Sorption of representative organic contaminants on microplastics: Effects of chemical physicochemical properties, particle size, and biofilm presence

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ABSTRACT

Microplastic pollution has attracted mounting concerns worldwide. Microplastics may concentrate organic and metallic contaminants; thus, affecting their transport, fate and organismal exposure. To better understand organic contaminant-microplastic interactions, our study explored the sorption of selected polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), α-hexabromocyclododecane (α-HBCDD), and organophosphate flame retardants (OPFRs) on high-density polyethylene (HDPE) and polyvinylchloride (PVC) microplastics under saline conditions. Sorption isotherms determined varied between chemicals and between HDPE and PVC microplastics. Log Freundlich sorption coefficients (Log K_F) for the targeted chemicals ranged from 2.01 to 5.27 L kg^{-1} for HDPE, but were significantly lower for PVC, i.e., ranging from Log K_F data (2.84 – 8.58 L kg^{-1}). Significant correlations between chemicals' Log K_F and Log K_{ow} (octanol-water partition coefficient) indicate that chemical-dependent sorption was largely influenced by their hydrophobicity. Sorption was evaluated using three size classes (< 53, $53 – 300$, and $300 – 1000$ μm) of lab-fragmented microplastics. Particle size did not significantly affect sorption isotherms, but influenced the time to reach equilibrium and the predicted maximum sorption, likely related to microplastic surface areas. The presence of biofilms on HDPE particles significantly enhanced contaminant sorption capacity, indicating more complex sorption dynamics in the chemical-biofilm-microplastic system. Our findings offer new insights into the chemical-microplastic interactions in marine environment.

1. Introduction

Plastic production and usage have been increasing rapidly worldwide (PlasticsEurope, 2016). Incentives and infrastructure for recycling are inadequate. As a consequence, environmental pollution from plastic wastes is increasing and has contaminated even remote regions. As of 2015 plastic waste had reached 6500 million tons (Mt), and by 2060 it is expected to surpass 12,000 Mt and continues to expand (Huang et al., 2022; Borrelle et al., 2020). Plastics can be degraded into fragments (including microplastics (MPs): particles size $\leq$ 5 mm) by physical, chemical and biological processes (Gao et al., 2022; Zhang et al., 2021; Zhao et al., 2019). Exposure to microplastics may result in adverse impacts at the organismal, population and ecosystem levels (Auta et al., 2017; Barboza and Gimenez, 2015; Li et al., 2016; Avio et al., 2017; Jang et al., 2020; Seeley et al., 2020).

Recent work has demonstrated that microplastics can not only release harmful organic monomers and additives, leading to pollution and accumulation in marine animals (Thompson, 2015; Van Wezel et al., 2016; Wu et al., 2019a), they also may sorb and transport water-borne contaminants (Andrady, 2011; Huffer and Hofmann, 2016). When microplastics are ingested by organisms, associated chemicals may be transferred and accumulated through the food chain, possibly threatening wildlife and even human health (Andrady, 2011; Nelms et al., 2018; Diepens and Koelmans, 2018). Alternatively, sorption to plastics

may reduce freely dissolved, highly bioavailable contaminants and thus reduce organismal exposure (Koelmans et al., 2016).

Studies have been conducted on the sorption behaviors of organic and metallic pollutants onto different types of microplastics, as well as the effects of environmental factors on chemical sorption processes (Bakir et al., 2014; Wang et al., 2015; Wu et al., 2016; Guo et al., 2020; Mei et al., 2020; Singh et al., 2021). Available data suggest that both the sorbent and the sorbate properties could influence the sorption outcomes. For instance, polymer properties such as polarity, abundance of rubbery regions and degree of crystallinity may impact sorption capacities for hydrophobic contaminants (Wang et al., 2015; Brennecke et al., 2016). The chemistry (e.g., hydrophobicity) of organic contaminants may also influence their sorption (Huffer and Hofmann, 2016; Wu et al., 2019b, 2020). Furthermore, sorption of organic pollutants on microplastics may vary between marine and freshwaters (Guo and Wang, 2019; Mei et al., 2020). Microplastics are present in the environment in a range of particle sizes and this could be another important factor influencing sorption. Previous studies have shown an effect of microplastic particle size on the sorption efficiency of various chemicals (Li et al., 2019a; Ma et al., 2019; Munoz et al., 2021; Cormier et al., 2022; Yu et al., 2022). Other authors (Mo et al., 2021; Yu et al., 2022) have attributed this observation to the combined influence of particle size (surface area) and agglomeration.

Within aquatic environments, microplastics are exposed to mixtures of chemicals, not individual contaminants in isolation (Velez et al., 2018; Moura et al., 2022). Thus, it is logical to examine their behavior as mixtures spanning a range of physicochemical properties in lab studies of sorption behavior. Additionally, plastic debris can interact with resident organisms including microorganisms, as well as dissolved and particulate organic matter. 'Bio-films' (enriched with proteins, lipids and polysaccharides) often form on surfaces (Fulaz et al., 2019). These films likely play a role in the fate of chemicals, e.g., changing sorption dynamics (Rummel et al., 2017; Johansen et al., 2019; Jang et al., 2020). However, such a hypothesis has only begun to be investigated.

