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Influence of a suite of environmentally relevant conditions on PBT leaching from, and sorption to, marine microplastic debris

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Marine Debris Program Final Report

Part I. Research Project Information

NA13NOS4630062

Project Title: Influence of a suite of environmentally relevant conditions on PBT leaching from, and sorption to, marine microplastic debris

Submitted by: Robert C. Hale, Professor

Date submitted: December 10, 2016

Project location: Virginia Institute of Marine Science (VIMS), 1208 Greate Road, Gloucester Point, VA 23062

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Report:

1. Introduction & Research Question

Background: Synthetic polymers (plastics) enter marine environments from terrestrial and marine-based sources. The manner of release, the plastic's composition/properties and ambient marine conditions determine debris fate and its impacts on living resources. It was long assumed that all plastics were persistent and inert, possessing negligible potential for chemical impacts. However, in reality, commercial polymers exhibit a range of potentials for interactions. Persistent, bioaccumulative and toxic (PBT) chemicals are lipophilic and may concentrate from ambient waters by orders of magnitude on polymer surfaces (Teuten et al., 2007). The type of polymer affects the degree of PBT sorption. Indeed, plastics have been found useful as passive samplers for measuring ambient concentrations of PBTs. Polymers also may be affected chemically or physically by weathering, e.g. exposure to ultraviolet (UV) radiation (Andrady, 2011), or fragmentation by abrasion, such as on a beach. While additives can leach from plastics into the water, migration studies pertinent to the marine environment are rare. The picture is complicated further as weathering itself may alter the extent of PBT leaching and sorption.

Historically, concerns about impacts on living resources have focused on physical interactions with large plastic debris (e.g. ingestion or entanglement in abandoned fishing gear). The chemical structures of most polymers render them difficult to identify and accurately quantify in complex environmental media, compromising tracking of microplastics plastic fragments of small size (<0.3 mm) and to assess their toxicological impact. Hence, to date, the fate and consequences of microplastics produced by the weathering of debris (as well as engineered polymeric micro- and nanomaterials), have received insufficient attention. Indeed, based on our limited field surveys of debris, a large portion of the plastics in the ocean appears to be missing (Cózar, A. et al. 2014.). Looking upgradient from the oceans, major types of plastics discarded in landfills include: high density polyethylene (HDPE:18%), low-density polyethylene (LDPE: 21%), polypropylene (PP: 16%), polyvinylchloride (PVC: 6%), polystyrene (PS: 9%), and polyethylene terephthalate (PET: 11%) (Saquing et al., 2010).

Many polymeric products in commerce are composites that contain % levels of additives. These are inserted to modify properties such as stability, appearance, plasticity and flame retardancy. It was generally assumed that such additives were permanently sequestered in polymer matrices; rendering their environmental mobility and bioavailability moot. However, recent studies suggest that these additives may pose chemical hazards, e.g. migration of chemicals to food from packaging (Muncke, 2009). Ingestion of microplastics may also be problematic as they can serve as carriers of PBTs.

Environmental scientists are typically concerned about water and sediment pollutant concentrations in the $\mu\text{g/L}$ and $\mu\text{g/kg}$ ranges, respectively. In contrast, plastics may contain percent by weight additive concentrations. Thus plastic debris may serve as discrete point sources to the environment, their impacts enhanced by their facile dispersal. While we generally focus on single chemical assessments, multiple additives may be present in a given plastic, resulting in simultaneous mixture exposure. This reality provides the opportunity of designing polymer experiments that include multiple chemicals (with a range of PBT properties) simultaneously. Reduction in polymer particle size via weathering enhances opportunities for environmental dispersal and ingestion by an increasingly large cadre of organisms (encompassing even those occupying lower trophic positions). The bioavailability of chemical additives within these particles is largely untested, but it has been hypothesized that digestive fluids may facilitate the accumulation of plastic-associated chemicals (Teuton, 2009).

The importance of the weathering of plastics and resultant decrease in particle size in modulating chemical impacts has to date not been systematically investigated. Weathering may also alter the hydrophobicity of plastic surfaces (via chemical oxidation or biofilm formation), affecting migration and sorption of HOCs. Size reduction may enhance particle environmental reactivity by increasing their surface area; as is exploited in many engineered nanomaterials (increasingly common in cosmetic, health and industrial applications). An increase in surface area may also alter the extent to which water-borne PBTs sorb to polymer surfaces. PBT sorption in the marine environment may be controlled by polymer type, surface area and ambient conditions.

