Potential for Plastics to Transport Hydrophobic Contaminants

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Plastic debris litters marine and terrestrial habitats worldwide. It is ingested by numerous species of animals, causing deleterious physical effects. High concentrations of hydrophobic organic contaminants have also been measured on plastic debris collected from the environment, but the fate of these contaminants is poorly understood. Here, we examine the uptake and subsequent release of phenanthrene by three plastics. Equilibrium distribution coefficients for sorption of phenanthrene from seawater onto the plastics varied by more than an order of magnitude (polyethylene ≫ polypropylene > polyvinyl chloride (PVC)). In all cases, sorption to plastics greatly exceeded sorption to two natural sediments. Desorption rates of phenanthrene from the plastics or sediments back into solution spanned several orders of magnitude. As expected, desorption occurred more rapidly from the sediments than from the plastics. Using the equilibrium partitioning method, the effects of adding very small quantities of plastic with sorbed phenanthrene to sediment inhabited by the lugworm (*Arenicola marina*) were evaluated. We estimate that the addition of as little as 1 μg of contaminated polyethylene to a gram of sediment would give a significant increase in phenanthrene accumulation by *A. marina*. Thus, plastics may be important agents in the transport of hydrophobic contaminants to sediment-dwelling organisms.

Introduction

Plastic litter contaminates marine and terrestrial habitats worldwide and is now present on some of the world's most remote beaches (*1*). In addition to being an eyesore, plastic debris presents a hazard to a variety of animals. More than 260 species including fish, seabirds, turtles, and marine mammals have been documented to ingest or become entangled in plastics (*2*). Instances of ingestion, which may result in ulceration or starvation (*3*), are increasing in many species of seabirds (*4*).

Many hydrophobic organic compounds have been detected on plastic pellets (1−5 mm in diameter) collected from the environment (*5−7*). Concentrations of polychlorinated biphenyls (PCBs) on polypropylene pellets were up to 10^6 times that in the surrounding water column (*7*). In a

deployment experiment, Mato et al. (*7*) demonstrated that uncontaminated polypropylene pellets readily accumulated PCBs, nonylphenol, and the pesticide metabolite 2,2-bis(*p*-chlorophenyl)-1,1-dichloroethene (DDE) over a period of 7 days. Subsequent transfer of these sorbed contaminants from plastics to organisms following ingestion has been suggested on many occasions (*3, 6−9*), but, surprisingly, we have found no published studies that address this possibility. However, a positive correlation between the amount of ingested plastic in seabirds and PCB tissue concentrations has been reported, providing indirect evidence for contaminant transport by plastics (*8*).

Microscopic plastic fragments (some as small as 20 μm; ref *9*) also litter the environment and are ingested by marine invertebrates including lugworms (*Arenicola marina*), barnacles (*Semibalanus balanoides*), and amphipods (*Orchestia gammarellus*) (*9*). Microplastic has been reported in sediments at numerous global locations (*9, 10*), including at an Indian ship-breaking yard, where it was present at concentrations of up to 81 ppm (*11*). These microplastics enter the environment directly both from use as "scrubbers" in cleaning products and as abrasive beads for cleaning ships (*11, 12*) and indirectly from deterioration of brittle, weathered macroscopic plastics (*13*). It seems likely that the increase in surface area accompanying fragmentation of weathered plastics will further increase their capacity for uptake and transport of hydrophobic compounds.

Many plastics are less dense than water and float at the sea-surface microlayer (SML) where hydrophobic compounds can be concentrated by up to 500 times that of the underlying water column (*14*). Buoyant plastics can be transported across oceans to remote locations (*1*); thus, plastics may provide a mechanism for transport of hydrophobic chemical contaminants to remote and pristine locations. Upon fouling, these plastics can sink (*15*), transporting any sorbed contaminants to the sediment. Given the rapid rate at which plastic debris is accumulating in the environment (*9*), plastics could therefore become important in contaminant transport at a global scale.

The work reported here investigates the potential for plastics to transport contaminants to organisms, focusing on the transport of phenanthrene, a priority pollutant, to a common benthic deposit feeder (*A. marina*). Equilibrium distribution coefficients (K_d) were determined for the sorption of phenanthrene to microscopic particles of three high production volume polymers: polyethylene, polypropylene, and polyvinyl chloride (PVC) (*16*). Desorption rates in seawater were also measured. The K_d values and rate constants of phenanthrene desorption were compared with those of natural sediments. Using the equilibrium partitioning method, tissue concentrations of phenanthrene in *A. marina* were predicted for sediment containing first, clean plastic and second, plastic contaminated in the SML prior to sedimentation.

