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# Impact of Polymer Colonization on the Fate of Organic Contaminants in Sediment

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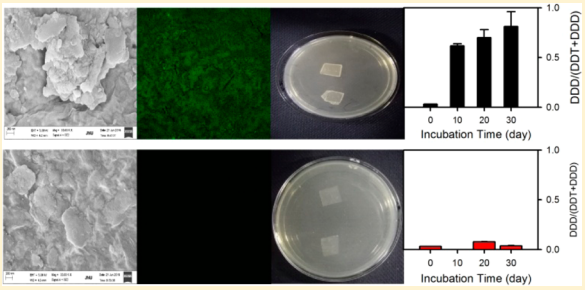
Supporting Information

**ABSTRACT:** Plastic pellets and microbes are important constitutes in sediment, but the significance of microbes colonizing on plastic pellets to the environmental fate and transport of organic contaminants has not been adequately recognized and assessed. To address this issue, low-density polyethylene (LDPE), polyoxymethylene (POM) and polypropylene (PP) slices were preloaded with dichlorodiphenyltrichloroethanes (DDTs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) and incubated in abiotic and biotic sediment microcosms. Images from scanning electron microscope, Lysogeny Broth agar plates and confocal laser scanning microscope indicated that all polymer slices incubated in biotic sediments were colonized by microorganisms, particularly the LDPE slices. The occurrence of biofilms induced higher dissipation rates of DDTs and PAHs from the LDPE slice surfaces incubated in the biotic sediments than in the abiotic sediments. Plastic colonization on LDPE slice surfaces enhanced the biotransformation of DDT and some PAHs in both marine and river sediments, but had little impact on PCBs. By comparison, PP and POM with unique properties were shown to exert different impacts on the physical and microbial activities as compared to LDPE. These results clearly demonstrated that the significance of polymer surface affiliated microbes to the environmental fate and behavior of organic contaminants should be recognized.




## INTRODUCTION

Plastic resin pellets, a group of man-made materials, have been ubiquitously identified in a variety of marine settings, ranging from populated areas to the shores of remote uninhabited regions.[1,2] These pellets can act as substrates for accumulating/leaching organic materials from/to surrounding marine environments and as platforms for microbial adhesion, and therefore may provide a pathway for transport of organic pollutants and microbes.[3−7] Recently we postulated that marine debris could mediate the distribution patterns of organic pollutants in coastal sediment.[8,9] It is also well-known that any surface exposed to seawater would be colonized by microorganisms, forming a thin layer of life (biofilm).[5,10] Recent studies indicated that the plastisphere microbes (the microbial community embedded in the surface of plastics) are distinct from those in the surrounding seawater and sediment.[5,10] In addition, some bacterium species have been demonstrated to hydrolyze plastics as the source of energy for growth,[11,12] although most plastics are chemically inert and resistant to biodegradation. However, the environmental fate and behavior of organic contaminants governed by the interaction between plastics and microbes (or plastic-attached microbial communities) have yet to be clarified,[13] particularly for what occurs on the surface of plastics.

Plastic strips, such as low-density polyethylene (LDPE) and polyoxymethylene (POM) sheets, have been increasingly used as passive samplers' sorbent phases for measuring organic pollutants in water, sediment, and air, largely thanks to their affinity and sorption capacity for organics.[14−16] Performance reference compounds (PRCs) have been used to correct biofouling effects from colonization by microorganisms during field deployment,[14−16] which requires further verification by additional experimental data.[17] Particularly, the fundamentals for the use of PRCs are related to isotropic exchange,[18] but many PRCs may not dissipate at all during deployments. For example, Fernandez et al.[19] reported that the dissipation rate of preloaded $^{13}$C-labeled *p,p′*-dichlorodiphenyldichloroethane (*p,p′*-DDD) in water-side LDPE deployed in the Palos Verdes Shelf was lower than that of $^{13}$C-labeled *p,p′*-dichlorodiphenyltrichloroethane (*p,p′*-DDT), whereas the dissipation rates were reversed in LDPEs exposed in sediment beds. The sediment bed-side dissipation processes were inconsistent with the exchange kinetics for the uptake of these compounds by

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passive sampling devices,[18] because DDT has a larger polymer−water partition coefficient than DDD.[19]

The primary goal of the present study was to investigate the sorption/desorption behavior of organic compounds linked to the interaction between three synthetic polymers, that is, LDPE, POM and polypropylene (PP) slices, and microbes. Among the selected plastics, LDPE and PP are commonly encountered in the marine environment,[20] while LDPE and POM are frequently selected as the sorbent phases in passive samplers.[19,21] The target analytes include dichlorodiphenyltrichloroethanes (DDTs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), which are commonly detected on marine plastic debris.[6,7] The polymer slices were preloaded with the target analytes and immersed in abiotic and biotic sediments to prepare incubation microcosms (brown glass jars). Potential impacts of microbes on the dissipation rates of preloaded target compounds from incubated polymer slices were examined. Finally, the biofouling effects on field applications of passive samplers with the use of PRCs were also assessed.