Dense plastics may enter sediments directly. Aggregation and biofouling of particles will facilitate their sedimentation. Therein, particle-associated chemicals will continue to act as exposure sources to benthic organisms. The characteristics of marine and fresh waters themselves (e.g., salinity, temperature, quality/quantity of dissolved organic matter (DOM)) vary widely in water bodies and will influence PBT sorption/migration. For example, we previously observed that humic acids decreased the apparent bioavailability and toxicity of some PBT chemicals (Mezin and Hale, 2004). DOM levels are typically much higher in sediment interstitial fluids than estuarine or marine waters. If this facilitates leaching of chemicals, concentrations therein may be elevated. In addition, some deposit-feeding organisms ingest large amounts of sediment, often several times their body weight per day. Thus, they may be exposed to high levels of sediment- and plastic-associated chemicals. From the above discussion, it is clear that chemical impacts from plastic debris will be controlled by the nature of the polymer particles, the PBTs, as well ambient environmental conditions.

Study Questions: To enhance understanding of the chemical impacts of PBTs with respect to marine debris, we proposed two in-lab experimental modules: 1) examining additive leaching (at VIMS) and 2) for PBT sorption to plastics from water (at Southern Illinois- Carbondale). Sequential examination of a suite of variables using these designs permits systematic hypothesis testing. It

allows evaluation of multiple variables (both polymer characteristics and environmental conditions) and the ability to extend study to additional variables or replication. The factorial hierarchy imparts experimental efficiency, i.e. reducing the number of experiments that had to be run due to overlapping test conditions. Experiments can also be conducted independently.

Our project focused on: 1) leaching of additives from 4 commercially produced polymer products (polyurethane foam (PUF), PS, PVC and PE); as a function of polymer particle size, UV weathering, water temperature, salinity, DOM and synthetic gut fluid composition; 2) sorption from water of two PBT mixtures (PCBs and halogenated flame retardants) to two model polymers (PE and PVC). Sorption experiments also examined the influence of particle size and biofilm formation.

Note that the sorption studies were conducted by Dr. Chen at University of Southern Illinois-Carbondale and applicable results are described after presentation of the leaching work done at VIMS. Sorption target compounds were PCBs (commonly detected in the marine environment) and current/recent-use halogenated flame retardants (FRs). Concerns over FRs have risen dramatically recently. Examination of mixtures of chemicals possessing a range of physical properties expanded data yields. Experiments were conducted in duplicate (and in some cases triplicate).

2. Methods

Selection of test materials: It was desirable to evaluate actual commercially distributed polymers to better represent materials that actually enter the environment. Unfortunately, additive compositions of such polymers are initially unknown and often maintained as confidential business information. This led to some trial and error in terms of selection of polymeric materials for testing. Desired polymers were flame-retarded polyurethane foam (PUF) used in cushioning, expanded polystyrene (EPS) used in insulation, high density polyethylene (PE) used in single use containers and plasticized polyvinyl chloride (PVC) found in number of applications from wiring to containers. PUF studied were originally used as cushioning in gymnastic studios. EPS was bought commercially. A MSDS indicated the presence of the flame retardant hexabromocyclododecane (HBCD) therein. The HDPE obtained was a post-consumer recycled resin or “regrind” product from Envision Plastics, i.e. plastic that had been recycled from multi-colored bottles. We felt that a regrind material would better encompass the diversity of discarded single-use PE products in the environment.

Three aliquots of each type of ground polymer (53-300 μm) were chemically analyzed to determine the targeted additive concentrations in the starting material. All solvents used were high purity HPLC or residue grade from Burdick & Jackson. Residual solids were removed by filtration (Whatman filter paper 11 μm , 7 cm diameter).

The resulting solvent extracts were purified to remove high molecular weight interferences by size exclusion liquid chromatography (Envionsep ABC column. 350 x 21.2 mm. Phenomenex Inc.) and then by elution through 2-g solid phase silica gel glass extraction columns (Isolute, International Sorbent Tech.; Hengoed Mid Glamorgan, U.K.) (La Guardia et al, 2013). Silica gel eluents were S1: 3.5ml (100% hexane-waste), S2: 6.5ml (60:40, hexane/methylene chloride-hydrophobic flame retardants) + 8mL (100% methylene chloride) and S3: 5ml (50:50, methylene chloride /acetone-polar compounds). The elution profiles of the additives were determined by running standards of the target chemicals. Purified extracts were diluted to produce chromatographic peak areas within the bounds of the LC/MS or GC/MS calibration curves.