Materials and Methods

Sample Collection, Preparation, and Characterization. PVC, polypropylene, and ultrahigh molecular weight (UHMW) polyethylene powder (Goodfellow, Huntington, U.K.) were sieved to the size range of 200−250 μm. Natural marine sediments (∼500 g) were collected from Mothecombe, Devon, U.K. and the Plym Estuary, Devon, U.K. in May and July 2006, respectively. The former is a sandy location, and the latter contains predominantly silt. Such locations in Devon have consistently low contents of microplastics (*9*). The sediments were air-dried and then γ-irradiated (25 kGy) to

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TABLE 1. Characterization of Plastics and Sediments

solid phase	particle size (μm)	% OC	BET surface area (m^2 g^{-1})	texture
		Polymers		
polyethylene	200−250	86[a]	4.37	granular polymer
polypropylene	200−250	86[a]	1.56	granular polymer
PVC$_{200-250}$	200−250	38[a]	n.d.[b]	granular polymer
PVC$_{130}$	127[c]	38[a]	1.76	granular polymer
		Sediments		
Plym	35[c]	0.67 ± 0.15	2.08	sand 40%; silt 57%; clay 3%
Mothecombe	191[c]	0.18 ± 0.09	1.37	sand 96%; silt 4%

[a] Calculated. [b] n.d.: Not determined. [c] Median particle size, determined by LALLS.

TABLE 2. Recovery of Phenanthrene in Each Phase in Sorption Experiments

	total PHE recovered in each phase (%)[a]			
	liquid	glass wall	solid	total recovery (%)
	In seawater			
polyethylene	4.6 ± 0.5	0.6 ± 0.3	80.5 ± 6.4	85.7 ± 6.5
polypropylene	37.4 ± 0.7	1.2 ± 0.4	35.6 ± 0.9	74.1 ± 1.2
PVC$_{200-250}$	67.6 ± 8.6	1.3 ± 0.2	27.3 ± 3.8	96.3 ± 4.8
Plym sediment	73.8 ± 2.0	2.4 ± 1.1	3.3 ± 0.5	79.5 ± 2.2
Mothecombe sediment	88.1 ± 3.9	2.0 ± 0.4	0.4 ± 0.1	90.5 ± 4.5
	In sodium taurocholate			
polyethylene	56.3 ± 1.3	0.7 ± 0.2	38.4 ± 0.8	95.4 ± 0.7
PVC$_{200-250}$	93.4 ± 5.1	0.5 ± 0.1	3.7 ± 1.3	97.7 ± 4.3
Mothecombe sediment	94.6 ± 6.9	0.6 ± 0.2	0.2 ± 0.2	95.4 ± 6.5

[a] Initial aqueous [PHE] = 3 μM.

eliminate microbial activity. Seawater was filtered (0.45 μm) and autoclaved before use.

Sediment organic carbon content (% OC) was measured using a CHN elemental analyzer, after first treating the samples with 1 M hydrochloric acid to remove inorganic carbon ($n = 9$). The surface area of plastics and sediments was determined from adsorption of N$_2$ to the surfaces, using the Brunauer−Emmett−Teller (BET) method (17), employing a Micromeritics Gemini 2375 Surface Area Analyzer. The median particle size was determined by low angle laser light scattering (LALLS) using a Malvern Long-bed Mastersizer X ($n = 5$). Surface areas, % OC, and particle size of the solid phases used in the sorption and desorption experiments are reported in Table 1.