## MATERIALS AND METHODS

**Materials.** Authentic standards of 28 PAHs (Supporting Information (SI) List S1) and benzo[*ghi*]perylene-$d_{12}$, five PCBs, that is, PCB-18, 61, 67, 82, and 191 were purchased from AccuStandard (New Haven, CT). Three isotopically labeled PAHs, that is, anthracene-$d_{10}$, benzo[*a*]anthracene-$d_{12}$ and benzo[*a*]pyrene-$d_{12}$, and eight $^{13}$C-labeled PCBs congeners, that is, $^{13}$C-PCB-1, 15, 28, 47, 101, 153, 180, and 202, were obtained from Cambridge Isotope Laboratories (Andover, MA). 2-Fluorobiphenyl, *p*-terphenyl-$d_{14}$, dibenzo[*a*,*h*]anthrancene-$d_{14}$, naphthalene-$d_8$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, and perylene-$d_{12}$ were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Four deuterated DDTs, *p*,*p*′-DDT-$d_8$, *o*,*p*′-DDT-$d_8$, *p*,*p*′-DDD-$d_8$ and *p*,*p*′-DDE-$d_8$, were purchased from C/D/N Isotopes (Quebec, Canada).

Low-density polyethylene (50 $\mu$m film thickness), POM (76-$\mu$m film thickness) and PP-type disposable food storage containers (370-$\mu$m thickness) were purchased from TRM Manufacturing (Corona, CA), CS Hyde Company (Lake Villa, IL) and a local supermarket, respectively. Before use, LDPE, POM, and PP-type food containers were cut into ∼25 × 25 mm slices, which were precleaned by dialysis in hexane twice over 48 h. The precleaned LDPE, POM and PP slices were immersed in water:methanol (50:50 in volume) solution spiked with various arrays of target compounds until use (at least for 2 weeks). Anthracene-$d_{10}$ was spiked at 30 $\mu$g L$^{-1}$ and all other target compounds were spiked at 3 $\mu$g L$^{-1}$. Two loaded polymer slices were processed to determine the initial concentration of each preloaded compound, and another two unloaded slices were used as laboratory blanks to monitor any possible external contamination during sample processing.

**Static Microcosm Incubation.** Two Hailing Bay marine sediments from sites 1 and 16, respectively, collected in a previous study[9] and one East River freshwater sediment[22] were used for microcosm incubation. Hailing Bay and East River sediments are known to contain abundant DDTs[9] and PAHs,[22] respectively. The sediments were sieved, prehomogenized and stored until use. Approximately 50 g of each wet sediment was added to a 100 mL microcosm containing 30 g of Milli-Q Millipore purified water, and the slurries were mixed by gentle agitation with a glass rod for approximately 2 min. The content in the microcosm was divided into two portions (abiotic and biotic sediments). The abiotic sediment, which also served as a control, was mixed with approximately 1 mg of sodium azide and sterilized by autoclave twice (2-week intervals) to inhibit bacterial activity.[23] The biotic sediment was not subject to any treatment. One preloaded polymer slice was added to each biotic or abiotic sediment microcosm. All the microcosms were incubated at room temperature (25 °C) and under ambient conditions. One polymer slice preloaded with different compounds was harvested each time.