We originally had contacted the Particle Technology Research Center at Western University (Ontario, Canada) and subsequently listed them in the proposal to mill the polymers into microplastics. Unfortunately, after we sent polymeric products to test-mill, they found they were unable to accomplish this. Thus we were forced to seek an alternative approach. We next contacted several additional commercial plastics milling operations, but they were unable to produce the modest levels of materials needed at a reasonable cost. We next researched and evaluated doing the milling in-house, thus providing us the ability to perform this for future studies. An equipment funding proposal was written and submitted to the Virginia Higher Education Equipment Trust Fund (administered by the VA State Council of Higher Education and the Virginia College Building Authority). It was successful. We then purchased a Retsch CryoMill and Retsch AS200 jet sieve.



Fig. 1. Retsch Cryomill uses liquid nitrogen to embrittle and mill polymer samples, via agitation and steel balls. Retsch AS200 Jet Sieve for selecting microparticles of discrete size ranges.

These units were used to cryogenically grind and sieve the polymers into three contiguous size fractions (<53 μm , 53-300 μm and 300-1000 μm), respectively. Polymer samples were placed in a closed metal grinding jar. The jar was continually cooled with liquid nitrogen before and during the grinding process. The liquid nitrogen circulated through the system and was continually replenished, maintaining the temperature at -196 $^{\circ}\text{C}$. Grinding was accomplished by a stainless steel ball and controlled shaking of the jar. Sufficient material (~10 g) of each polymer type was ground at one time (in multiple batches due to limited grinding jar capacity) from one source to encompass the anticipated leaching experiments. This reduced the heterogeneity of the materials tested. The amount ground at a time was a function of the polymer density, i.e. lower on a gram basis for the less dense foams (e.g. PS and PUF).

After grinding, the desired size fraction of each polymer was obtained using a Retsch AS200 air jet-sieving machine. The AS200 is suitable for sieving low density microplastics, which tend to agglomerate, to particle sizes in the low to sub mm size range. The size fraction retained for testing was 53 to 300 μm (as determined by retention on stainless steel sieves). The unit was operated at 20 rpm for 4 minutes. Initially, ground polymer particles were sieved thru a 1 mm sieve and particles <1 mm collected via a cyclone and attached glass collection jar. These retained particles were then re-

sieved and those passing thru a 300 μm sieve were again collected in the cyclone. The $<300 \mu\text{m}$ particles were then re-sieved using the 53 μm sieve. The retained fraction (53-300 μm) from multiple batches of grindings was composited into a single aliquot. Subsamples for individual column leaching experiments were removed from this, following homogenization.

Polymer UV weathering was performed by the Particle Technology Research Center. Polymer microplastics (53 to 300 μm size) were subjected to accelerated weathering in a Q-Sun Xenon Test Chamber for 0, 500 and 1000 hr (equivalent to $\sim 0, 6$ and 12 months of sunlight).



Fig. 2. Q-Sun Xenon Test Chamber for accelerated UV weathering of microplastics.

Surface areas of microparticles were determined using the Brunauer, Emmett and Teller (BET) approach. This method is based on measurements of the amount of nitrogen gas that adsorbs as a monomolecular layer on the particle surface at the temperature of liquid nitrogen (<http://www.particletechlabs.com/services/surface-area-and-pore-size-analysis>). The specific surface area result is expressed in units of area per mass of sample (m^2/g). Samples were analyzed on a Micromeritics Gemini V series surface area analyzer. Samples were placed in pre-cleaned tubes overnight and dried/degassed at 650°C under nitrogen flow. A balance tube with glass beads was used for samples with a surface area $< 1 \text{ m}^2$. Surface area was measured using a 10-point curve with the relative pressure (P/P_0) from 0.05 to 0.5. P is the pressure of the adsorbate and P_0 is the saturated pressure of adsorbate. All samples were analyzed a minimum of three times. Liquid nitrogen was refilled prior to each sample. P_0 was set each day prior to the first analysis. Particle surface microscopic inspections were done by scanning electron microscopy (SEM: LEO 435VP).

