55.7 ng/L, which were significantly greater than those in soil containing microplastics at 0.1% (3.4–7.7 ng/L). The C_{free} values further varied among the different types of plastic polymers as well as HOCs.

To better relate bioavailability of HOCs as a function of plastic types, amendment rate, and HOCs, the free fraction (ff) of HOCs was calculated by dividing the C_{free} over the total concentration (C_{total}) of HOCs in the soil⁴⁴

$$ff = \frac{C_{\text{free}}}{C_{\text{total}}} \times D \quad (3)$$

where C_{total} was obtained by multiplying the initial HOC concentration in microplastics (C_{plastic}) and the microplastic mass fraction (f_{plastic}), and D (L/kg) was the ratio of the water volume to the soil weight. In comparison with PE, the ff values of PS treatments were consistently smaller for most HOCs at the same amendment rate (Figure 3). For example, the mean ff

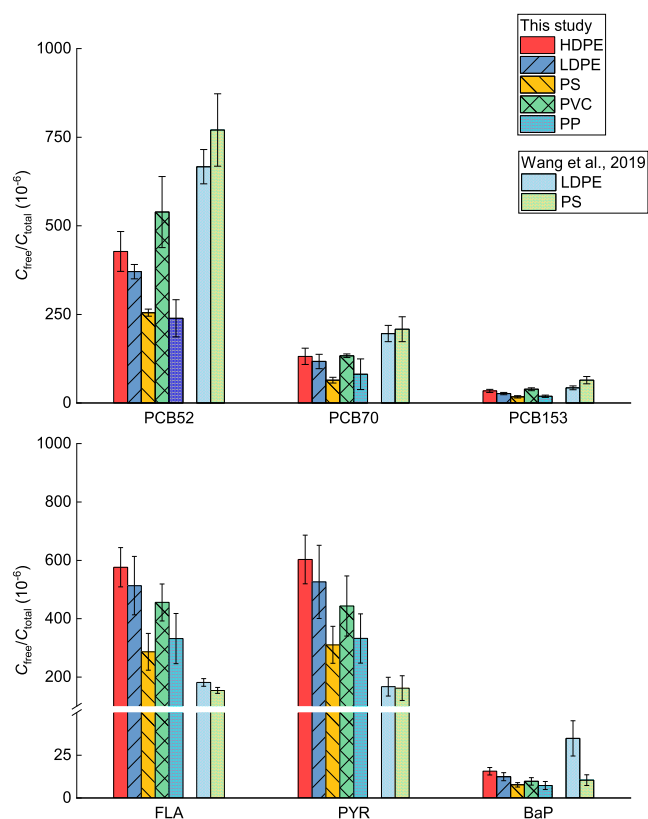


Figure 3. Comparison of HOC free fractions in the current study and a previous study where clean plastics were amended in HOC-contaminated soils ($n = 6$). HDPE = high-density polyethylene; LDPE = low-density polyethylene; PS = polystyrene; PP = polypropylene; PVC = polyvinyl chloride.

values of PCB52, PCB70, and PCB153 were 3.40×10^{-4} , 8.83×10^{-5} , and 2.18×10^{-5} , respectively, in the soil amended with PS, which were statistically smaller than those in the HDPE amended soil (6.22×10^{-4} , 1.88×10^{-4} , and 5.42×10^{-5} , respectively). According to their glass transition temperatures, polymers may be categorized into rubbery (e.g., HDPE, LDPE, and PP) or glassy (e.g., PVC and PS) polymers.^{45–47} Due to the cross-linking of chains, PS is known to have a dense glassy structure and may form internal pores.⁴⁸ Moreover, PS has benzene molecules in the polymeric backbone, restricting the segmental mobility of HOCs within the PS chains.⁴⁹ These properties of PS may have contributed to irreversible sorption or very slow desorption, resulting in decreased HOC release from PS into the soil in this study. Although PVC is also a type of glassy amorphous polymer, the ff values were relatively high. For instance, the ff values of PCB52 in the different microplastic treatments followed the order of HDPE (6.22×10^{-4}) > PVC (5.52×10^{-4}) > LDPE (5.02×10^{-4}) > PS (3.40×10^{-4}) \approx PP (3.39×10^{-4}), suggesting that other factors,

such as cohesive density of PVC, may also affect HOC desorption from plastics. Previous studies suggested that the cohesive density may create attractive forces between the individual PVC chains and therefore reduce the free volume when compared with other polymers.⁴⁹ The lack of free volume in PVC may have inhibited the diffusion of HOCs into PVC, limiting sorption to mostly interfacial deposition on the particle surfaces and allowing easier desorption of the sorbed HOCs.

In addition, for the same plastic type, a decreasing trend (Figure S2) in ff values was observed with increasing octanol–water partition coefficients (K_{ow}) and molecular weights (MW) among the six HOCs ($P < 0.05$), indicating that desorption of HOCs from the same microplastics decreased with increasing hydrophobicity or MW.⁵⁰ While there was no significant difference between FLA and PYR, a pair of isomers, in the derived ff values, BaP, with substantially greater hydrophobicity, displayed ff values of only about 2% of those for FLA or PYR.