The first batch of LDPE slices was preloaded with either *p*,*p*′-DDT-$d_8$ or *p*,*p*′-DDD-$d_8$ and *p*,*p*′-DDT-$d_8$ for the coastal marine sediment and PCB-61, anthracene-$d_{10}$, benzo[*a*]-anthracene-$d_{12}$ and benzo[*a*]pyrene-$d_{12}$ for the river sediment. Incubated LDPE slices were collected from the coastal marine sediment after 10, 20, and 30 days and from the river sediment after 7, 20, and 40 days (SI Table S1). To further examine the possibility of biotransformation/biodegradation of the target compounds during incubation, the second batch of LDPE slices was preloaded separately with *p*,*p*′-DDT-$d_8$, *p*,*p*′-DDD-$d_8$, *p*,*p*′-DDE-$d_8$, *p*,*p*′-DDT-$d_8$ and *p*,*p*′-DDD-$d_8$, *p*,*p*′-DDT-$d_8$ and *p*,*p*′-DDE-$d_8$, and *o*,*p*′-DDT-$d_8$ and *p*,*p*′-DDD-$d_8$ for coastal marine sediment, and *p*,*p*′-DDT-$d_8$ and *p*,*p*′-DDD-$d_8$ also separately for river sediment. Loaded LDPE slices were retrieved upon 20 days of incubation (SI Table S1). The third batch contained POM and PP slices loaded with *p*,*p*′-DDD-$d_8$ and *p*,*p*′-DDT-$d_8$, or $^{13}$C-*p*,*p*′-DDT (only for the POM slice) for coastal marine sediment and LDPE slices loaded with PCB 61 and eight $^{13}$C-labeled PCB congeners or naphthalene-$d_8$, acenaphthene-$d_{10}$, fluorene-$d_{10}$, phenanthrene-$d_{10}$, pyrene-$d_{10}$, chrysene-$d_{12}$, perylene-$d_{12}$ and benzo[*ghi*]perylene-$d_{12}$ for river sediment (SI Table S1). For the first and second batches of plastic slices, 2-fluorobiphenyl, *p*-terphenyl-$d_{14}$, dibenzo[*a*,*h*]anthrancene-$d_{14}$ and PCB-82 were used as internal standards and PCB-67, PCB-191, naphthalene-$d_8$, acenaphthene-$d_{10}$, phenanthrene-$d_{10}$, chrysene-$d_{12}$, perylene-$d_{12}$, and benzo[*ghi*]perylene-$d_{12}$ were used as surrogate standards. 2-Fluorobiphenyl, *p*-terphenyl-$d_{14}$ and PCB 82 were used as internal standards and PCB-18, PCB-67, PCB-191, anthracene-$d_{10}$ and benzo[*a*]anthracene-$d_{12}$ were used as surrogate standards for the third batch of samples.

**Sample Characterization.** To identify any microbial activity on polymer surfaces, LDPE, PP and POM slices from biotic river sediment (SI Figure S1a, b, f, and g), LDPE slice from biotic (SI Figure S1c and h) and abiotic (SI Figure S1d and i) marine sediment and procedural blank (SI Figure S1e and j) after 20 day exposure were randomly selected. All the polymer slices were cut and fixed on copper stubs with double coated carbon conductive tabs. Samples were subsequently coated with platinum and imaged by a Zeiss Ultra 55 scanning electron microscope (SEM, Oberkochen, Germany). To further visualize the adherent microbes and microbial colonization on polymer surfaces, the polymer slices upon 10 day culturing were randomly selected, cut and rinsed with sterile phosphate buffered saline (Life Technology, Grand Island, NY). The traditional Lysogeny Broth agar plates were further used to incubate microbes adhered on polymer surfaces for 48 h at 30 °C aerobically. Coatings of extracellular polymeric substance, one of the principal structural components of biofilms, on the surfaces of plastic strips were visualized by staining with fluorescent wheat germ agglutinin conjugate.[24] Briefly, the polymer slices were fixed with 4% paraformaldehyde for 1 h at 30 °C. Samples were subsequently washed once with sterile phosphate buffered saline and stained with 5 $\mu$g mL$^{-1}$ wheat


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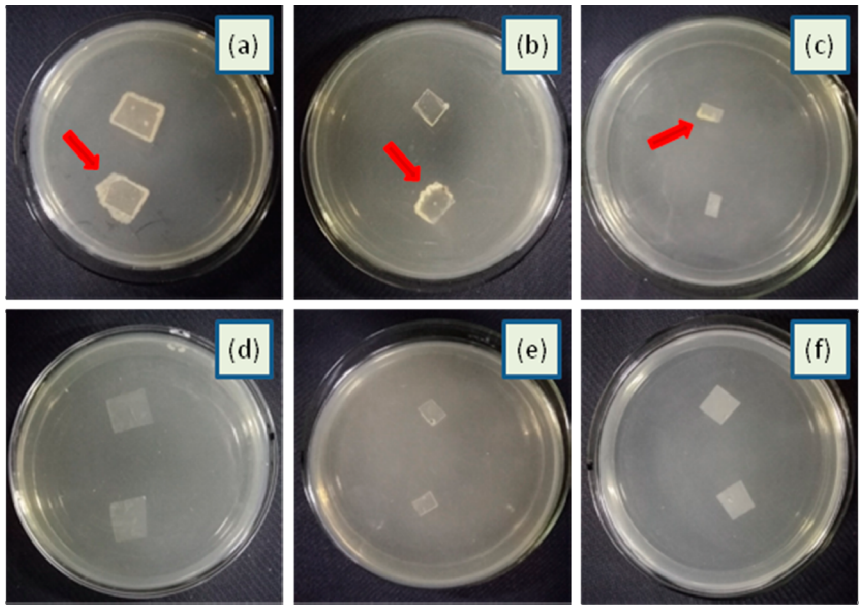