Aldrich humic acid (HA) (Sigma-Aldrich, St. Louis, MO) was used as the DOM in leaching studies. To prepare HA solutions, 100 mg of HA were added to 1L reverse osmosis (RO) water. The humic acid solution was mixed for 20 minutes at 500+ RPM using a magnetic stirrer/stir bar. It was then filtered through a 1 μm glass fiber filter (Gelman #61635, 14.2 cm diameter). After filtration, the solution pH

was adjusted to 7.0 using 0.01M NaOH or 0.1M HCl. The % carbon of 100 mg/L solutions was measured as 29.6 mg/L (SD 0.181) by combustion. Sodium taurocholate (STC), a vertebrate bile salt and sodium dodecyl sulfate (SDS) at 10 mM were used as surrogate deposit feeder digestive fluids (Voparil et al. 2004).

Polymer leaching (migration) experiments: Our experimental approach employed dispersing the milled microplastics (0.4 g) of the pre-determined size ranges in small amount of sand, in turn packed into stainless steel HPLC columns. The column was then topped up with sand. Microplastics are similarly dispersed in sediments or landfills. The sand (Quikrete® pool filter grade; 400-800 µm/20-50 mesh) for the columns was pre-cleaned by baking in a muffle oven at 450°C overnight (> 12 hours). Polymers of the desired characteristics (e.g. particle size, polymer type, degree of weathering) were sequentially evaluated. Columns containing microplastics were then eluted with waters possessing a range of selected characteristics. In this way the desired values of a given parameter (e.g. salinity) could be varied, while other factors (e.g. polymer type and size, temperature, dissolved organic carbon, degree of polymer weathering) could be held constant. Stainless steel HPLC columns (250 x 4.6 mm), equipped with stainless steel end caps were used. Use of polyether ether ketone (PEEK) column fittings permitted reuse of the caps and columns. A 2 µm stainless steel frit (Valco Instruments Co. Inc.) and end cap were used to seal the column top (exit end). A new column frit was used for each experiment to reduce the potential for cross-contamination. The pump, column, and eluent reservoir were connected by inert tubing.

Eluent water (reverse osmosis (RO), pH 7: adjusted with 0.01 M NaOH or 0.1 M HCL solution, < 3 ug/L total organic carbon) was delivered to the column using a Waters 600 HPLC pump. Desired water temperature was maintained by placement of the column and an inlet loop of stainless steel tubing inside an environmental chamber (Associated Environmental System LH6) capable of maintaining temperature within +/- 10C. A water flow rate of ~1 mL/min through the HPLC column was used and ~1 liter of eluent (measured to 1 ml) collected over a 17 hour period in amber glass, pre-cleaned bottles.

In experiments to evaluate leaching one liter samples were collected. Our primary research goal was to compare and contrast the influence of selected environmentally pertinent conditions on leaching, not to exhaustively extract the chemicals from the polymer.