The ff values calculated in the current study were subsequently compared with those in Wang et al. (2019) where a precontaminated soil was amended with clean microplastic particles (Figure 3). The ff values were consistently smaller in the same soil–plastic combinations in this study, with exception of FLA and PYR. The lower ff values for HOCs with greater hydrophobicity in this study may be again attributed to the fact that HOCs were far from attaining phase equilibrium between the plastic particles and soil under the experimental conditions. From previous studies on the partition of HOCs between plastic films and water, very long-time intervals are needed to achieve phase equilibrium. For example, for the strongly hydrophobic DDT compounds, equilibrium was not achieved for a 51 μm PE film even after one year under field conditions.³⁶ Choi et al. (2016) reported that only 20% of PCB192 preloaded onto a 17 μm PE film was desorbed after 265 d in a sediment.⁵¹ Several studies further showed slow mass transfer from microplastics to the surrounding environments under static conditions. For instance, Endo et al. (2013) evaluated desorption of PCBs from field-collected PE pellets via long-term desorption and diffusion modeling, and estimated that the time to reach equilibrium spanned from 2.8 yr for PCB8 and up to 3500 yr for PCB209 under near static conditions.⁵² Therefore, given that the precontaminated microplastics were in contact with the soil for only 28 d in this study, HOCs on the microplastics may be assumed to be in the state of “over-equilibrium”, while soil (and soil porewater) were in the state of “under-equilibrium”. The deviations from equilibrium were greater for PS than for PE for the same HOC and also greater for more hydrophobic HOCs (Figure 3). Given that HOCs in soil and soil porewater are more bioavailable to the earthworm than in microplastics, lower ff values in this study likely contributed to the lower earthworm bioaccumulation than in the previous study.

Evaluation of Relative Importance of Uptake Pathways. Passive samplers have been used in previous studies to predict bioavailability and further tissue concentrations of HOCs in sediments or soils (e.g., Joyce et al., 2016; Wang et al., 2018).^{39,53} The concentrations of HOCs in earthworms in the current study were first predicted from C_{free} and individual bioconcentration factor (BCF) values

$$C_{\text{worm}} = C_{\text{free}} \times \text{BCF} \quad (4)$$

where the BCF values were calculated using the empirical relationships in Connell and Markwell (1990).⁵⁴ After log transformation, the predicted HOC concentrations were plotted against the measured earthworm tissue levels in this study (Figure 4). A significant linear correlation was observed

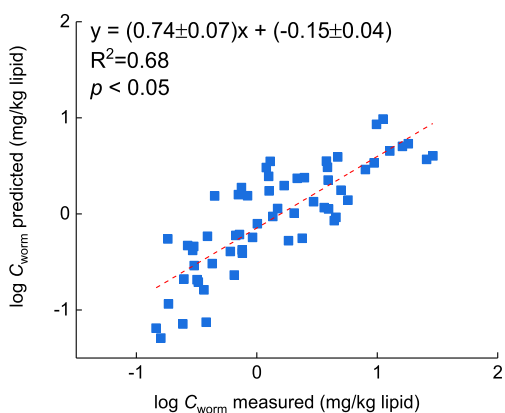


Figure 4. Relationship between C_{free} predicted tissue concentrations and experimentally measured tissue concentrations in *E. fetida*.

with $R^2 > 0.68$ ($P < 0.05$). However, the slope of this linear relationship (0.74 ± 0.07) was statistically smaller than 1, suggesting that on average, dermal absorption accounted for about 74% of bioaccumulation. However, there was considerable data scattering, implying that ingestion of microplastics and/or soil particles was also a significant source for the accumulation of HOCs in earthworms in some plastic-HOC treatments under the experimental conditions.

The mass balance of chemical uptake and loss processes was subsequently evaluated using the modified biodynamic model in eq 2. The results indicated that the modeled tissue concentrations on day 28 agreed well with the measured C_{worm} values (Figure 5), with a highly significant linear correlation ($R^2 = 0.97$, $P < 0.001$). In particular, the slope of the linear regression (0.98 ± 0.02) was statistically equal to 1 indicating that the biodynamic model was capable of accounting for the different exposure pathways in predicting HOC concentrations in earthworm in a soil with precontami-

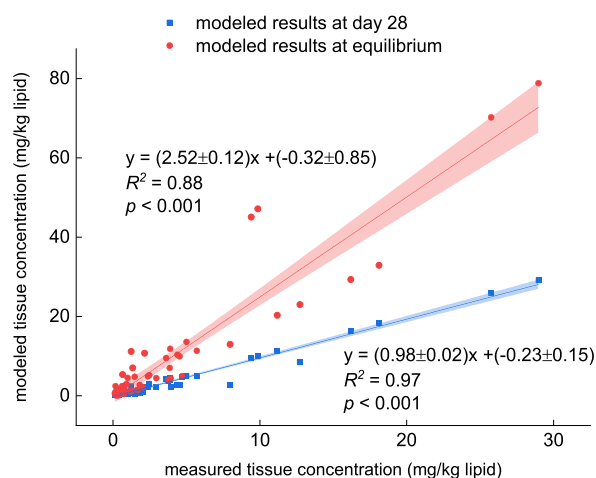


Figure 5. Relationship between biodynamic modeled tissue concentrations and experimentally measured tissue concentration in *E. fetida*.