**Figure 1.** Images of colonized polymer plastic strips on the Lysogeny Broth agar plates after 48 h incubation: (a), (b), and (c) display LDPE, PP and POM slices, respectively, immersed in 10 day static marine biotic sediment microcosm and (d), (e), and (f) display LDPE, PP and POM slices, respectively, immersed in 10 day static marine abiotic sediment microcosm. The red arrows indicate biofouling associated with the polymer plastic strips.

germ agglutinin Alexa Fluor 647 fluorescent conjugate solution (Molecular Probes, Eugene, OR) and incubated for 1 h at 30 °C in the dark. Upon removal of unbound dyes by rinsing with sterile phosphate buffered saline, the samples with extracellular polymeric substance coatings were imaged by a confocal laser scanning microscope (LSM 700; Carl Zeiss, Germany).

An aliquot of each sediment sample was acidified with 10% HCl overnight to remove carbonate. The samples were subsequently washed with purified water to remove chlorine ion and dried at 60 °C to determine total organic carbon (TOC) contents by an Element Analyzer Vario EL III (Elementar, Hanau, Germany).

**Sample Extraction.** Prior to extraction, loaded polymer slices were rinsed with water and wiped with filter paper. They were cut to small pieces (~5 × 5 mm), wrapped with filter paper, spiked with the surrogate standards and extracted in hexane (soaking) twice over 24 h. Each extract was dried with sodium sulfate, concentrated to 1 mL with a Zymark TurboVap 500 (Hopkinton, MA) and spiked with the internal standards before instrumental analysis. Detailed procedures for instrumental analysis and quality assurance and quality control results are provided in SI Text S1.

## RESULTS AND DISCUSSION

**Characteristics of Surface of Polymer Slices.** After 20 day incubation, the surface of LDPE slices exposed to biotic river and marine sediments became rough (SI Figures S1a, S1c, and S1h), while the surfaces of all other samples remained smooth (SI Figures S1d and S1i). The Lysogeny Broth agar plates for the plastic strips from the biotic sediments were colonized by microbes (Figure 1a–c), that is, the biotic sediments indeed produced biofilms on the plastic strips. By comparison, the Lysogeny Broth agar plates for the plastic strips from the sterilized sediments remained smooth and were not colonized (Figure 1d–f), indicating the effectiveness of abiotic treatments. The extracellular polymeric substance coatings only occurred on the slices from the biotic sediments (SI Figures S2a–c); particularly, LDPE slices (SI Figure S2a) were more colorful than PP and POM slices (SI Figure S2b and c). Among the polymer slices under investigation, POM was less susceptible to biofouling probably because of its smoother and denser surfaces as compared to PP and LDPE, which are manufactured with rough or sticky surfaces.[25] All microscopic analyses suggested that the surfaces of polymer slices could be colonized by microorganisms, particularly the LDPE slices forming biofilm rapidly.