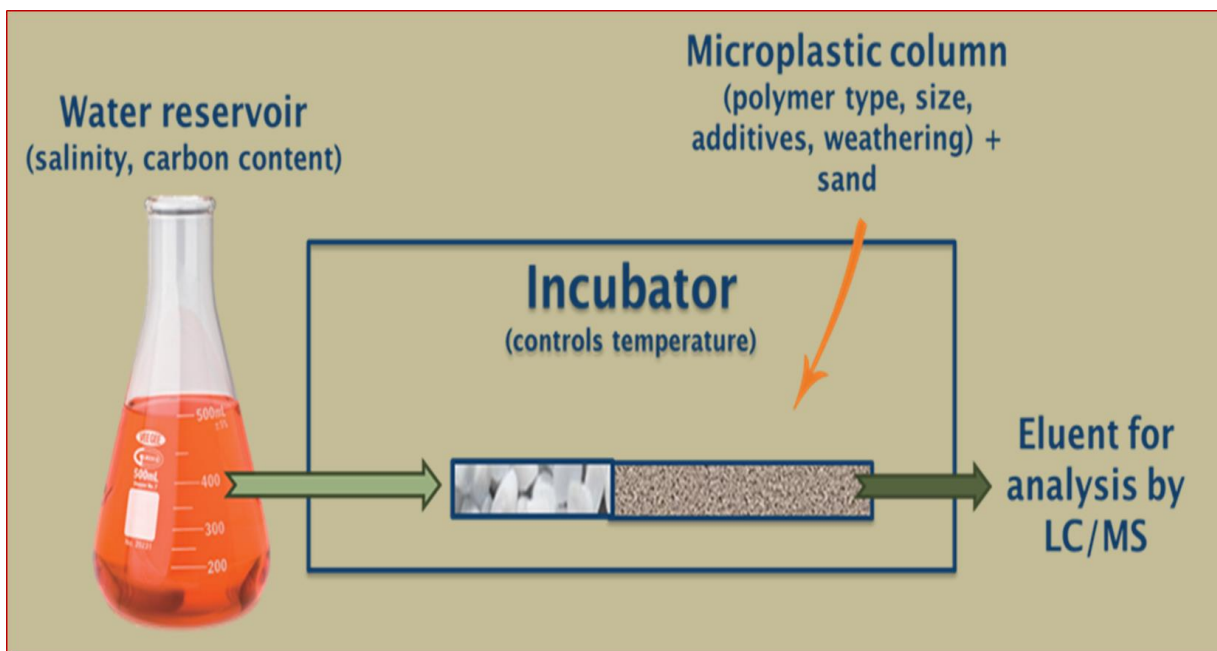


Fig. 3. Setup for performance of microplastic leaching experiments. The desired microplastic (0.4 grams) was dispersed in sand and in turn placed onto a sand bed in a HPLC column. The column was capped with a 2 μm frit to eliminate possible escape of microplastics. The column could then be eluted with fluids of the desired characteristics. The column was placed in an incubator, allowing precise temperature control.

To isolate additives from the leachates, 1L water samples were solvent extracted (three sequential aliquots) with methylene chloride, after the addition of a surrogate standard, in separatory funnels. Extracts were purified by silica gel chromatography.

Identification and quantitation of the target additives from PUF, PE, PVC and PS and associated leachates was accomplished by ultra-high performance liquid chromatography/mass spectrometry (UHPLC/MS). The UHPLC (Acquity UHPLC, Waters Corporation, Milford, MA, U.S.A.) was operated in the gradient mode and equipped with a C_{18} UPLC analytical column (Acquity UPLC BEH C_{18} , 1.7 μm particle diameter, 2.1 \times 150 mm, Waters Corp. or equivalent). The UHPLC column temperature was maintained at 45°C and the mobile phase consisted of 100% water (A1) and 100% methanol (B1). The initial mobile phase composition was 95:5 A1/B1 at a flow rate of 250 $\mu\text{L}/\text{minute}$, held for 3 minutes. This was followed by a linear gradient to 30:70 A1/B1 over the next 12 minutes. The flow rate was then increased to 300 $\mu\text{L}/\text{minute}$, followed by a 5-minute linear solvent gradient to 100% methanol. The column was regenerated by a 3-minute linear gradient back to 95:5 A1/B1, followed by a 2 minute hold at a flow rate of 250 $\mu\text{L}/\text{minute}$. Analytes were subjected to atmospheric pressure

photoionization (APPI), the dopant (acetone) was introduced at 150 $\mu\text{L}/\text{min}$ by a liquid chromatography pump (LC-20AD, Shimadzu Corporation, Kyoto, Japan), and product ions detected on a triple quadrupole mass spectrometer (3200 QTrap, AB Sciex, Framingham, MA, U.S.A.) operated in the multiple reaction monitoring (MRM) mode. The following parameters were used: curtain gas 15 psi (N_2), probe temperature 300°C, nebulizer gas 55 psi (Zero air), auxiliary gas 40 psi (Zero air), interface heater on, collision gas medium (N_2), ion spray -850 V . The purified extracts were also analyzed for TPP and the surrogate d15-TPP by UPLC-APPI-MS/MS operated in the positive ion mode (ion spray 850 V). The analytical method has been validated previously for FRs in complex environmental media (La Guardia et al., 2013).

Phthalates in PVC and associated leachates were analyzed by GC/MS (Agilent 5975C MS coupled with a 7890A GC). Carrier gas was helium. The GC was equipped with a DB-5 column (Agilent Technologies: 60 m x 0.1 μm film thickness). Analytes were injected in the splitless mode and subjected to electron impact ionization mode at 70 eV. Ion mass-to-charges were obtained at unit resolution. Compound concentrations were calculated based on the area of selected ions (p-terphenyl m/z 230, DEHP m/z 149 and BDE166 m/z 484).

3. Results

Surface areas of microplastics: Microplastics of different polymeric composition, but the same nominal size (e.g. 53-300 μm) exhibited substantially different surface areas. This was not unexpected. PS and PUF have cellular structures, so these were expected to have highest surface areas (Fig 2). Surprisingly however, we observed that ultra high molecular weight PE (UHMWPE) had the highest surface area. SEM indicated that this material possessed a smaller size than the reported value (mean 150 μm) indicated by the manufacturer (Goodfellow Cambridge Ltd.). This material has been used by other researchers (e.g. Teuten et al, 2007) as a model HDPE for PBT sorption experiments. While not part of the original study design, acrylonitrile butadiene styrene (ABS) was also evaluated. ABS and PVC possessed the lowest surface areas.