nated microplastic particles. The tissue concentrations of HOCs were further predicted using the biodynamic model under complete phase equilibrium conditions and plotted against the measured tissue concentrations (Figure 5). A highly significant linear correlation ($R^2 = 0.88$, $P < 0.001$) was also observed; however, the slope (2.52 ± 0.12) was substantially greater than 1, suggesting that the desorption of HOCs from microplastics to soil, and/or during passage in the gut of earthworm, was likely far from equilibrium under the experimental conditions. This observation was consistent with the above finding for C_{free} that long-time intervals would be needed for attaining phase equilibrium of HOCs among microplastics, soil, and soil porewater. Previous studies suggested that desorption of HOCs from the ingested microplastics may be divided into two stages, i.e., a relatively fast release from the outer reservoir of the plastic and a much slower release governed by intrapolymer transport. Mohamed Nor and Koelmans⁵⁵ reported that more than 50 d was required to achieve equilibrium for PCB desorption from PE and PVC microplastics to artificial gut fluid at the slower stage. Therefore, over the time scale of 28 d in this study, it was unlikely for the redistribution of HOCs between microplastics and soil particles to reach equilibrium, particularly for HOCs with larger $\log K_{\text{ow}}$ values and for some of the plastic types such as PS. Given the short passage time in the earthworm gut for ingested particles (about 6 h),⁴³ desorption of HOCs from microplastics into the gut fluid after uptake was likely even further away from equilibrium.

The relative contributions via dermal uptake, soil ingestion, and plastic ingestion were consequently estimated by dividing each term in eq 2 over the total predicted tissue concentration (Figure 6). The contribution of soil ingestion to the total bioaccumulation was relatively small, with the exception of PCB153 and BaP in the soil with the microplastics amended at 0.1%, indicating that bioaccumulation via soil ingestion was closely linked to the hydrophobicity of HOCs. This may be attributed to the fact that the strong hydrophobicity of PCB153 and BaP led to significant sorption to soil particles and hence a greater relative contribution. Interestingly, the relative contribution of soil ingestion decreased when microplastics were amended at 1%, likely due to the fact that microplastics were a stronger competitive sorbent phase than soil. Compared to Wang et al. (2019), the relative contributions of soil ingestion were consistently smaller under the current experimental conditions.³⁴ For example, in the soils amended with LDPE at 1%, the relative contributions of soil ingestion for PCB52, PCB70, and BaP were 0.3, 0.8, and 3.11%, respectively, while in the previous case, the contributions were 15.9, 37.5, and 63.9%, respectively. Similar trends were also observed for the soils amended with PS particles in the two studies. This observation may be again attributed to the lack of phase equilibrium of HOCs between microplastics and soil. In the present study, the HOCs needed to desorb from microplastics particles into soil porewater, and some of the desorbed HOCs was then adsorbed by soil particles and subsequently accumulated in earthworm via soil ingestion. However, the slow mass transfer of HOCs from microplastics likely led to relatively low HOC concentrations in soil porewater and on the soil solids, thus decreasing the relative contribution of soil ingestion to the bioaccumulation in the earthworm.

It is evident that although the average contribution of dermal uptake was about 74%, it varied greatly among the different