Sorption of Phenanthrene to Plastics and Sediments. Glass centrifuge tubes were charged with 20 μL of ^{14}C-labeled phenanthrene dissolved in methanol (phenanthrene-9-^{14}C, Sigma-Aldrich, specific activity = 8.2 mCi/mmol, 17 μM), and the methanol was allowed to evaporate. Plastic particles (10 mg) and seawater (25 mL) were added. The tubes were capped and equilibrated in the dark for 24 h at 18 °C, with continuous horizontal, rotary agitation (200 rpm). Analysis of samples over a period of 72 h showed that equilibrium concentrations in the aqueous phase and on the plastic were reached after 24 h. The concentration of phenanthrene in each phase was determined by counting the β decay from the ^{14}C-phenanthrene by liquid scintillation counting (LSC) in an Ultima Gold (PerkinElmer) scintillation cocktail. To measure the aqueous phenanthrene concentration, 5 mL of seawater was added to the scintillation cocktail and counted by LSC. To determine the phenanthrene concentration on the sorbent, the plastic particles were collected by filtration, added to 5 mL of scintillation cocktail, and counted directly by LSC; analysis of standards indicated that the presence of ≤10 mg of plastic did not quench the signal or affect the count rate. For experiments involving the plastics, cessation of agitation 1 min before sampling allowed the suspended particles to settle, as indicated by control experiments.

Sediment samples were centrifuged before collection of the sediment by filtration. The sediment could not be counted directly by LSC due to internal quenching; therefore, the filtered sediment was shaken vigorously with 5 mL of methanol, and the methanol extract was counted by LSC. To conduct a complete mass balance, the amount of phenanthrene sorbed to the tube walls was also measured; the walls were rinsed with 5 mL of methanol, which was added to the scintillation cocktail and counted by LSC. Sorption experiments were repeated in triplicate, using at least four concentrations of phenanthrene in the initial aqueous concentration range of 0.6−6.1 μg L^{-1}. Separate experiments were conducted using polyethylene, polypropylene, and PVC. Total phenanthrene recoveries are listed in Table 2.

Sorption isotherms were generated using both a linear model and the Freundlich model. For the linear model, the slope of the aqueous concentration (μg L^{-1}) plotted against the solid phase concentration (μg kg^{-1}) generated the distribution coefficient (K_d) as the gradient. For comparison, the data were also analyzed with the Freundlich model using eq 1

$$\log C_i = \log K_F + n \log C_{aq} \qquad (1)$$

where C_i is the solid phase concentration (μg kg^{-1}), C_{aq} is the aqueous concentration (μg L^{-1}), K_F is the Freundlich constant, and n is the Freundlich exponent.

Desorption of Phenanthrene from Plastics and Sediments. Phenanthrene was sorbed to plastics and sediments as described previously, giving final sorbate concentrations of 1.3−2.8 μg g^{-1}. The filtered solid phase (10 mg) was transferred to a 100 mL amber jar, and 75 mL of seawater was added. The jar openings were foil lined, capped, and equilibrated in the dark at 18 °C, with rotary agitation (200 rpm). Aliquots (1 mL) were removed at recorded times, and the aqueous concentration of phenanthrene was determined by LSC. Aqueous samples from sediment desorption experiments were centrifuged before counting. Plastics were

allowed to settle for 1 min before sampling as described previously. The concentration of phenanthrene on the solid phase was calculated by difference, taking into account both the amount sorbed to the walls and the total recovery. Desorption experiments were repeated with 15.5 mM sodium taurocholate in seawater. All kinetic experiments were conducted in triplicate. Pseudo-first-order rate analyses were used to determine the rate constant for initial desorption, where the extent of resorption was assumed to be negligible. The rate constant (k) for the loss of phenanthrene from the solid phase was determined from the gradient of plots of $\ln(C_i/C_{i,0})$ versus time. Errors were estimated from the standard deviation of the slope, determined by linear regression.

Modeling. A model system was developed to estimate the concentration of phenanthrene in *A. marina*, following exposure to a sediment−plastic mixture containing porewater contaminated with a low level of phenanthrene. Two scenarios were investigated: (i) the effect of adding clean plastic to sediment and (ii) the effect of adding previously contaminated plastic to sediment. The equilibrium aqueous phase phenanthrene concentration (C_{aq}) was calculated using a mass balance approach shown in eq 2, where M_{PHE} is the mass of phenanthrene in the system (μg), M_i is the mass of the solid phase i (kg), and V is the porewater volume (L)

$$C_{aq} = \frac{M_{PHE}}{\sum K_{di}M_i + V} \qquad (2)$$

The system employed 1.5 kg of the total solid phase containing 400 mL of water and one 1.2 g worm, which was 5% lipid by mass. Solid phase concentrations were determined using the distribution coefficients. The distribution coefficient for the lipids was estimated from K_{ow} using eq 3 (18)