In light of the above, we hypothesized that the physicochemical properties of chemicals, particle size and biofilm would affect the sorption of microplastics on pollutants. Our present study aimed to explore the interactions between a range of environmentally important chemical contaminants and microplastics (HDPE: high density polyethylene and PVC: polyvinyl chloride) in simulated seawater. HDPE and PVC differ compositionally and are widely used worldwide as commercial polymers, and commonly encountered in environmental water samples (Brignac et al., 2019). As such, they are often used as model sorbents for microplastic sorption research (Wang et al., 2019a; Li et al., 2021). Three families of contaminants were examined in the present study. They span a range of physicochemical properties. Polychlorinated biphenyls (PCBs) were removed from production in the mid-1970 s, but remain an environmental and human health concern due to their persistent, bioaccumulative and toxic (PBT) properties. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (α-HBCDD) were widely used as flame retardant polymer additives. Due to their PBT properties, PBDE use was discontinued about 10 – 15 years ago (as a function of formulation), but increased use of α-HBCDD occurred during this period (Chen et al., 2011; Liu et al., 2018). These PBDE mixtures and α-HBCDD have all been included in the Stockholm Convention on Persistent Organic Pollutants (POPs) list (www.pops.int). In contrast, organophosphate flame retardants (OPFRs) have been used as plasticizers and flame retardants and their production and use has actually risen. While less persistent and hydrophobic, OPFRs are an increasing environmental concern (Li et al., 2019b). These are chemically similar to tris(2,3-dibromopropyl)phosphate, a flame retardant used in children's pajama in the 1970 s. It and a metabolite were found to be mutagenic (Blum et al., 1978). Specific objectives of the study were to: (1) characterize chemical-dependent sorption isotherms for selected PCBs, PBDEs, α-HBCDD and OPFRs as components of mixtures (as such contaminants do not occur in isolation in the environment); and (2)

investigate factors that might influence sorption, including polymer type, particle size, and existence of biofilms. Our findings extend the knowledge on the "real-world" of environmental chemicals by microplastics and contribute to better assessments of wildlife and human exposure risks.

2. Materials and methods

2.1. Chemicals and reagents

Reference standards of α-HBCDD, 10 PCB congeners (PCB-3-5, -28, -74, -118, -138, -180, -203, -206, -209) and 10 PBDE congeners (BDE-3, -15, -28, -47, -85, -99, -153, -183, -208, -209) were purchased from AccuStandard (New Haven, CT, USA). OPFRs included tris(2-chloroethyl)phosphate-d_{12} (d_{12}-TCEP), tris(1,3-dichloro-2-propyl)phosphate-d_{15} (d_{15}-TDCPP), tri-n-butyl phosphate-d_{27} (d_{27}-TBP), triphenyl phosphate-d_{15} (d_{15}-TPP), and tris(2-butoxy-[13C2]-ethyl)phosphate (M_6-TBEP) were purchased from Wellington Laboratories (Guelph, Canada). The 4'-fluoro-2,3',4,6-tetrabromodiphenyl ether (F-BDE69), 4'-fluoro-2,3,3',4,5,6-hexabromodiphenyl ether (F-BDE160), 2,2',3,3',4,5,5',6,6'-nonabromo-4'-chlorodiphenyl ether (4PC-BDE208), 2,4,6-trichlorobiphenyl (PCB-30), 2,3,5,6-tetrachlorobiphenyl (PCB-65), 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB-204), and 13C18-triphenyl phosphate (MTPP) were employed as surrogate standards, while 3'-fluoro-2,2',4,4',5,6'-hexabromodiphenyl ether (F-BDE154), decachlorodiphenyl ether (DCDE), and coumaphos-d_{10} were used as internal standards. They were purchased from AccuStandard, Wellington, or Cambridge Isotope Laboratories (Andover, MA, USA).

2.2. Sorption experiments

Sorption studies were conducted on microplastics generated from HDPE and nonplasticized PVC pellets (Goodfellow Inc, Coraopolis, PA, USA). Pellets were fragmented using a cryogenic grinder (Retsch Cryo-Mill, Verder Scientific, Inc., Newtown, PA, USA) charged with liquid nitrogen. The desired size ranges (< 53, 53 – 300, and 300 – 1000 μm) were obtained using a Retsch AS200 air jet sieve. Mixtures of target chemicals (Table S1), each at one of the four pre-determined concentrations (10, 20, 50, or 100 ng each), were added to glass tubes containing 25 mL of salt water (35 ppt; Instant Ocean® Sea Salt, Blacksburg, VA) and 10 mg of microplastic particles, at each of the three size ranges. The above four different concentrations were employed for determining the sorption isotherms. Acetone was used as a vehicle (< 0.5%) to expedite aqueous dissolution. Each mixture was thoroughly mixed in a water bath shaker (Benchmark Scientific, USA) at a rate of 50 rpm and 25 °C for up to 8 or 20 days. Light was excluded. Three replicates were processed for each polymer type (PVC and HDPE) and microplastic size classes. Triplicate tubes were sampled at days 0, 1, 2, 4, 8, 14, and 20 to determinate sorption isotherms and equilibrium time. Microplastics and water were separated by filtration through a Whatman GF/C filter (pore size 0.45 μm, GE Life, UK). Both microplastics and filtered water were kept at 4 °C until chemical analysis.