**The Retained Fractions of Pre-Loaded Target Analytes from Plastics Under Abiotic Conditions.** The retained fractions of preloaded DDTs, PAHs and PCBs from LDPE slices after incubation were controlled by the target compounds' physicochemical properties and sediment TOC contents. For example, the retained fractions of preloaded *p,p′*-DDD-$d_8$, *p,p′*-DDT-$d_8$, *o,p′*-DDT-$d_8$, and *p,p′*-DDE-$d_8$ in marine sediments from sites 1 and 16 were positively related to log $K_{ow}$ or log $K_{pew}$ (5.08 for *p,p′*-DDD; 5.82 for p,*p′*-DDT; 6.00 for *o,p′*-DDT, and 6.20 for *p,p′*-DDE; SI Table S2) (Figure 2a). For the river sediment, the measured losses of preloaded PAHs and PCBs after 7, 20, and 40 day incubation of LDPE slices under abiotic conditions followed diffusion-mediated patterns (SI Figure S3). In addition, the retained fractions of *p,p′*-DDD-$d_8$ and *o,p′*-DDT-$d_8$ at site 1 were significantly different ($p < 0.05$) from those at site 16 (Figure 2a), whereas the TOC contents in both marine sediments were 1.1% and 0.6%, respectively. Because all sediment samples were taken from a relatively small area, organic materials were expected to derive from the same sources. The different sediment structures may have stemmed from TOC or other organic carbon constituents, such as black carbon. On the other hand, *p,p′*-DDE, with a large log $K_{pew}$ (6.20; SI Table S2) compared to those of DDTs and DDDs, more favorably sorbed to the LDPE slices. Slight variability in sediment organic contents appeared to have little impact on the desorption of *p,p′*-DDE-$d_8$ (Figure 2a). The desorption profiles of benzo[*a*]pyrene-$d_{12}$ and PCB-155 (log $K_{pew}$ = 6.64 and 6.14, respectively; SI Table S2)


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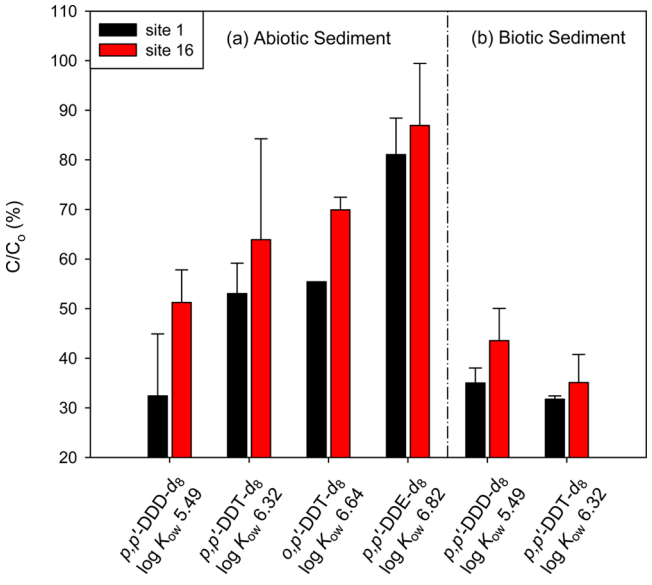


**Figure 2.** Retained fraction ($C/C_0$) of preloaded DDTs from LDPE slices upon exposure in the first batch of (a) abiotic and (b) biotic marine sediments. Coastal marine sediments at sites 1 and 16 were previously collected from an aquaculture base containing historical DDTs.

apparently reached equilibrium after 7 day exposure (SI Figure S3), similar to that of anthracene-$d_{10}$ with lower log $K_{pew}$ (4.37; SI Table S2). This was probably caused by the limited microcosm volume.[26]

**Biotransformation of Pre-Loaded DDT on LDPE Slice in Coastal Marine Sediment.** DDDs are known to be transformed by microbes from DDTs under anaerobic condition.[27−29] The retained fractions of *p,p′*-DDT-$d_8$ preloaded on LDPE slices in the first batch were smaller in biotic microcosms than in abiotic microcosms (Figure 2). In addition, *p,p′*-DDD-$d_8$ was detected in the biotic microcosms, with its contents increasing with incubation time (Figure 3). The values of DDD/(DDD+DDT) in sterilized marine sediment from sites 1 and 16 were similar to the initial value

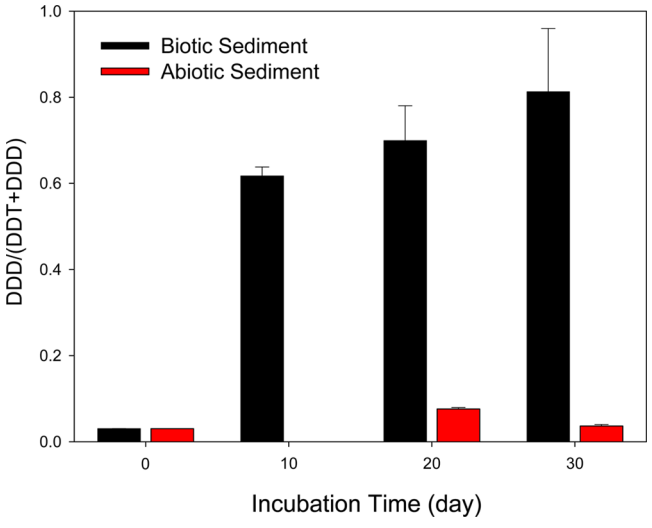


**Figure 3.** Values of DDD/(DDD+DDT) in LDPE slices loaded with *p,p′*-DDT-$d_8$ upon exposure in the first batch of abiotic/biotic marine sediments.