$$K_{d,lipid} = 3.2K_{ow}^{0.91} \qquad (3)$$

Phenanthrene concentrations reported in the bulk water and the SML at Chesapeake Bay were used as a guideline for M_{PHE} (19). Simulations used to predict *A. marina* tissue concentrations in the presence of contaminated plastic allowed a prior equilibration of phenanthrene between plastic and seawater in 10 cm² of the sea-surface microlayer (60 μm thick). The additional phenanthrene sorbed to the plastic was incorporated into the mass balance (eq 2) when assessing the effect of contaminated plastic. The Supporting Information contains a thorough description of the mathematics used in the model.

Results and Discussion

An experimental system was developed to investigate the relative contribution of plastic as compared to sediment for the transport of hydrophobic contaminants to sediment-dwelling organisms under environmental conditions. Polyethylene, polypropylene, and PVC were selected as model plastics, as these are produced in the highest volumes in Western Europe (16); these polymers also represent a significant proportion of plastic debris in the environment. For example, polyethylene and polypropylene accounted for 97% of the total plastic present in fur seal scat (20). Plastic particles in the size range of 200−250 μm were used to provide a high surface area for sorption and to address concerns about the impact of microscopic plastic debris on the environment (9).

Sorption of Phenanthrene to Plastics. Sorption studies were conducted using initial aqueous concentrations of phenanthrene in seawater in the range of 0.6−6.1 μg L⁻¹. This is a relevant environmental concentration range for phenanthrene, which predominantly enters aquatic systems

TABLE 3. Isotherm Parameters for Sorption of Phenanthrene to Plastics and Sediments

solid phase	Freundlich model[a]		linear model[a]	
	log K_F[b]	n[c]	K_d[d]	K_{oc}[e]
Polymers				
polyethylene	4.60 ± 0.12	1.03 ± 0.11	38100 ± 5600	44500
polypropylene	3.33 ± 0.01	1.05 ± 0.06	2190 ± 170	2560
PVC$_{200-250}$	3.00 ± 0.03	1.50 ± 0.09	1650 ± 200	4340
PVC$_{130}$	3.24 ± 0.03	1.03 ± 0.20	1690 ± 310	4450
Sediments				
Plym	2.11 ± 0.03	0.97 ± 0.07	135 ± 16	20100
Mothecombe	1.17 ± 0.06	1.07 ± 0.14	19 ± 3	10400

[a] ± SD. [b] Freundlich constant; log (L kg⁻¹). [c] Freundlich exponent. [d] Distribution coefficient (L kg⁻¹). [e] $K_{oc} = K_d$/fraction organic carbon (L kg⁻¹).

in large pulses during storm events. Concentrations of up to 69 μg L⁻¹ have been reported in urban runoff waters in the U.S. (21). Under the conditions used, no significant change in K_d was observed after 24 h, indicating that equilibrium had been reached. Sorption isotherms were generated using both linear and Freundlich models (Table 3). As illustrated by the Freundlich exponents (n), for which deviation from unity indicates nonlinearity, the isotherms were generally linear within the concentration range examined. The larger PVC particles showed a slight nonlinearity. The K_d and K_F values show comparable trends and clearly indicate preferential uptake onto plastics, as compared to sediments. Furthermore, polyethylene sorbed an order of magnitude more phenanthrene than either polypropylene or PVC. Although polyethylene has a larger surface area than the other plastics (Table 1), this difference alone is insufficient to account for the large variation in K_d. Nonetheless, the distribution coefficient obtained for UHMW polyethylene particles in this study (log $K_d = 4.6$) is comparable to those determined previously for low density polyethylene membranes (log $K_d = 4.2–4.3$; refs 22 and 23). A similar preference was observed for the uptake of tri- to hexa-chlorinated biphenyls by polyethylene as compared to PVC (log $K_d = 5.0–5.3$ for polyethylene and 2.8–3.8 for PVC; ref 24). Pascall et al. (24) suggested that the higher affinity of polyethylene was a result of the larger volume of the internal cavities, allowing facile diffusion of compounds into the polymer. However, Wu et al. (25) showed that two alkylbenzenes sorbed more strongly to PVC than to polyethylene (log $K_d = 1.8–2.4$ for polyethylene and 2.7–2.9 for PVC), indicating that such trends should not be broadly applied to all organic contaminants. Linear free energy relationships (LFERs) have been invoked to explain the equilibrium partitioning of organic compounds between polymers and aqueous phase (26) and may account for the differences observed.