To explore the influence of biofilm on chemical sorption on microplastics, we compared the sorption isotherms on HDPE particles (300 – 1000 μm) with and without the presence of biofilm. Biofilm was developed by incubating HDPE particles with marine algae *Dunaliella salina* in a re-circulated water system at the Southern Illinois University Fisheries Laboratory for a period of 20 days. Sufficient amounts of HDPE were placed in nylon bags (pore size = 50 mesh; approximately 0.28 mm) and incubated for biofilm formation to ensure that the microplastics could be separated from the algal suspension. The HDPE particles with biofilm from nylon bags were transferred to Petri dishes, rinsed three times with seawater, and dried under natural temperature conditions, and finally confirmed by scanning electron microscopy (SEM; ULTRA55, Carl Zeiss Jena Ltd., Germany) (Fig. 1). Sorption experiments were conducted with the above-described methodology for the same
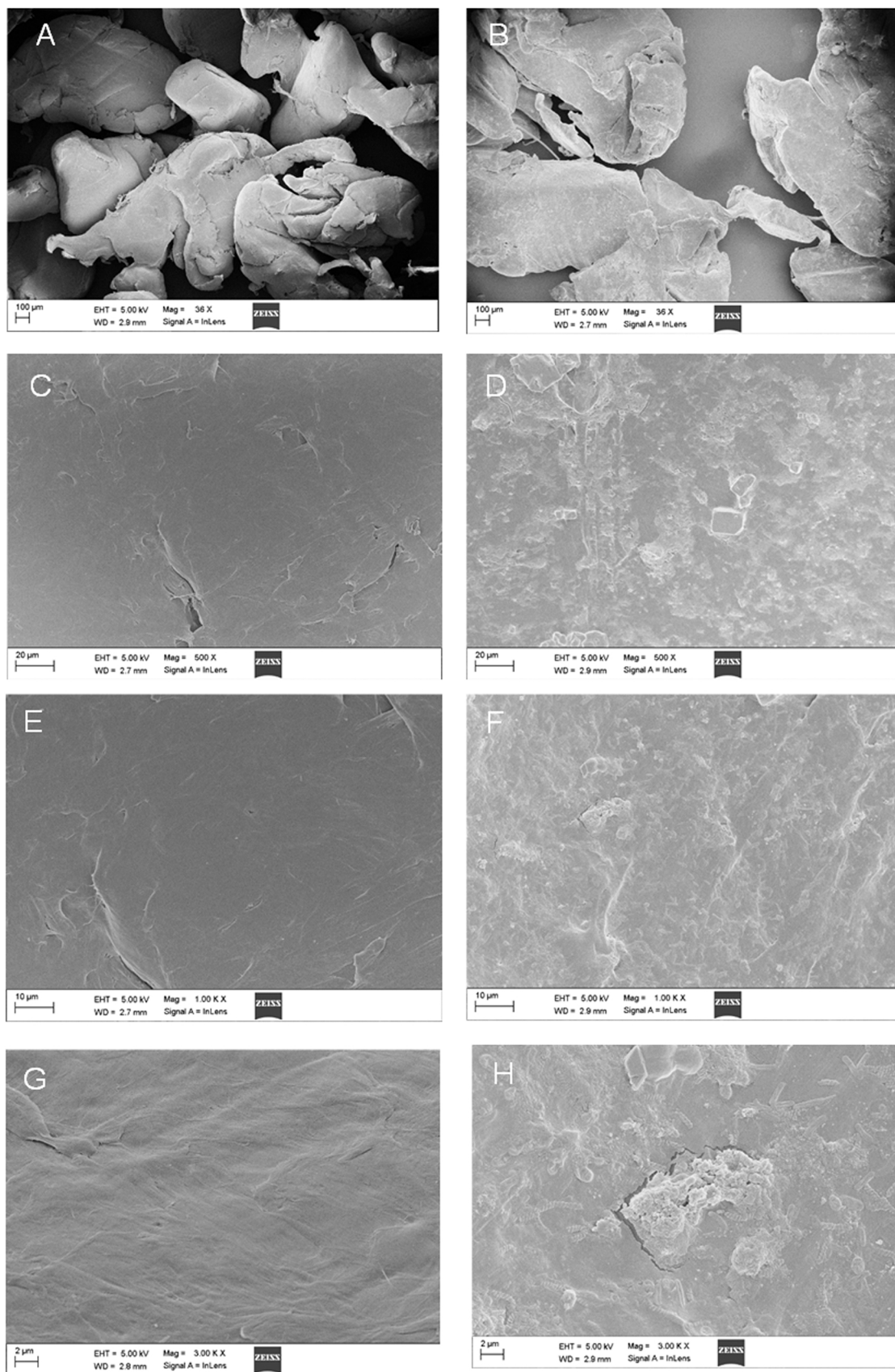
Fig. 1. SEM images of HDPE polymer particles (300 – 1000 μm) with (right) and without (left) the presence of biofilm at 36X (A,B), 500X (C,D), 1000X (E,F), and 3000X (G,H).

suite of chemicals at four different concentrations.

2.3. Chemical analysis

Microplastics retained on filters were amended with a mixture of surrogate standards and subjected to enhanced solvent extraction (ASE 350, Dionex, CA, USA) with dichloromethane at 100 ℃ and 1500 psi. Each extract was passed through solvent-rinsed, activated sodium sulfate to remove moisture, and then concentrated and filtered (centrifugal filter, VWR International). Internal quantitation standards were added to the final extract prior to instrumental analysis.

Filtered water was transferred to a 50 mL separatory funnel. After the surrogate standards were added, water was sequentially extracted three times with 20, 10, and 10 mL of dichloromethane. These aliquots were combined, passed through sodium sulfate, concentrated and spiked with internal standards prior to instrumental analysis.

Detection of PBDE and PCB congeners was conducted on an Agilent 7890B gas chromatography (GC) coupled to a 5977 A mass spectrometer (MS; Agilent Technologies, Palo Alto, CA). OPFRs and α-HBCDD were determined on an Agilent 1260 HPLC equipped with a Kinetex EVO C18 column (2.1 mm × 100 mm, 5 µm particle size) or Waters Xterra® phenyl column (2.1 mm × 100 mm, 3.5 µm particle size), which was interfaced with a 3200 Q Trap® triple quadrupole MS (Applied Biosystems/MDS SCIEX; Toronto, Canada). Further details of the instrumental analysis are summarized in the Supporting Information (SI).