in LDPE slices samples preloaded with *p,p′*-DDT-$d_8$, that is, they were both lower than 0.20 (Figure 3). By comparison, the ratio of DDD/(DDD+DDT) increased from 0.62 in 10 days to 0.81 in 30 days in the biotic marine sediment (Figure 3). The values of DDD/(DDD+DDT) for LDPE slices preloaded with *p,p′*-DDT-$d_8$ in the second batch of biotic marine sediments were also greater than 0.2 (SI Figure S4). The values of DDD/(DDD+DDT) for LDPE slices preloaded with *p,p′*-DDT-$d_8$ were different between the first and second batches, which may have stemmed from the time interval (i.e., nine months) between the two experiments. Meanwhile, the value of DDD/(DDD+DDT) for LDPE slices preloaded with *o,p′*-DDT-$d_8$ and immersed in biotic microcosms was similar to that with *p,p′*-DDT-$d_8$, which increased from 0 to 0.12 (SI Figure S4). Conversely *o,p′*-DDD-$d_8$ was not detected in the same LDPE slices which were immersed in sterilized marine sediment. The indigenous microorganisms in the marine sediment had been chronically exposed to high levels of DDTs before being collected,[9] and therefore have strong potential to effectively degrade desorbed deuterated DDT. Accordingly, the biotransformation of DDT to DDD possibly occurred in the incubated sediment resulting in an increase of DDD concentrations in the sediment. This effect implied a higher dissipation rate of DDT in biotic marine sediment than in abiotic marine sediment.

The mean values of DDD/(DDD+DDT) in LDPE slices loaded with *p,p′*-DDT-$d_8$ and *p,p′*-DDD-$d_8$ were 0.47, 0.47, 0.53, 0.58, and 0.53 (data not shown), respectively, for the biotic and sterilized river sediments, sterilized marine sediments from site 1 and 16 and biotic sediment from site 16, which were all smaller than the initial value in LDPE slices (0.63). It is interesting to note that the DDD/(DDD+DDT) value (0.75) in the LDPE slices sampled from biotic marine sediment from site 1 was greater than the initial value (0.63) in LDPE slices (SI Figure S4). Because the dissipation rate was inversely related to the magnitude of log $K_{pew}$, that is, 5.08 for *p,p′*-DDD and 5.82 for *p,p′*-DDT (SI Table S2), DDD was expected to desorb faster than DDT in the sterilized marine sediments (Figure 2a). However, the dissipation rates of *p,p′*-DDD-$d_8$ from LDPE slices incubated in biotic marine sediment were similar to those of *p,p′*-DDT-$d_8$ (Figure 2b). Furthermore, it was difficult for *p,p′*-DDD-$d_8$ biotransformed from *p,p′*-DDT-$d_8$ to resorb to LDPE slice from sediment, because *p,p′*-DDD-$d_8$ was also preloaded in the LDPE slices. Moreover, DDTs can be degraded in natural anaerobic sedimentary environments, but the half-lives were predicted to be on the time scale of years.[30,31] All the results suggested that desorption of *p,p′*-DDT-$d_8$ from LDPE slice to sediment, followed by transformation to *p,p′*-DDD-$d_8$, could not explain why the values of DDD/(DDD+DDT) in the LDPE slices from biotic sediments were elevated.