The considerably higher uptake of phenanthrene onto plastics than onto natural sediments has a potential significance in geochemical determinations of contaminant concentrations in soils and sediments. The presence of small amounts of contaminated plastic could result in a large increase in the concentrations of hydrophobic contaminants in the sediment. The sorptive properties of soils and sediment are affected by their plastic content, and plastics should therefore be considered as constituent components in sediment and soil analyses. Possibly of more importance, however, is the subsequent fate in the environment of the plastic-sorbed pollutants.

Environmental Fate of Plastic-Sorbed Contaminants. The large distribution coefficients for phenanthrene and other environmentally persistent contaminants (Table 3; ref 24) indicate that these compounds have a high affinity for plastics and suggest a potential for plastics to transport these

TABLE 4. First-Order Rate Constants (k) for Desorption of Phenanthrene

	k (day^{-1})[a]		surfactant rate enhancement
solid phase	seawater	surfactant[b]	
Polymers			
polyethylene	0.61 ± 0.41	4.09 ± 0.39	6.7
polypropylene	0.50 ± 0.22	9.70 ± 2.10	19.4
PVC$_{200-250}$	1.04 ± 0.05	2.29 ± 1.40	2.2
PVC$_{130}$	0.85 ± 0.16	2.30 ± 0.36	2.7
Sediments			
Plym	8.4 ± 1.9	n.d.[c]	
Mothecombe	68 ± 6.3	n.d.[c]	

[a] ± SD. [b] 15.5 mM sodium taurocholate in seawater. [c] Desorption rates in surfactant were not determined due to the rapid release in seawater.

chemicals. The nature and environmental significance of this transport will be determined by the fate of the plastic.

Many plastics are less dense than water (i.e., they float on water), thereby allowing geographical transport by river and ocean currents. This may be then followed by deposition of both the plastics and their sorbed pollutant load onto the high tide strand line and subsequent incorporation into littoral sediments. Fouling of the plastic surfaces in the water column, however, may result in subsequent sinking of buoyant plastics (15). Sedimentation of these plastics and sorbed contaminants may consequently lead to sequestration of these contaminants in offshore sediments, with minimal microbial degradation due to strong binding to the plastic (microbial degradation of phenanthrene has been shown to be reduced by a factor of 6 when the phenanthrene is associated with polyethylene; ref 27). Thus, it is important to ascertain how readily the sorbed pollutant burden might subsequently desorb from plastics in sediments and seawater, especially when the sediments and plastics are taken up by sediment-dwelling organisms such as lugworms.

First-order rate constants for the desorption of phenanthrene from PVC, polyethylene, polypropylene, and two sediments into seawater are reported in Table 4. The rate of desorption from plastics in seawater is significantly lower than from the sediments. However, due to the high phenanthrene uptake by plastics (Table 3), when moved to a clean or closed system, even a small amount of contaminated plastic may release a considerable amount of the sorbed compound.

Transport of Contaminants to Organisms by Plastics. Plastics are mistaken as food by numerous animals, including birds, fish, turtles, marine mammals, and marine invertebrates (2, 9). Given the high capacity of the plastics to sorb phenanthrene (as illustrated by the large K_d values; Table 3), plastics may be an important vehicle for transporting contaminants to organisms. Based on our in vitro observations, the potential for plastic to transport phenanthrene to the ubiquitous benthic deposit feeder, *A. marina*, was evaluated. *A. marina* has been shown to ingest microscopic plastic fragments (9) and therefore may be affected by contaminants sorbed to plastic surfaces. Since *A. marina* is at the base of the food chain, and eaten by numerous other species, contamination of *A. marina* also presents a high potential for the transfer of contaminants throughout the food web. To better understand the relative contributions of sediment and plastics in transporting contaminants to *A. marina*, K_d values and desorption rates were measured for two sediments (Tables 3 and 4). A sandy sediment of low organic carbon content and a sediment with a higher silt and moderate organic carbon content were chosen as representative sediment types. These samples were both collected from areas inhabited by *A. marina*.
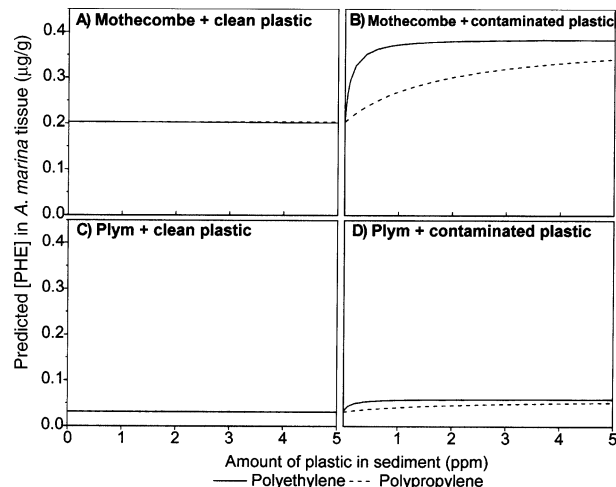