Quality assurance and control (QA/QC) procedures included the evaluation of background contamination in laboratory procedural blanks and recoveries of target analytes in spiking experiments, and of surrogate standards in authentic samples. QA/QC data are summarized in the Supporting Information.

2.4. Data analysis

The maximum sorption on microplastics were predicted using an exponential regression (Eq. 1) (Gonzalez-Lopez et al., 2022).

$$Y = Y_0 + A \times \exp(R_0 \times X) \tag{1}$$

Where X is the sorption time (day); Y is the sorption amount at X; Y_0 is the predicted maximum sorption amount; R_0 is the sorption rate constant; and A is a constant.

To determine the sorption isotherm, experimental data were input into the Freundlich model (Eq. 2).

$$\text{Log } C_s = \text{Log } K_F + 1/n \text{ Log } C_{aq} \tag{2}$$

Where C_s (µg chemical/kg microplastics) is the solid phase concentration, C_{aq} (µg chemical/L simulated marine water) is the aqueous concentration, K_F (L kg^{-1}) is the Freundlich sorption coefficient which indicates sorption capacity, and 1/n (dimensionless) is the Freundlich isotherm exponent, and a linearity index of sorption isotherms. d_{12}-TCEP, PCB-74, 118, 138, 180, 203, 206, and 209, as well as BDE-85, 99, 153, 183, 208, and 209, were excluded from the sorption isotherm model as they were below quantification limits in the aqueous phases.

Statistical analyses were performed with Origin version 9.0 and PASW Statistics 18.0. Differences between different types or size classes of microplastics were determined with the Paired-Samples t Test and Kruskal-Wallis analyses of variance (ANOVA). The octanol/water partition coefficient (K_{ow}) for each chemical was calculated by the U.S. Environmental Protection Agency Estimation Program Interface (EPI) Suite Version 4.11. Pearman's correlation analysis was used to evaluate correlations between the K_{ow} coefficient and maximum sorption, Freundlich sorption coefficient (K_F) or Freundlich isotherm exponent (1/n).

3. Results and discussion

3.1. Sorption kinetics

Sorption kinetics for the targeted PCBs, PBDEs, α-HBCDD and OPFRs on HDPE were investigated for three different microplastic size classes. Times required to reach sorption equilibria were determined (Fig. 2 and Fig. S2). Our data revealed that the α-HBCDD, PBDEs, PCBs and OPFRs reached sorption equilibrium within 1 – 4 days. Interestingly, time to reach equilibrium was longer for particles < 53 µm for most target chemicals, relative to those 53–300 and 300–1000 µm (Fig. 2). This may result from a greater surface area (SSA) of the < 53 µm HDPE particles than those of the larger sizes, as demonstrated in Table 1.

Previous studies have investigated the sorption kinetics of a variety of organic chemicals onto microplastic, but equilibration times varied greatly and depended on the chemicals, polymeric composition, and environmental conditions under investigation. Bakir et al. (2014) reported that sorption of phenanthrene, perfluorooctanoic acid (PFOA), and di-2-ethylhexyl phthalate (DEHP) onto PE microplastics in seawater and under simulated gut conditions (pH 4 at 38 ℃) generally reached equilibrium within 24 h, while the highly hydrophobic 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT) required up to 48 h. Our results also indicated that there were some differences between the required equilibration times of different classes of compounds. The time required for some OPFRs (e.g., d_{27}-TBP) to reach sorption equilibrium were longer than that for PBDEs and PCBs (Fig. 2 and Fig. S2). The larger affinity of the nonpolar PCBs and PBDEs for microplastics (HDPE), as well as the greater water solubility of OPFRs compared to that of PCBs and PBDEs, likely contributed to the results. Zhan et al. (2016) reported an equilibration time of ~8 h for the sorption of PCB-77 on PP, whereas Rochman et al. (2013) reported 6 – 12 months were needed for PCB congeners to reach steady state on PVC, PP, and polyethylene terephthalate (PET) in natural marine waters (where exposure levels were dynamic), implying that environmental conditions play an important role in determining the equilibration times of pollutants. Even under similar conditions, sorption of polycyclic aromatic hydrocarbons (PAHs) on PP appeared to be faster than that on PE (Teuten et al., 2007). However, Karapanagioti et al. (2010) reported similar rates for PAHs sorption between PE and PVC.

Based on the sorption kinetics data, the theoretical maximum sorption capacity of each chemical on HDPE under our simulated conditions was predicted using an exponential regression model. Maximum sorption exhibited a significant relationship with a chemical's Log K_{ow} (octanol-water partition coefficient) within each group of PBDEs or PCBs ($p < 0.05$; Fig. 3). The relationships indicate that a chemical with Log K_{ow} between 7 and 9 exhibited the greatest sorption onto HDPE. The maximum sorption of OPFRs also exhibited an increasing, but not significant trend (Fig. 3), along with the Log K_{ow} during the Log K_{ow} range of 1.63 – 4.7.

3.2. Sorption isotherms

Based on the above sorption equilibration experiments with HDPE, we chose day 8 as the time point for evaluating sorption isotherms for PBDEs, PCBs, α-HBCDD and OPFRs by HDPE and PVC microplastics.