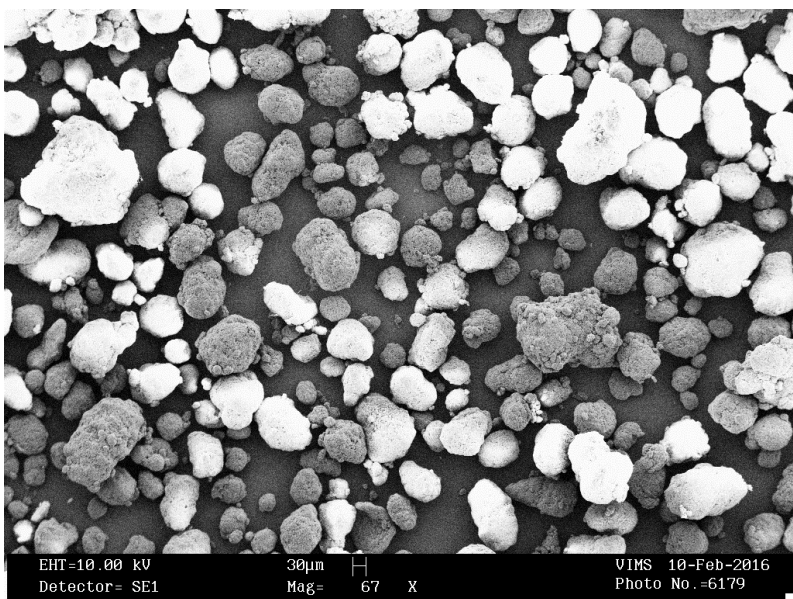


Fig. 4. SEM micrograph of the UHMW PE (Goodfellow Cambridge Ltd) product. According to the manufacturer mean particle size was 150 μm . However, examination of the scale (30 μm) on this micrograph suggests many particles are smaller than 150 μm . This material exhibited a surprisingly large BET surface area. Close examination of particles also suggests a rough or pitted surface texture.

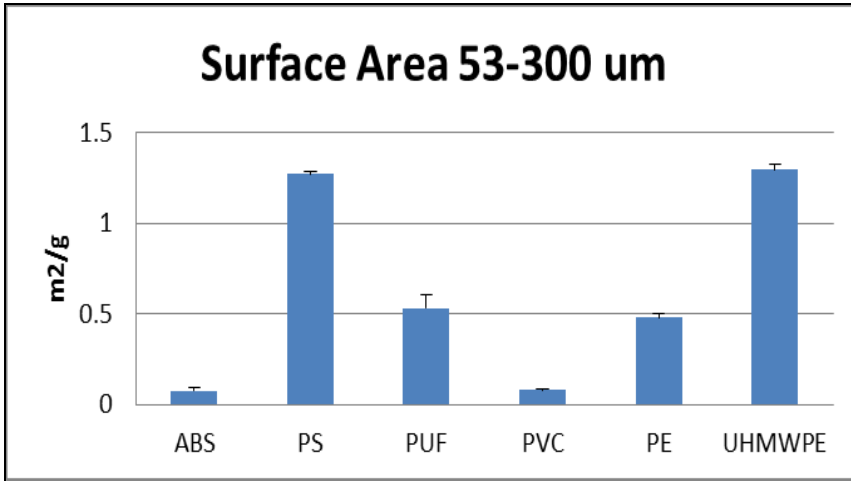


Fig. 5. BET surface areas of various polymer microplastics (nominal 53-300 μm). All were cryogenically ground and air jet sieved at VIMS, except for the UHMWPE, which was examined as received from the manufacturer, as it supposedly had a mean particle size of 150 μm .

It was assumed that surface areas of microplastics would be a more important criteria affecting both leaching of additive and sorption of hydrophobic pollutants from water, than sieve-determined particle sizes. For most polymers surface areas increased as nominal particle size decreased. However, this was not always the case. This likely was experimental error, i.e. the expected particle size distributions were likely not obtained by the sieving step.