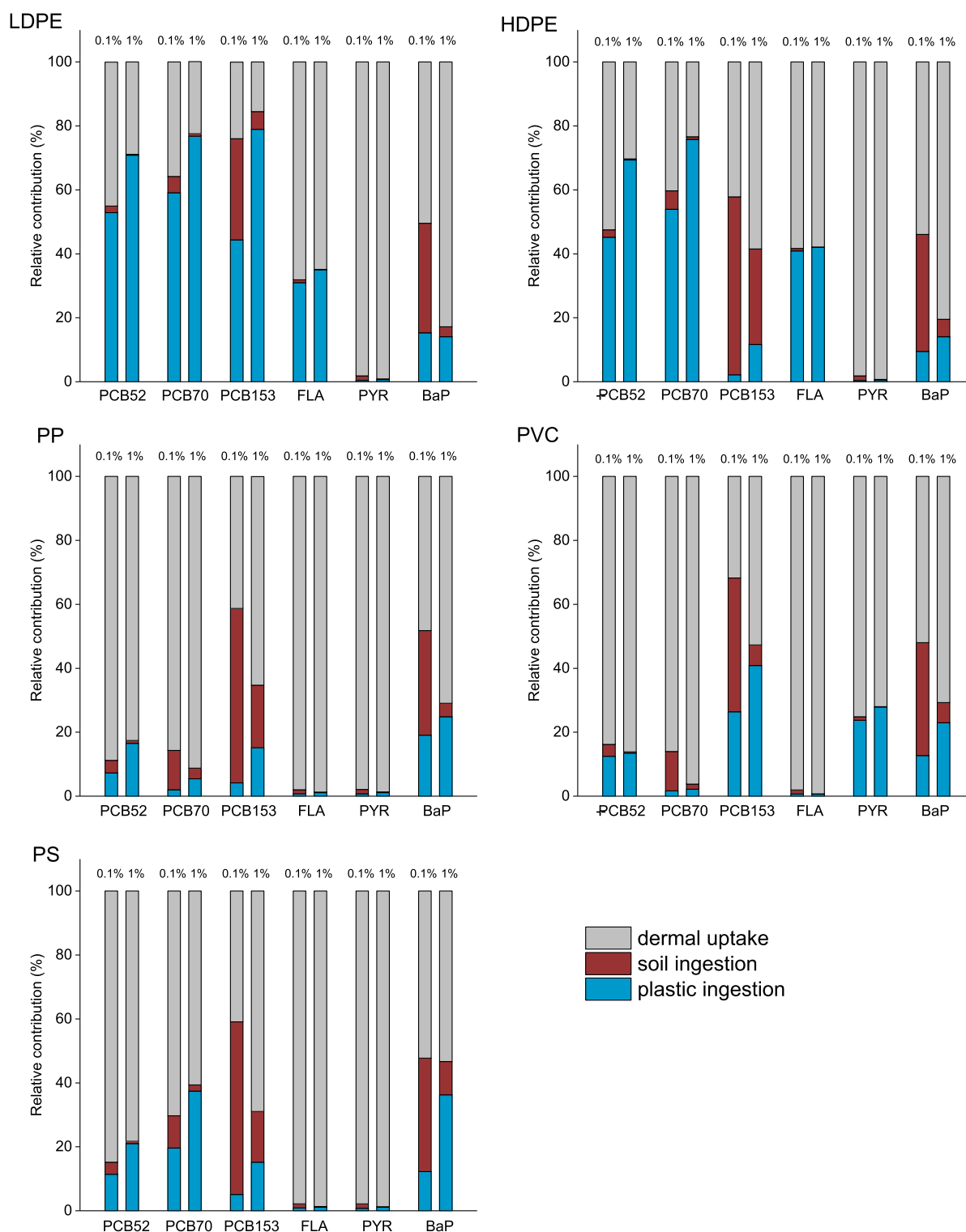


Figure 6. Relative contribution of the various uptake pathways for HOC bioaccumulation in *E. fetida* in different treatments. HDPE = high-density polyethylene; LDPE = low-density polyethylene; PS = polystyrene; PP = polypropylene; PVC = polyvinyl chloride.

plastic and HOC types, ranging from 15.5 to 98.7% (Figure 6). In general, dermal uptake contributed more predominantly for PS, PP, and PVC than PE plastics and for the same types of plastics, for lower molecular weight PAHs and PCBs. For example, for PP or PS, dermal uptake contributed >97% to the total bioaccumulation of FLA and PYR (Figure 6). Concurrently, the relative contribution of plastic ingestion also varied, and was greater for LDPE and HDPE than for the

other plastics, especially for the higher molecular weight PCBs and PAHs. For example, the relative contribution of microplastic ingestion for PCB153 accumulation in soil amended with 1% LDPE was 78.9% but was negligible for FLA and PYR in the soil amended with 1% PS or PP (Figure 6). Again, due to the long time needed for the precontaminated HOCs to reestablish phase equilibrium, HOCs on microplastics were likely in an “over-equilibrium” state when the plastic particles

were passing through the earthworm gut. This could have led to the elevated contribution to the overall bioaccumulation through ingestion of PE particles.⁵⁶ However, sorption of HOCs on PS or PP was likely irreversible, resulting in limited contribution from ingestion of PS or PP microplastics. Additionally, relatively small diffusion coefficients of HOCs have been documented in PS or PP than PE,⁵⁷ and the low diffusivities may have also added to the limited contribution. In contrast to the generally important contribution from plastic ingestion in the current study, Wang et al. (2019) reported that the contribution of plastic ingestion was very limited in the scenario where clean microplastics were added at 0.1% and 1% into a precontaminated soil.³⁴ For example, in the contaminated soils amended with 1% LDPE particles, the relative contribution of plastic ingestion for PCB153 accumulation was only 1.03%, which was significantly smaller than the values in the current study. When clean microplastics were added to a HOC-contaminated soil, HOCs must desorb from soil particles into porewater, and a fraction of the desorbed HOCs is then sorbed onto the microplastics. However, as a long time is needed for the HOCs to reach distribution equilibrium, the microplastic particles in the latter case would be in a state of “under-equilibrium”, and microplastics would continually sorb HOCs from the system, e.g., during the passage through the gut of earthworm, leading to a net decrease in HOC bioaccumulation. Therefore, the relative contribution of microplastic ingestion to the overall HOC bioaccumulation by soil-dwelling organisms may differ greatly depending on the fugacity gradients of the HOCs between the earthworm and the ingested microplastics.

It must be emphasized that under field conditions, the contact time of microplastics and soil could be substantially longer, and thus the distribution of HOCs between microplastics, soil, and soil porewater under field conditions may be expected to be closer to phase equilibrium than the laboratory exposure. Considering that the lifetime of earthworm can be up to 4 years,⁵⁸ the bioaccumulation of HOCs may be several times greater than that derived via short-term (e.g., 28 d) exposure tests. Thus, short-term laboratory experiments may represent a significant underestimation of the actual bioaccumulation of HOCs from contaminated plastics under field conditions. Additionally, ideal geometries (i.e., spheres) were assumed for the microplastics used in this study, while plastic particles detected in the environment are usually irregular in shape.⁵⁹ These irregular microplastics have various cross-sectional areas, which may further influence the diffusion and sorption of HOCs in microplastics.⁶⁰ Furthermore, previous studies documented that weathering can affect the sorption properties of microplastics by eroding the surface and generating oxygen functional groups.^{61–63} For instance, Muller et al.⁶⁴ reported that weather aging induced the generation of oxidized surface layer on PS microplastics and decreased the sorption of fuel aromatics. Weathering may also change the size, color, and surface biofilm of microplastics, which potentially influence the ingestion of microplastics by organisms.⁶⁵ Therefore, how processes such as weathering under environmentally relevant conditions affect the interactions of microplastics and contaminant cycling merits further investigation.