FIGURE 1. Predicted amount of phenanthrene accumulated in *A. marina* from (A) Mothecombe (low % OC) sediment with clean plastic, (B) Mothecombe sediment with plastic contaminated in the SML, (C) Plym (moderate % OC) sediment with clean plastic, and (D) Plym sediment with plastic contaminated in the SML. An enrichment factor of 61 was used for the phenanthrene concentration in the SML as compared to the bulk water (19). Note that when x = 0, the sediment contains no plastic. An expanded version (0−500 ppm) is shown in Supporting Information Figure S1.

Determination of the thermodynamic equilibrium concentration of a contaminant between sediment, water, and animal lipids is an effective method for estimating contaminant burden in biota (28, 29). Using the equilibrium partitioning method (28), the concentration of phenanthrene in *A. marina* was estimated for sediments containing 0−500 ppm plastic by mass (Figure 1). Aqueous phenanthrene concentrations measured in Chesapeake Bay were used in the calculations (19).

Addition of clean plastic to the sediment decreases the bioavailability of the phenanthrene present, as compared to a sediment−seawater mixture containing phenanthrene but no plastic (Figures 1A and 1C and Supporting Information Figures S1A and S1C). This can be viewed as scavenging of the phenanthrene by the highly sorbent plastic, which reduces the equilibrium concentrations in the other phases, including the organism. The effect is most pronounced for polyethylene, particularly in sediment with a low % OC since the latter has little capacity to sorb phenanthrene onto natural organic matter. Addition of 81 ppm polyethylene (the highest reported sediment content of microplastic; ref 11) to low % OC sediment is predicted to give a 13% reduction in phenanthrene tissue concentrations in *A. marina* (Figure S1A). However, due to the high uptake of contaminants onto plastics, and the longevity of plastics in the environment, it is unlikely that plastic debris will remain clean for any extended period of time. Hence, this predicted beneficial effect of plastics in reducing contaminant concentrations in benthic organisms will likely be short-lived, if it operates at all. For example, buoyant microplastics including polyethylene and polypropylene have been documented in hydrophobic contaminant-rich SML (10).

Phenanthrene concentrations in the SML at Chesapeake Bay have been reported to be up to 61 times higher than in the bulk water column (19). Hence, plastics floating in the SML have the potential to become enriched in phenanthrene and other hydrophobic contaminants. Fouling of floating plastics causes them to become negatively buoyant (15), which may result in sedimentation and thus act as a transporter of contaminants into offshore as well as strandline sediments. Many buoyant microplastics, including those examined herein, have been reported in sediments (9).
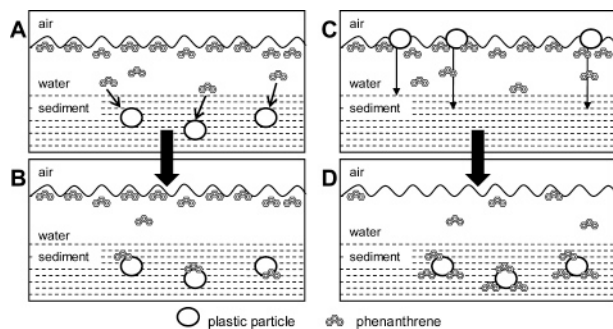
FIGURE 2. Schematic illustrating the additional effects of plastics in the transport of phenanthrene. (A) Sorption of phenanthrene to clean plastic in sediment resulting in (B) subsequent accumulation of phenanthrene in the sediment, as compared to (C) sorption of phenanthrene to plastic in the SML and subsequent sinking, resulting in (D) accumulation of phenanthrene in the sediment. Note that C → D results in higher sediment phenanthrene concentrations than A → B. Although not shown in the schematic, sorption to the sediment also occurs.