Sorption isotherms varied between PVC and HDPE (Table 1). Other than those chemicals whose concentrations fell below analytical quantitation limits in aqueous phases (see Section 2.4), log Freundlich sorption coefficients (Log K_F) of target chemicals ranged from 2.01 to 5.27 L kg^{-1} on the three size classes of HDPE granules. These were significantly lower than the Log K_F data (2.84–8.58 L kg^{-1}) determined on PVC ($p < 0.05$) (Table 1). The differences in sorption affinities between PVC and HDPE may be attributable to their dissimilar physicochemical properties. Chemically, PVC differs from HDPE by the substitution of chlorine for a hydrogen atom, which increases the polarity of PVC compared with HDPE. This, in turn, may enhance the
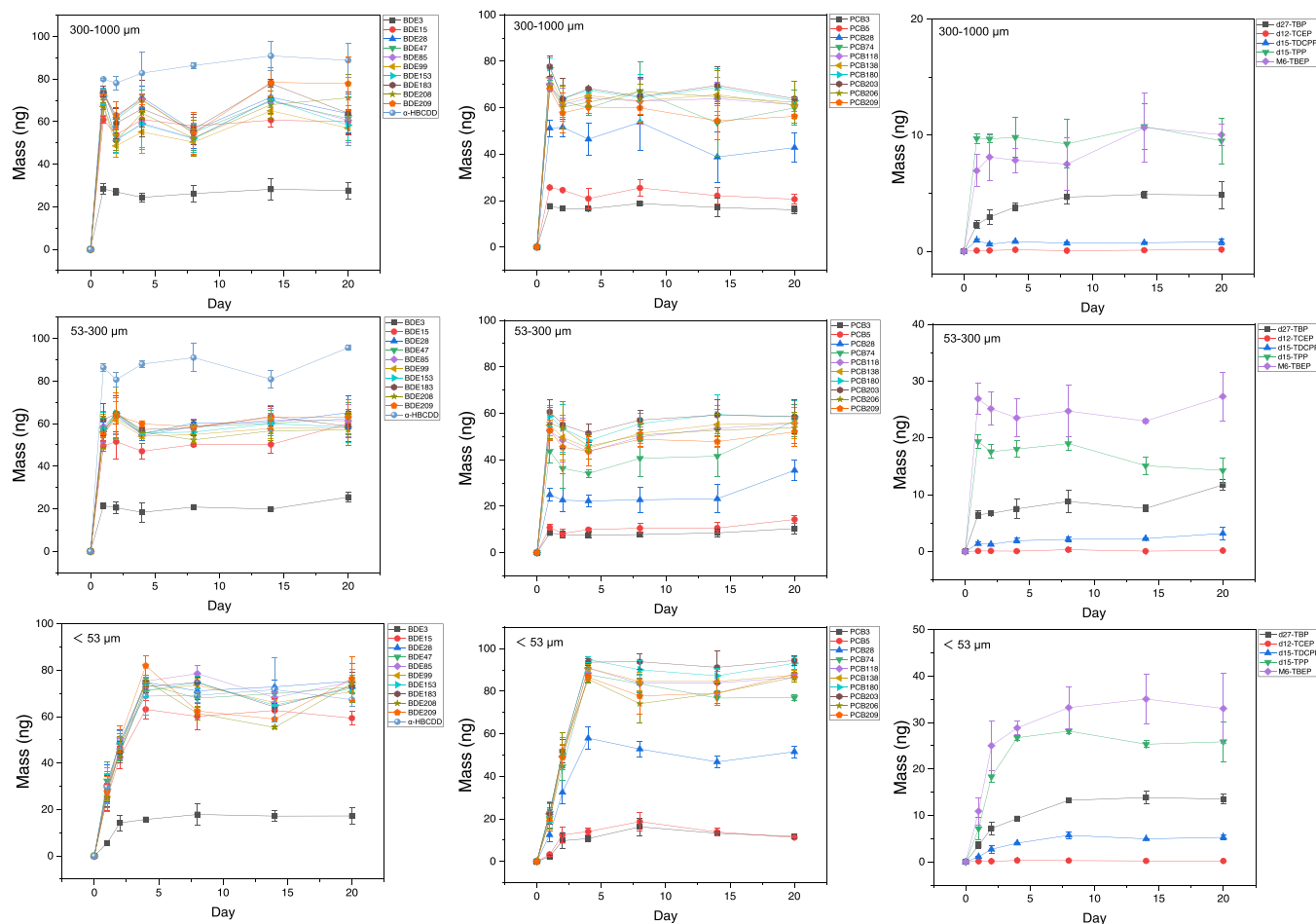
Fig. 2. Masses (ng) of α-HBCDD, PBDEs, PCBs and OPFRs sorbed onto HDPE microplastics of three size ranges over time (days).

Table 1
Parameters of Freundlich model-based sorption isotherm fitting for selected analytes sorbed onto HDPE and PVC.