This study simulated a more probable exposure scenario for microplastic-borne contaminants to soil-dwelling organisms. The results showed that earthworm *E. fetida* was capable of accumulating HOCs when a soil was amended with HOC-

contaminated microplastics. The tissue concentrations varied greatly among different types of plastics and HOC compounds. Analysis of freely dissolved fractions of HOCs in soil suggested that desorption of HOCs from glassy polymers, such as PS, PVC, and PP, was more limited than the rubbery polymer PE, likely due to partially irreversible sorption. Evaluation of the relative contributions of the different uptake routes using a biodynamic model highlighted a predominant role of dermal absorption for bioaccumulation of HOCs by *E. fetida* for most plastic-HOC combinations, with an average contribution of about 74%. However, the relative contribution of plastic ingestion increased substantially for PE particles and became predominant for PCBs. The enhanced contribution of PE particles was attributable to “over-equilibrium” of HOCs on the plastics due to slow desorption, while the limited contribution of PS, PP, or PVC particles was likely caused by irreversible sorption of HOCs on these plastics. Ingestion of soil particles played a relatively small role. When clean microplastics were amended to HOC-contaminated soil, bioaccumulation of HOCs by *E. fetida* was generally greater than that observed in this study. In addition, the relative contributions of the different uptake routes to the overall bioaccumulation differed significantly between the two scenarios. Therefore, the influence of microplastics as a vector on bioaccumulation of contaminants such as HOCs by soil fauna depends closely on the sequence of contamination between microplastics and soil. Although not considered in this study, the slow sorption/desorption kinetics for many hydrophobic contaminants on plastics may play a similarly important role in bioaccumulation and toxicity in other systems, such as water column and sediment. These findings also imply that due to slow sorption kinetics of many contaminants on plastics, short-term exposure experiments produce incorrect predictions of bioaccumulation of persistent contaminants and ecotoxicological effects in systems polluted with microplastics.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c02922>.

Section S1, materials; Section S2, measurement of HOC concentration in microplastics; Section S3, measurement of HOC concentration in earthworm; Section S4, measurement of HOC concentration in fibers; Section S5, instrumental analysis; Section S6, biodynamic model for the accumulation of HOCs; Table S1, total concentration of HOCs on microplastics; Table S2, freely dissolved concentration of HOCs; Table S3, species-specific parameters for the model; Table S4, chemical-specific parameters for the model; Figure S1, comparison of tissue concentration; Figure S2, relationship between $\log K_{ow}$ values and K_{ow} and MW (PDF)