It is well documented that the presence of biofilm may promote interfacial physicochemical reactions, that is, biocorrosion or microbially influenced corrosion.[32,33] For example, Harms et al.[14] suggested that bacterial biofilm around solid or sorbed substrates may generate high dissolution fluxes because they drive dissolution from inside the diffusion layer surrounding the substrate source. Wick et al.[34] reported that PAH-degrading bacteria grew approximately 10 times faster with solid anthracene than with DMSO-dissolved anthracene under laboratory cultural conditions. DDD-containing biofilm attached on LDPE slice surfaces may be one of the causes that artificially inflated the value of DDD/(DDD+DDT) in LDPE


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slices sampled from biotic sediments. In fact, spots of biofilm were observed to attach tightly on the surface of LDPE slices (SI Figures S1a, h and S2a ), although the LDPE slices had been washed with water and immersed in hexane for more than 24 h before (SI Figure S1e and j). In addition, a broad sulfur peak was noticed in the sterilized LDPE slices, which continued to grow with increasing incubation time (data not shown). Dechlorination of DDTs coupled with reduction by sulfate-reducing bacteria in hostile low-nutrient environments is well documented.[35−37] Therefore, microbes grown directly on the LDPE slice surfaces may have driven the biotransformation of DDTs observed in the present study.

**Bacterial Control of Pre-Loaded PAHs and PCBs Retained on LDPE Slice in Freshwater River Sediment.** Unlike DDTs, the pathways for biodegradation and biotransformation of PAHs and PCBs are variable,[38,39] dependent on the type of microbes. Hence only the data of retained fractions were presented. As expected, the retained fractions of preloaded deuterated PAHs and PCBs increased with increasing molecular weight (Figure 4 and SI Figure S5). For

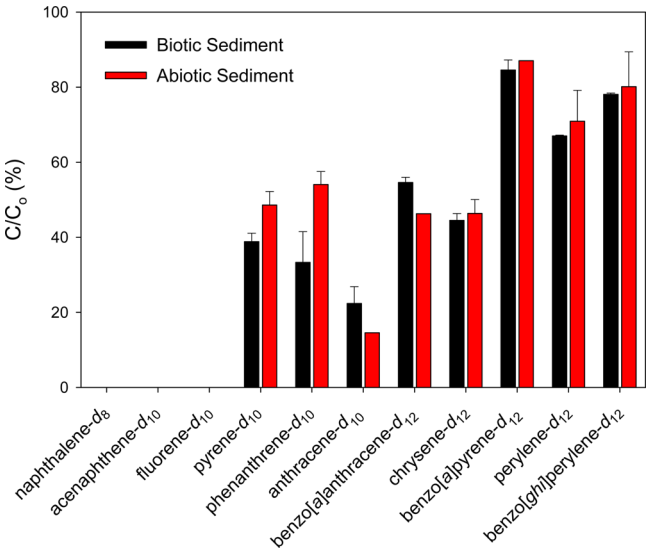


**Figure 4.** Retained fraction ($C/C_o$) of preloaded PAHs from LDPE slices upon exposure in the first and third batches of abiotic/biotic river sediments.

example, the retained fractions were less than 20% for the low molecular weight PAHs (naphthalene-$d_8$, acenaphthene-$d_{10}$ and fluorene-$d_{10}$) and PCBs ($^{13}$C-PCB-1 and $^{13}$C-PCB-15), but more than 30% for the high molecular weight PAHs (benzo[*a*]pyrene-$d_{12}$ and benzo[*ghi*]perylene-$d_{12}$). Meanwhile, the retained fractions for preloaded anthracene-$d_{10}$, benzo[*a*]-anthracene-$d_{12}$, benzo[*a*]pyrene-$d_{12}$, PCB-67 and $^{13}$C-labeled PCBs were similar in biotic and abiotic sediments (Figure 4 and SI Figure S5). It is interesting to note that the dissipation rates of preloaded phenanthrene-$d_{10}$ and pyrene-$d_{10}$ in biotic river sediments were significantly different from those in the abiotic river sediments ($p < 0.05$). Furthermore, the ratios of the concentrations of sorbed phenanthrene, fluoranthene and pyrene on the LDPE slices incubated in biotic and abiotic river sediments substantially deviated from the 1:1 line (Figure 5), which perhaps suggested the occurrence of a potential selective degradation process. In fact, Willumsen et al.[40] reported that a PAHs-degrading bacterium (*Mycobacterium frederiksbergense* sp.) was able to mineralize phenanthrene,