|	BDE-3	BDE-15	BDE-28	BDE-47	PCB-3	PCB-5	PCB-28	d_{27}-TBP	d_{15}-TDCPP	d_{15}-TPP	M_6-TBEP	a-HBCDD
HDPE < 53 μm; Surface area (n = 3): 1.820 ± 0.091 m²/g												
$LogK_F$	3.56	3.74	3.97	4.35	4.15	3.79	4.72	2.70	2.04	3.06	3.49	4.03
1/n	0.42	0.39	0.34	0.41	1.14	1.10	0.83	1.04	0.27	1.04	0.97	1.26
r^2	0.99	0.99	0.99	0.98	0.88	0.96	0.98	0.93	0.98	0.88	0.87	0.99
HDPE 53 – 300 μm; Surface area (n = 3): 0.340 ± 0.012 m²/g												
$LogK_F$	3.63	3.86	4.18	4.70	4.44	4.30	5.27	2.53	2.03	2.79	3.21	4.19
1/n	0.42	0.54	0.44	0.56	1.37	1.06	1.05	0.65	0.23	0.83	0.98	1.21
r^2	0.87	0.91	0.92	0.90	0.99	0.98	0.99	0.97	0.88	0.93	0.93	0.99
HDPE 300 – 1000 μm; Surface area (n = 3): 0.464 ± 0.019 m²/g												
$LogK_F$	3.60	3.96	4.48	4.76	4.06	4.18	4.92	2.53	2.01	2.60	3.20	4.31
1/n	0.49	0.61	0.67	0.67	1.00	0.89	0.86	0.89	0.59	0.67	0.66	1.19
r^2	0.94	0.97	0.98	0.95	0.99	0.99	0.97	0.95	0.89	1.00	0.93	0.97
HDPE-Biofilm 300 – 1000 μm												
$LogK_F$	3.81	4.65	5.00	5.04	4.18	4.22	5.18	2.58	2.36	2.41	3.40	4.05
1/n	0.69	0.79	0.87	0.97	0.92	0.92	0.90	0.91	0.28	1.07	0.95	1.08
r^2	0.99	0.99	0.95	0.93	0.99	1.00	1.00	1.00	1.00	1.00	0.99	0.99
PVC < 53 μm; Surface area (n = 3): 0.155 ± 0.015 m²/g												
$LogK_F$	4.89	6.87	7.52	8.58	4.18	4.53	4.72	2.70	3.39	4.89	3.06	8.41
1/n	0.81	1.43	1.40	2.26	0.52	0.62	0.62	0.47	0.72	1.43	1.22	2.22
r^2	0.99	0.98	0.95	0.96	0.99	0.87	0.98	0.87	0.99	1.00	0.88	1.00
PVC 53 – 300 μm; Surface area (n = 3): 0.078 ± 0.005 m²/g												
$LogK_F$	5.57	7.58	6.80	7.39	5.04	5.23	6.21	2.93	3.46	4.33	3.00	7.79
1/n	1.11	1.93	1.28	1.61	0.90	0.85	1.18	0.81	0.86	1.12	0.95	2.02
r^2	0.95	0.96	1.00	0.99	0.96	1.00	1.00	0.97	1.00	1.00	0.98	0.95
PVC 300 – 1000 μm; Surface area (n = 3): below the detection limit												
$LogK_F$	5.38	7.64	5.98	8.07	5.82	5.76	5.08	2.90	3.33	4.85	2.84	8.16
1/n	0.82	1.80	1.04	1.98	1.30	1.15	0.69	1.21	1.69	1.70	0.65	2.53
r^2	0.90	0.98	0.88	0.96	0.99	0.98	0.99	1.00	0.93	0.92	0.98	1.00
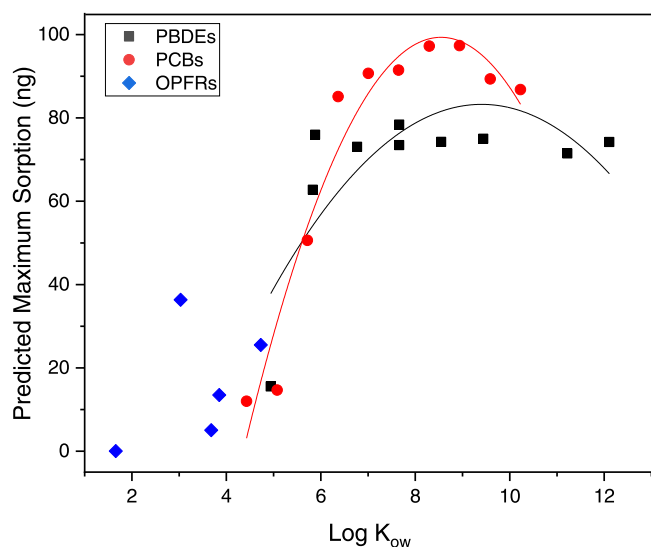
Fig. 3. Changes of the predicted maximum sorption along with Log K_{ow}. Curve represents the fitting result of K_{ow} and PCBs or PBDEs ($p < 0.01$).

sorption affinity of PVC for the targeted chemicals (i.e., PBDEs, PCBs, and some OPFRs). However, not all published studies revealed the same trend. For example, K_F values of phenanthrene, DDT, and PFOA on PE were reported to be higher than those on PVC (Bakir et al., 2014; Wang et al., 2019a), whereas tylosin, naphthalene, nitrobenzene, and DEHP exhibited higher K_F on PVC versus PE (Bakir et al., 2014; Wang et al., 2019a; Guo et al., 2018). Other sorption experiments reported greater sorption capacity of PCBs by PE than PVC (Pascall et al., 2005; Rochman et al., 2013), but the simulated sorption conditions differed from those in our experiments. Polymers in commercial use, as well as those commonly employed in published scientific studies, exhibit substantial diversity in matrix composition, physical form, surface areas, additive composition and other characteristics. The contribution of additives in test materials especially may be unknown to researchers but nonetheless alter outcomes of fate and toxicological studies (Hale et al., 2021). For example, Hummel et al. (2021) observed that the presence of additives in PVC enhanced sorption of oestrone, 17-α-ethinyloestradiol and nor-ethisterone by increasing sorbent hydrophobicity and particle void volume. Hydrophobic and electrostatic interactions are the dominant mechanisms for the sorption of many chemical contaminants onto MPs (Tourinho et al., 2019). Therefore, additives may affect the sorption of PCBs, PBDEs, and OPFRs by microplastics similar. Additionally, the form of the polymer itself, e.g., low density versus high density PE, can also alter sorption (Uber et al., 2019). In some cases, ultra-high density PE

(containing additives) has been used in sorption experiments (e.g., Bakir et al., 2012). These studies collectively suggest sorption capacities by microplastics are affected by the type of microplastics, sorbent chemicals, as well as sorption conditions. Additionally, competitive interactions between chemicals and surfaces may also lead to different sorption outcomes (Bakir et al., 2012; Velez et al., 2018; Wu et al., 2019b). As contaminants occur together in the environment, our experiments utilized sorbate mixtures.