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Notes

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REFERENCES

- (1) Cole, M.; Lindeque, P.; Halsband, C.; Galloway, T. S. Microplastics as contaminants in the marine environment: A review. *Mar. Pollut. Bull.* **2011**, *62*, 2588–2597.
- (2) Galloway, T. S.; Lewis, C. N. Marine microplastics spell big problems for future generations. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 2331–2333.
- (3) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. Plastic waste inputs from land into the ocean. *Science* **2015**, *347*, 768–771.
- (4) Law, K. L.; Moret-Ferguson, S.; Maximenko, N. A.; Proskurowski, G.; Peacock, E. E.; Hafner, J.; Reddy, C. M. Plastic accumulation in the North Atlantic subtropical gyre. *Science* **2010**, *329*, 1185–1188.
- (5) Sussarellu, R.; Suquet, M.; Thomas, Y.; Lambert, C.; Fabioux, C.; Pernet, M. E. J.; Goïc, N. L.; Quillien, V.; Mingant, C.; Epelboin, Y.; Corporeau, C.; Guyomarch, J.; Robbens, J.; Paul-Pont, I.; Soudant, P.; Huvet, A. Oyster reproduction is affected by exposure to polystyrene microplastics. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113*, 2430–2435.
- (6) Wright, S. L.; Kelly, F. J. Plastic and human health: A micro issue? *Environ. Sci. Technol.* **2017**, *51*, 6634–6647.
- (7) Nelms, S. E.; Galloway, T. S.; Godley, B. J.; Jarvis, D. S.; Lindeque, P. K. Investigating microplastic trophic transfer in marine top predators. *Environ. Pollut.* **2018**, *238*, 999–1007.
- (8) Amelineau, F.; Bonnet, D.; Heitz, O.; Mortreux, V.; Harding, A. M. A.; Karnovsky, N.; Walkusz, W.; Fort, J.; Gremillet, D. Microplastic pollution in the Greenland Sea: Background levels and selective contamination of planktivorous diving seabirds. *Environ. Pollut.* **2016**, *219*, 1131–1139.
- (9) Lusher, A. L.; McHugh, M.; Thompson, R. C. Occurrence of microplastics in the gastrointestinal tract of pelagic and demersal fish from the English Channel. *Mar. Pollut. Bull.* **2013**, *67*, 94–99.
- (10) Neves, D.; Sobral, P.; Ferreira, J. L.; Pereira, T. Ingestion of microplastics by commercial fish off the Portuguese coast. *Mar. Pollut. Bull.* **2015**, *101*, 119–126.
- (11) Caron, A. G. M.; Thomas, C. R.; Berry, K. L. E.; Motti, C. A.; Ariel, E.; Brodie, J. E. Ingestion of microplastic debris by green sea turtles (*Chelonia mydas*) in the Great Barrier Reef: Validation of a sequential extraction protocol. *Mar. Pollut. Bull.* **2018**, *127*, 743–751.
- (12) Lee, K. W.; Shim, W. J.; Kwon, O. Y.; Kang, J. H. Size-dependent effects of micro polystyrene particles in the marine copepod *Tigriopus japonicus*. *Environ. Sci. Technol.* **2013**, *47*, 11278–11283.
- (13) Rehse, S.; Kloas, W.; Zarfl, C. Short-term exposure with high concentrations of pristine microplastic particles leads to immobilisation of *Daphnia magna*. *Chemosphere* **2016**, *153*, 9199.
- (14) Huerta Lwanga, E.; Gertsen, H.; Gooren, H.; Peters, P.; Salanki, T.; van der Ploeg, M.; Besseling, E.; Koelmans, A. A.; Geissen, V. Microplastics in the terrestrial ecosystem: Implications for *Lumbricus terrestris* (Oligochaeta, lumbricidae). *Environ. Sci. Technol.* **2016**, *50*, 2685–1672.
- (15) Huerta Lwanga, E.; Gertsen, H.; Gooren, H.; Peters, P.; Salanki, T.; van der Ploeg, M.; Besseling, E.; Koelmans, A. A.; Geissen, V. Incorporation of microplastics from litter into burrows of *Lumbricus terrestris*. *Environ. Pollut.* **2017**, *220*, 523–531.
- (16) Rodriguez-Seijo, A.; da Costa, J. P.; Rocha-Santos, T.; Duarte, A. C.; Pereira, R. Oxidative stress, energy metabolism and molecular responses of earthworms (*Eisenia fetida*) exposed to low-density polyethylene microplastics. *Environ. Sci. Pollut. Res.* **2018**, *25*, 33599–33610.
- (17) Rodriguez-Seijo, A.; Lourenço, J.; Rocha-Santos, T. A. P.; Costa, J. D.; Duarte, A. C.; Vala, H.; Pereira, R. Histopathological and molecular effects of microplastics in *Eisenia andrei* Bouche. *Environ. Pollut.* **2017**, *220*, 495–503.
- (18) Al-Odaini, N. A.; Shim, W. J.; Han, G. M.; Jang, M.; Hong, S. H. Enrichment of hexabromocyclododecanes in coastal sediments near aquaculture areas and a wastewater treatment plant in a semi-enclosed bay in South Korea. *Sci. Total Environ.* **2015**, *505*, 290–298.
- (19) Gauquie, J.; Devriese, L.; Robbens, J.; De Witte, B. A qualitative screening and quantitative measurement of organic contaminants on different types of marine plastic debris. *Chemosphere* **2015**, *138*, 348–356.
- (20) Rochman, C. M.; Manzano, C.; Hentschel, B. T.; Simonich, S. L. M.; Hoh, E. Polystyrene plastic: A source and sink for polycyclic aromatic hydrocarbons in the marine environment. *Environ. Sci. Technol.* **2013**, *47*, 13976–13984.
- (21) Hartmann, N. B.; Rist, S.; Bodin, J.; Jensen, L. H.; Schmidt, S. N.; Mayer, P.; Meibom, A.; Baun, A. Microplastics as vectors for environmental contaminants: Exploring sorption, desorption, and transfer to biota. *Integr. Environ. Assess. Manage.* **2017**, *13*, 488–493.
- (22) Bakir, A.; O' Connor, I. A.; Rowland, S. J.; Hendriks, A. J.; Thompson, R. C. Relative importance of microplastics as a pathway for the transfer of hydrophobic organic chemicals to marine life. *Environ. Pollut.* **2016**, *219*, 56–65.
- (23) Besseling, E.; Foekema, E. M.; van den Heuvel-Greve, M. J.; Koelmans, A. A. The effect of microplastic on the uptake of chemicals by the lugworm *Arenicola marina* (L.) under environmentally relevant exposure conditions. *Environ. Sci. Technol.* **2017**, *51*, 8795–8804.
- (24) Chua, E. M.; Shimeta, J.; Nuggeoda, D.; Morrison, P. D.; Clarke, B. O. Assimilation of polybrominated diphenyl ethers from microplastics by the marine amphipod, *Allorchestes compressa*. *Environ. Sci. Technol.* **2014**, *48*, 8127–8134.
- (25) Herzke, D.; Anker-Nilssen, T.; Nost, T. H.; Gotsch, A.; Christensen-Dalsgaard, S.; Langset, M.; Fangel, K.; Koelmans, A. Negligible impact of ingested microplastics on tissue concentrations of persistent organic pollutants in northern fulmars off coastal Norway. *Environ. Sci. Technol.* **2016**, *50*, 1924–1933.
- (26) Koelmans, A. A.; Bakir, A.; Burton, G. A.; Janssen, C. R. Microplastic as a vector for chemicals in the aquatic environment: Critical review and model supported reinterpretation of empirical studies. *Environ. Sci. Technol.* **2016**, *50*, 3315–3326.
- (27) Rochman, C. M. Microplastics research - From sink to source. *Science* **2018**, *6384*, 28–29.
- (28) Nizzetto, L.; Futter, M.; Langaas, S. Are agricultural soils dumps for microplastics of urban origin? *Environ. Sci. Technol.* **2016**, *50*, 10777–10779.
- (29) Nizzetto, L.; Langaas, S.; Futter, M. Pollution: do microplastics spill on to farm soils? *Nature* **2016**, *537*, 488–488.