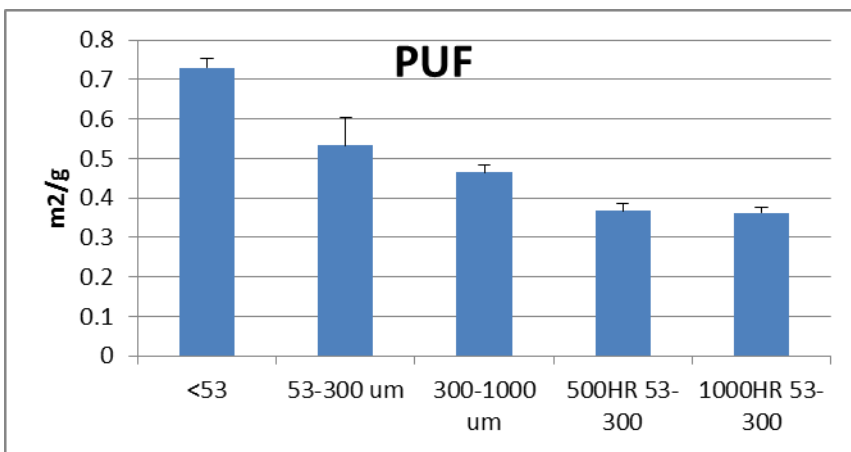


Fig. 6. BET surface areas of cryogenically ground flexible PUF. Aliquots of the 53-300 μm fractions were also UV weathered for 500 and 1000 hrs. PUF surface areas decreased with increasing particle size. Exposure to UV for 500 or 1000 hrs appeared to decrease surface areas, although the longer UV duration did not appear to exacerbate the effect. UV-exposed PUF was visibly yellowed (which increased with UV duration), indicating chemical degradation.

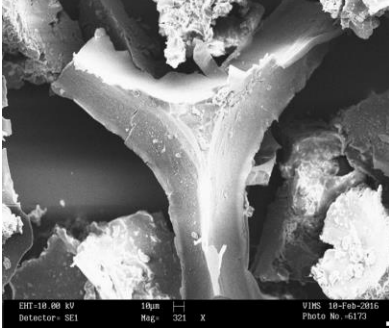


Fig. 7. A representative SEM of 53-300 μm PUF is shown, illustrating the remnants of its cellular structure.

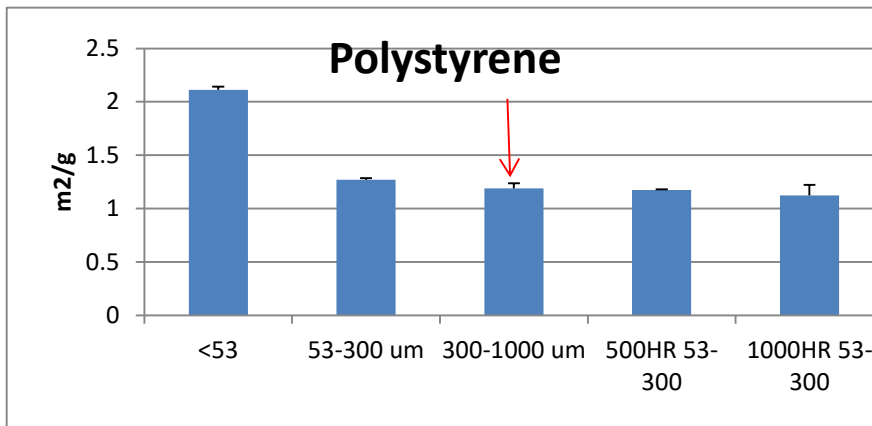


Fig. 8. Unexpectedly similar surface areas were observed between PS microparticles of nominal 53-300 and 300-1000 μm (latter indicated by red arrow in figure). UV exposure did not appear to affect PS surface area. UV-exposed PS showed visible yellowing (which increased with duration). File Source: surface area092716

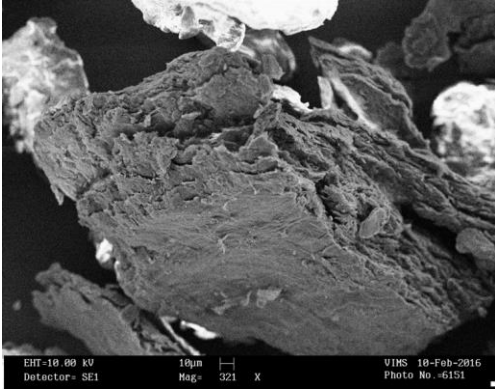


Fig. 9. SEM indicated PS exhibited a flattened, asymmetric shape and this might have confounded the air jet sieves' abilities to separate the particles into the desired size categories.