Therefore, to examine the possibility of transport of contaminants from the SML to sediments via plastics, a two-box equilibration model was used. In the initial step, the equilibrium concentration of phenanthrene on plastic floating in the SML was calculated. The second step of the model determined the equilibrium concentrations in the sediment, porewater, plastic, and *A. marina* lipids for phenanthrene introduced both from the water and from the plastic. For clarity, Figure 2 displays a simple schematic illustrating the differences between this model approach and that described previously for addition of clean plastic to sediment. Parts B and D of Figure 1 show results from a scenario in which the plastic was pre-exposed to an SML 61-fold enriched in phenanthrene over the bulk water before equilibrating with the sediment (Figure 2C → D). Only a small quantity of plastic is required to sorb a significant amount of phenanthrene from the SML and transport it into the sediment. This increases the total phenanthrene in the benthic environment and results in higher *A. marina* tissue concentrations. As compared to plastic-free sediment, addition of 1 ppm contaminated polyethylene, or of 14 ppm contaminated polypropylene, is predicted to increase the phenanthrene tissue concentration by 80%. These plastics concentrations are lower than those reported in the environment (*11*). This indicates the potential for plastics to transport contaminants at plastic abundances already present at polluted sites.

The presence of digestive surfactants in polychaetes is known to increase the bioaccessibility of sediment-bound polycyclic aromatic hydrocarbons (PAHs) (*30*). To examine the effect of surfactants on plastic-bound phenanthrene, desorption rate constants were measured in the presence of sodium taurocholate, a cholesterol-derived bile salt known to mimic solubilization of phenanthrene by *A. marina* gut fluid (*31*). The presence of sodium taurocholate led to higher liquid equilibrium concentrations of phenanthrene than in seawater (Table 2) and up to a 20-fold increase in the desorption rate as compared to desorption from plastic in seawater (Table 4). An increased desorption rate indicates that equilibrium will be attained more quickly than in the absence of the surfactants. The position of the equilibrium, however, will be determined by the chemical activity of phenanthrene in each of the phases (*32*).

In preparing risk assessments, the European Commission advises that the equilibrium partitioning method may underestimate tissue concentrations of contaminants with log K_{ow} values in the range of 3−5 (*29*). Numerous studies have highlighted the importance of sediment ingestion in the uptake of hydrophobic contaminants by deposit feeders

(*33−35*), which can ingest several times their body weight in sediment daily. For example, the deposit feeding oligochaete *Ilyodrilus templetoni* was shown to obtain 80% of its total phenanthrene burden (log K_{ow} = 4.6; ref *36*) from porewater, while the remaining 20% originated from sediment-bound phenanthrene (*33*). For compounds with log K_{ow} > 5, sediment ingestion is the dominant uptake route (*29, 33*). Such contaminants likely sorb to plastics more strongly than phenanthrene, and gut surfactant mediated desorption may play an important role in their transfer to benthic deposit feeders.

In view of our findings, the potential for plastics to transport contaminants to a variety of organisms now warrants further investigation. In particular, there is a need to consider a range of contaminants, plastic types, and the effects of environmental exposure on the sorption characteristics. Weathering of polymers increases their surface area through cracking and fragmentation, while photo-oxidation functionalizes the surface (*13*). Aging of plastics may decrease the rate of release of sorbed contaminants, a well-known phenomenon for sediment and soil natural organic matter (*37*). Sorption characteristics may also be altered by biofouling of the surfaces. Finally, sorption of contaminants to plastics may preserve the contaminants in the environment by inhibiting microbial degradation (*27*).

Supporting Information Available

Expanded version of Figure 1, showing predicted tissue phenanthrene concentrations in *A. marina* for 0−500 ppm plastic in the sediment. Examples of sorption isotherms and desorption kinetics and additional information about the mathematical modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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