The Log K_F values determined also varied greatly between different chemicals. Regardless of the polymer composition or microparticle sizes, OPFRs generally exhibited lower Log K_F than PBDEs, PCBs and α-HBCDD (Table 1), and lower sorption affinities. The sorption by microplastics is largely determined by partitioning between the hydrophobic and aqueous phases. Indeed, linear relationships were observed between individual chemical Log K_{ow} (octanol-water partition coefficient) and their Log K_F ($p < 0.05$; Fig. 4) for different microplastic size ranges and polymers. In addition, no significant relationships were observed between Log K_{ow} and the Freundlich isotherm exponent (1/n) for PVC and HDPE sorption ($p > 0.1$). The Freundlich isotherm exponent (1/n) values of target chemicals exhibited substantial variation between chemicals, i.e., 0.27 – 1.37 for HDPE sorption and 0.47 – 2.53 for PVC sorption (Table 1). As a heterogeneity factor, 1/n values below 1.0 suggest that the sorption process is mainly chemical, while 1/n > 1 implies a substantial role for physical processes (Gimbert et al., 2008; Jiang et al., 2002). Therefore, large variations in 1/n may indicate dissimilar sorption processes between chemicals, attributable to chemical-specific sorption isotherms.

3.3. Particle size effect on sorption

A particle size effect was observed for the sorption of target chemicals onto HDPE. The predicted maximum sorption amounts of PBDEs and PCBs on < 53 μm HDPE particles were all significantly greater than those on the two larger size groups of HDPE (Fig. 5). The trend for OPFRs was similar, although no statistical significance was observed ($p = 0.20$). The size effect was consistent with the greater specific surface area (SSA) of the < 53 μm HDPE particles compared with the 53–300 and 300 – 1000 μm HDPE granules. Interestingly, the measured SSA of the latter two size groups did not differ significantly (Table 1).

By contrast, significant size-effects were not observed for Log K_F (the p values of Paired-Samples t Test ranging from 0.14 to 0.46 for HDPE and 0.49–0.82 for PVC) or Freundlich Exponent (1/n) (0.81 – 0.99 for HDPE; 0.12 – 0.51 for PVC), indicating that the sorption isotherms were less influenced by the microplastic sizes we evaluated. This finding was consistent with those from other studies (Wang et al., 2019b; Li et al., 2019a). For instance, Wang et al. (2019b) reported no obvious variation in Log K_F values of phenanthrene (3.52 – 3.74 L kg^{-1}) and nitrobenzene

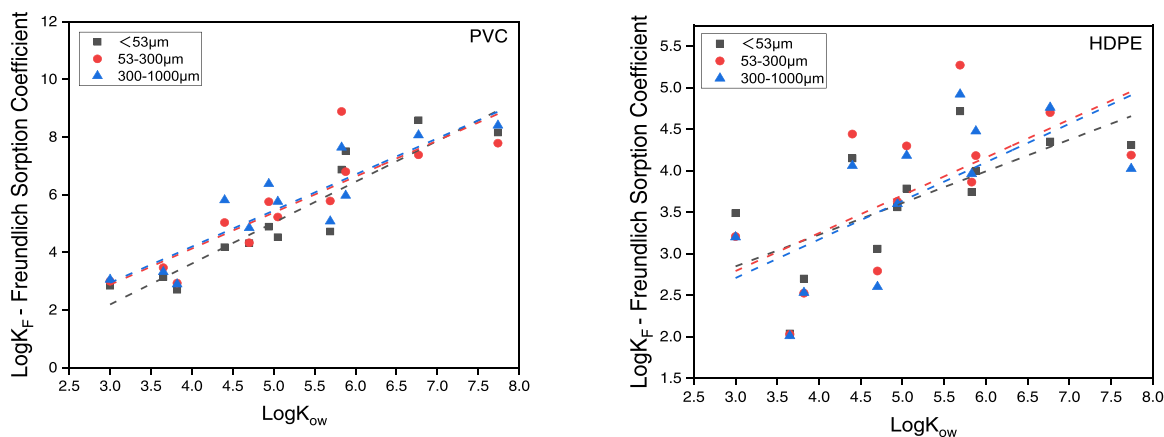**Fig. 4.** Linear regression between Log K_{ow} and Log K_F for chemical sorption on three size ranges of PVC (left) and HDPE (right) ($p < 0.05$).
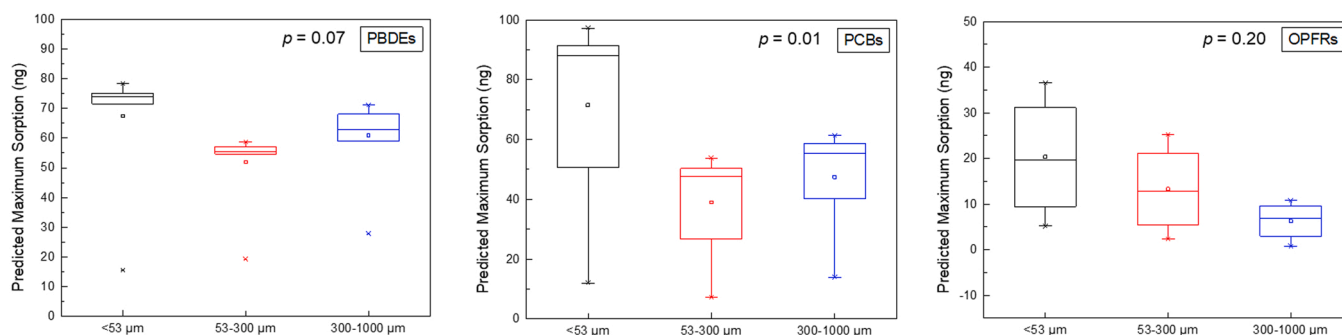
Fig. 5. Comparison of the predicted maximum sorption of PBDEs, PCBs, and OPFRs on different size ranges of HDPE. $p \leq 0.05$ represents a significant difference among three particle sizes.