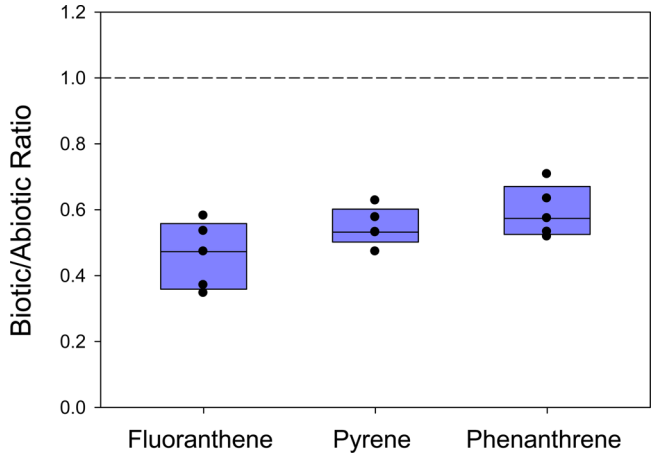


**Figure 5.** Ratios of sorbed PAHs on LDPE slices incubated in abiotic and biotic freshwater river sediments in the third batch.

fluoranthene and pyrene, but observed no growth or mineralization of anthracene, fluorene or benzo[*a*]pyrene. All these findings suggest that the occurrence of surface-associated microbes capable of selectively utilizing PAHs may result in underestimated or overestimated concentrations of the analytes if LDPE slices preloaded with isotopically labeled PAHs and/or DDTs as PRCs are used as sorbents in field deployment. For example, the freely dissolved concentrations from abiotic microcosms were greater than those from biotic microcosms, that is, 2.5 times for phenanthrene in the third batch of freshwater river sediments and 2.5 and 1.6 times for *p,p′*-DDT and *p,p′*-DDD in the first batch of marine sediments (data not shown). This would definitely undermine the data analysis and interpretation when using LDPE in passive sampling of organic pollutants in sediment porewater, which must be carefully addressed.

**Polymer Properties Control the Physical and Microbial Processes.** Different from the kinetic processes associated with the biotransformation of DDTs in the LDPE slices in DDTs-polluted marine sediment discussed above, desorption of preloaded deuterated *p,p′*-DDTs from thick PP and POM slices in the same marine sediments was primarily controlled by diffusion with no apparent microbial facilitation. For example, the retained fractions of *p,p′*-DDT-$d_8$ and *p,p′*-DDD-$d_8$ on the PP slices remained unchanged in both biotic and abiotic marine sediments after 20 day incubation (SI Figure S6a). Thicker polymer slices are known to require longer time for analytes to approach sorption equilibrium; hence diffusion in the polymer becomes the limiting step of dissipation.[41] Microbes may attach on the PP surface (SI Figure S1b) and promote surface erosion.[42]

The smoother surfaces of POM, shown by SEM after 20 day incubation (SI Figures S1f and g), may not be easily sorbed by microbes, reducing the likelihood of biofouling and DDT biotransformation on the POM surfaces. Unlike LDPE slices, the retained fractions of $^{13}$C-*p-p′*-DDT on POM slices were not significantly different ($p = 0.12$) between the biotic and abiotic marine sediments (SI Figure S6b), and $^{13}$C-*p-p′*-DDD was not detected in either sample. The retained fractions of *p-p′*-DDT-$d_8$ and *p-p′*-DDD-$d_8$ were also not significantly different between the biotic and abiotic marine sediments (SI Figure S6b). Conversely, Fernandez et al.[19] observed more deletion of $^{13}$C-labeled *p,p′*-DDT preloaded on POM slices deployed in sediment of the Palos Verdes Shelf, California compared to


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$^{13}$C-labeled *p,p′*-DDD (except in sediment at station 8C). All these results indicate that the role of polymer properties in plastic colonization and their potential effects upon the fate and behavior of organic contaminants merits further examination.

Overall, the present study addressed the significance of microplastic colonization. The acquired data logged at least three findings. First, bacterial biofilms around LDPE slice surfaces can generate high dissolution fluxes of DDTs, artificially inflating the desorption rates of DDTs. Second, colonization of LDPE slice surfaces by microbes can govern the biotransformation of DDTs in DDTs-polluted marine sediment, which may undermine the utility of DDTs-related diagnostic tools in source tracking. Finally, microbes are capable of selectively utilizing PAHs. These findings solidify the importance of plastic surface affiliated microbes to mediating the environmental fate and behavior of organic contaminants. It should also be noted that the experiments conducted in the present study were laboratory-controlled. Hence further studies should be conducted under conditions more closely mimicking the natural environmental settings, including the use of weathering and abrasive microcosms, to obtain more realistic results. In addition, the microbial ecology and/or species-energy relationships, such as competition, cooperation, and mutualism, should also be assessed.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b03310.

Additional tables and figures as mentioned in the main text (PDF)

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### Notes

The authors declare no competing financial interest.

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