- (30) Mahon, A. M.; Connell, B. O.; Healy, M. G.; Connor, I. O.; Officer, R.; Nash, R.; Morrison, L. Microplastics in sewage sludge: Effects of treatment. *Environ. Sci. Technol.* **2017**, *51*, 810–818.
- (31) Rillig, M. C. Microplastic in terrestrial ecosystems and the soil? *Environ. Sci. Technol.* **2012**, *46*, 6453–6454.
- (32) Mai, L.; Bao, L. J.; Shi, L.; Liu, L. Y.; Zeng, E. Y. Polycyclic aromatic hydrocarbons affiliated with microplastics in surface waters of Bohai and Huanghai Seas, China. *Environ. Pollut.* **2018**, *241*, 834–840.
- (33) Besseling, E.; Wegner, A.; Foekema, E. M.; van den Heuvel-Greve, M. J.; Koelmans, A. A. Effects of microplastic on fitness and PCB bioaccumulation by the lugworm *Arenicola marina* (L.). *Environ. Sci. Technol.* **2013**, *47*, 593–600.
- (34) Wang, J.; Coffin, S.; Sun, C. L.; Schlenk, D.; Gan, J. Negligible effects of microplastics on animal fitness and HOC bioaccumulation in earthworm *Eisenia fetida* in soil. *Environ. Pollut.* **2019**, *249*, 776–784.
- (35) Rochman, C. M.; Hoh, E.; Hentschel, B. T.; Kaye, S. Long-term field measurement of sorption of organic contaminants to five types of plastic pellets: Implications for plastic marine debris. *Environ. Sci. Technol.* **2013**, *47*, 1646–1654.
- (36) Lohmann, R. Critical review of low-density polyethylene's partitioning and diffusion coefficients for trace organic contaminants and implications for its use as a passive sampler. *Environ. Sci. Technol.* **2012**, *46*, 606–618.
- (37) Beekingham, B.; Ghosh, U. Differential bioavailability of polychlorinated biphenyls associated with environmental particles: Microplastic in comparison to wood, coal and biochar. *Environ. Pollut.* **2017**, *220*, 150–158.
- (38) Bakir, A.; Rowland, S. J.; Thompson, R. C. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions. *Environ. Pollut.* **2014**, *185*, 16–23.
- (39) Lee, H.; Lee, H. J.; Kwon, J. H. Estimating microplastic-bound intake of hydrophobic organic chemicals by fish using measured desorption rates to artificial gut fluid. *Sci. Total Environ.* **2019**, *651*, 162–170.
- (40) Scheurer, M.; Bigalke, M. Microplastics in Swiss floodplain soils. *Environ. Sci. Technol.* **2018**, *52*, 3591–3598.
- (41) Wang, J.; Taylor, A.; Xu, C. Y.; Schlenk, D.; Gan, J. Evaluation of different methods for assessing bioavailability of DDT residues during soil remediation. *Environ. Pollut.* **2018**, *238*, 462–470.
- (42) Belfroid, A. C.; Seinen, W.; Van Gestel, K.; Hermens, J. L. M.; Van Leeuwen, K. J. Modelling the accumulation of hydrophobic organic chemicals in earthworms: Application of the equilibrium partitioning theory. *Environ. Sci. Pollut. Res.* **1995**, *2*, 5–15.
- (43) Jager, T.; Fleuren, R. H. L. J.; Hogendoorn, E. A.; de Korte, G. Elucidating the routes of exposure for organic chemicals in the earthworm, *Eisenia andrei* (Oligochaeta). *Environ. Sci. Technol.* **2003**, *37*, 3399–3404.
- (44) Gouliarmou, V.; Smith, K. E. C.; de Jonge, L. W.; Mayer, P. Measuring binding and speciation of hydrophobic organic chemicals at controlled freely dissolved concentrations and without phase separation. *Anal. Chem.* **2012**, *84*, 1601–1608.
- (45) Guo, X. Y.; Wang, X. L.; Zhou, X. Z.; Kong, X. Z.; Tao, S.; Xing, B. S. Sorption of four hydrophobic organic compounds by three chemically distinct polymers: Role of chemical and physical composition. *Environ. Sci. Technol.* **2012**, *46*, 7252–7259.
- (46) Huffer, T.; Weniger, A. K.; Hofmann, T. Sorption of organic compounds by aged polystyrene microplastic particles. *Environ. Pollut.* **2018**, *236*, 218–225.
- (47) Xing, B. S.; Pignatello, J. J. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol.* **1997**, *31*, 792–799.