$(1.73 - 2.57 \text{ L kg}^{-1})$ on different sizes $(30 - 170 \text{ μm})$ of polystyrene microplastics.

The lack of a size effect on sorption isotherms could indicate that sorption isotherms are primarily determined by interactive processes (physical or chemical) between the contaminants and microplastics. Hydrophobic and electrostatic interactions have been reported to be the predominant mechanisms for the sorption of many chemical contaminants onto microplastics (Tourinho et al., 2019). Other interactions also may be involved, including van derWaals and π-π interactions (Tourinho et al., 2019; Fu et al., 2021). Microplastic, dissolved chemical contaminant, and surrounding medium characteristics can affect the above processes (Tourinho et al., 2019). Alternatively, size effects could exist, but may not be resolvable until the particle sizes differ substantially, i.e., by orders of magnitude (e.g., nanometer versus micrometer). It is noted that the three microplastic size ranges we examined were contiguous.

3.4. Impacts of biofilm on sorption

The sorption of organic contaminants to microplastics in the "real environments" is likely complicated by additional factors (Velez et al., 2018). These include the formation of an "eco-corona" consisting of organic coatings, as well as algae, bacteria and fungi on surfaces. These have been hypothesized to interfere with sorption (Rummel et al., 2017, Wang et al., 2021; Nava and Leoni, 2021; Nava and Leoni, 2021). Biofilm formation occurs rapidly on most submerged surfaces. For this reason, sorption isotherms for HDPE particles $(300 - 1000 \text{ μm})$ with and without the presence of biofilm were compared.

An obvious biofilm formed on the HDPE surface (Fig. 1) after incubating particles with the alga Dunaliella salina for 20 days. Surface roughness increased relative to that of unbiofilmed HDPE (Fig. 1). The Log K_F values for PBDEs, PCBs, α-HBCDD and OPFRs on HDPE in the presence of biofilms ranged from 2.36 to 5.18 L kg^{-1} (Table 1), significantly greater than those on virgin HDPE (Log K_F: $2.01 - 4.92 \text{ L kg}^{-1}$) $(p = 0.035)$. This implies that here biofilm formation enhanced the association of these chemicals with HDPE microplastic complexes. It should be noted that the chemicals for which data are presented possessed moderate water solubilities, i.e., concentrations of the highly hydrophobic sorbates were below quantitation limits in the aqueous phase due to the modest water volumes available for extraction. Biofilms are enriched with endogenous chemicals (lipids and proteins), and thus may facilitate the adsorption of these compounds. Some studies also suggest that biofilm formation could influence microplastic surface characteristics/behavior/fate by modifying the physical properties of the particles (Rummel et al., 2017; Liu et al., 2020). Indeed, the HDPE surface appeared more irregular following biofilm formation (Fig. 1). The resulting enhanced surface area could alter the adsorption of environmental contaminants, which was supported by the greater Log K_F values for these compounds relative to unbiofilmed HDPE. A recent study by Bhagwat et al. (2021)) revealed that aged microplastic fibers (MFs) exhibited enhanced surface areas relative to unbiofilmed fibers;

resulting in $4 - 25 \%$ and $20 - 85 \%$ higher adsorbed lead and perfluorooctane sulfonate concentrations, respectively. Wang et al. (2021) also recently reported that biofilm-enveloped microplastics can sorb more pollutants than the virgin ones, then act as vectors to introduce pollutants and attached microorganisms to aquatic environments and to organisms. These findings could support our conclusion.

Biofilm formation may affect the physical and chemical properties of microplastics, such as surface micro-morphology and roughness, surface charge, specific surface area, and density, which may further affect the vertical migration, weathering, and adsorption-desorption of chemical pollutants and pathogens on microplastics in the environment (Wang et al., 2021; Tu et al., 2020; Jacquin et al., 2019). Thus, future efforts are needed to elucidate the dynamic processes in the chemical-biofilm-microplastic system, underlying mechanisms, and influencing factors such as extent of weathering of plastic surfaces.

4. Conclusion

Our study explored the sorption of representative environmental contaminants on HDPE and PVC microplastics under controlled marine water conditions. The results demonstrated that the sorption isotherms varied greatly between contaminant types and polymeric materials. Contaminant sorption was influenced by their relative hydrophobicity, as well as the physical and chemical characteristics of the polymers. In our work, microplastic size (utilizing contiguous size distributions) did not appear to affect sorption isotherms, but influenced the time to sorption equilibrium and the predicted maximum sorption. Presence of a biofilm on HDPE particles significantly enhanced sorption capacity, indicating more complex sorption dynamics in the "real world" contaminant-biofilm-microplastic system. Our findings thus offer new insight into the chemical-microplastic interactions in marine environment.

CRediT authorship contribution statement

Wenxuan Cui: Investigation, Writing – original draft. **Robert C. Hale**: Conceptualization, Methodology, Foundation, Writing – review & editing. **Yichao Huang**: Writing – review & editing. **Fengli Zhou**: Investigation, Validation. **Yan Wu**: Investigation, Validation. **Xiaolin Liang**: Validation. **Liu Yang**: Validation. **Hongli Tan**: Conceptualization, Investigation, Visualization, Writing – review & editing. **Da Chen**: Foundation, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgement

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2023.114533.

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