- (48) Liu, J.; Ma, Y.; Zhu, D. Q.; Xia, T. J.; Qi, Y.; Yao, Y.; Guo, X. R.; Ji, R.; Chen, W. Polystyrene nanoplastics-enhanced contaminant transport: Role of irreversible adsorption in glassy polymeric domain. *Environ. Sci. Technol.* **2018**, *52*, 2677–2685.
- (49) Pascall, M. A.; Zabik, M. E.; Zabik, M. J.; Hernandez, R. J. Uptake of polychlorinated biphenyls (PCBs) from an aqueous medium by polyethylene, polyvinyl chloride, and polystyrene films. *J. Agric. Food Chem.* **2005**, *53*, 164–169.
- (50) Bakir, A.; Rowland, S. J.; Thompson, R. C. Transport of persistent organic pollutants by microplastics in estuarine conditions. *Estuarine Coastal Shelf Sci.* **2014**, *140*, 14–21.
- (51) Choi, Y. J.; Wu, Y. W.; Luthy, R. G.; Kang, S. Non-equilibrium passive sampling of hydrophobic organic contaminants in sediment pore-water: PCB exchange kinetics. *J. Hazard. Mater.* **2016**, *318*, 579–586.
- (52) Endo, S.; Yuyama, M.; Takada, H. Desorption kinetics of hydrophobic organic contaminants from marine plastic pellets. *Mar. Pollut. Bull.* **2013**, *74*, 125–131.
- (53) Joyce, A. S.; Portis, L. M.; Parks, A. N.; Burgess, R. M. Evaluating the relationship between equilibrium passive sampler uptake and aquatic organism bioaccumulation. *Environ. Sci. Technol.* **2016**, *50*, 11437–11451.
- (54) Connell, D. W.; Markwell, R. D. Bioaccumulation in the soil to earthworm system. *Chemosphere* **1990**, *20*, 91–100.
- (55) Mohamed Nor, M. H.; Koelmans, A. A. Transfer of PCBs from microplastics under simulated gut fluid conditions is biphasic and reversible. *Environ. Sci. Technol.* **2019**, *53*, 1874–1883.
- (56) Diepens, N. J.; Koelmans, A. A. Accumulation of plastic debris and associated contaminants in aquatic food webs. *Environ. Sci. Technol.* **2018**, *52*, 8510–8520.
- (57) Lee, H.; Byun, D. E.; Kim, J. M.; Kwon, J. H. Desorption modeling of hydrophobic organic chemicals from plastic sheets using experimentally determined diffusion coefficients in plastics. *Mar. Pollut. Bull.* **2018**, *126*, 312–317.
- (58) Edwards, C. A.; Bohlen, P. J. *Biology and Ecology of Earthworms*; Springer: Netherlands, Dordrecht, Netherlands, 1995.
- (59) Song, Y. K.; Hong, S. H.; Jang, M.; Kang, J. H.; Kwon, O. Y.; Han, K. M.; Shim, W. J. Large accumulation of micro-sized synthetic polymer particles in the sea surface microlayer. *Environ. Sci. Technol.* **2014**, *48*, 9014–9021.
- (60) Lee, H.; Byun, D. E.; Kim, J. M.; Kwon, J. H. Desorption of hydrophobic organic chemicals from fragment-type microplastics. *Ocean Sci. J.* **2018**, *53*, 631–639.
- (61) Huffer, T.; Wenger, A. K.; Hofmann, T. Sorption of organic compounds by aged polystyrene microplastic particles. *Environ. Pollut.* **2018**, *236*, 218–225.
- (62) Jahnke, A.; Arp, H. P. H.; Escher, B. I.; Gewert, B.; Gorokhova, E.; Kuhnle, D.; Ogonowski, M.; Potthoff, A.; Rummel, C.; Schmitt-Jansen, M.; Toorman, E.; MacLeod, M. Reducing uncertainty and confronting ignorance about the possible impacts of weathering plastic in the marine environment. *Environ. Sci. Technol. Lett.* **2017**, *4*, 85–90.
- (63) Johansen, M. P.; Cresswell, T.; Davis, J.; Howard, D. L.; Howell, N. R.; Prentice, E. Biofilm-enhanced adsorption of strong and weak cations onto different microplastic sample types: Use of spectroscopy, microscopy and radiotracer methods. *Water Res.* **2019**, *158*, 392–400.
- (64) Muller, A.; Becker, R.; Dorgerloh, U.; Simon, F. G.; Braun, U. The effect of polymer aging on the uptake of fuel aromatics and ethers by microplastics. *Environ. Pollut.* **2018**, *240*, 639–646.
- (65) Rummel, C. D.; Jahnke, A.; Gorokhova, E.; Kuhnle, D.; Schmitt-Jansen, M. Impacts of biofilm formation on the fate and potential effects of microplastic in the aquatic environment. *Environ. Sci. Technol. Lett.* **2017**, *4*, 258–267.