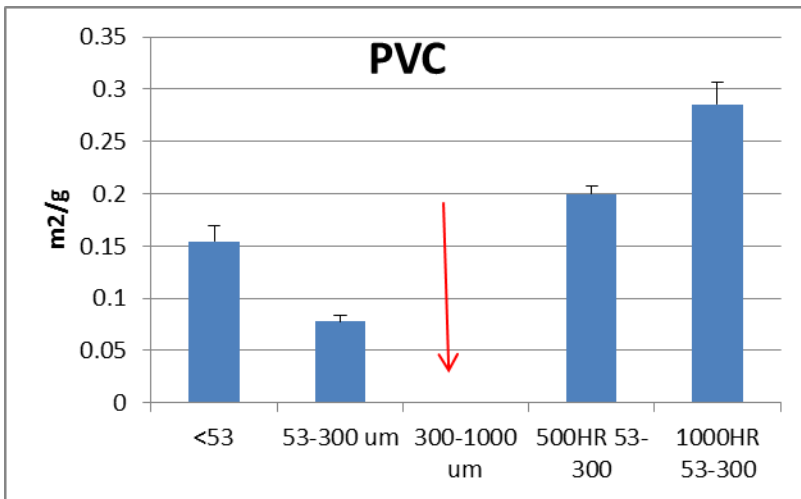


Fig. 10. PVC BET surface areas decreased with increasing nominal particle size. However, the 300-1000 µm sample possessed too low a surface area for the Micromeritics Gemini V series analyzer to measure (indicated by the red arrow). Interestingly, UV exposure increased surface areas, especially after 1000 hrs of exposure. The original PVC was yellow in color, but the 1000 hr UV weathered material was lighter in color.

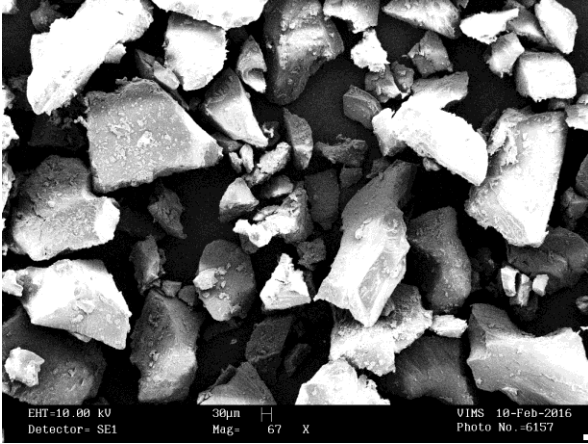


Fig. 11. SEM of PVC microplastics. Particles were angular and textures were relatively smooth.

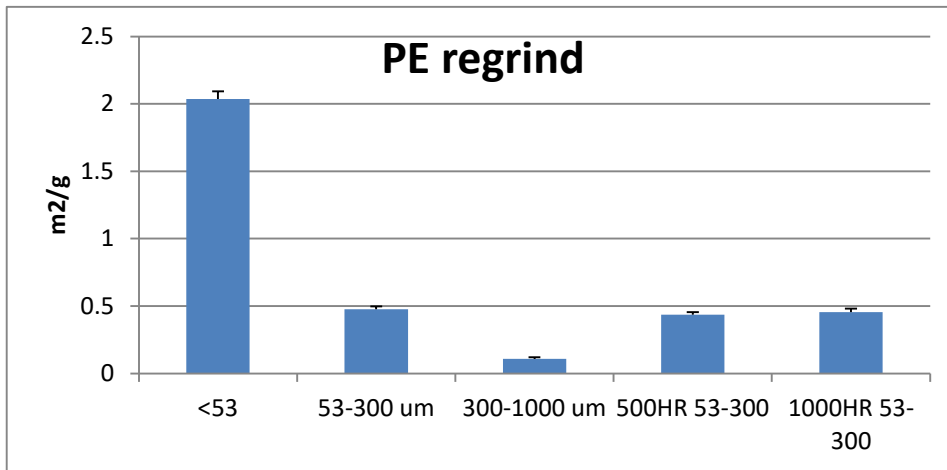


Fig 12. PE regrind exhibited a similar pattern of increasing surface area with decreasing nominal particle size; and increased surface area following weathering (although areas were similar between 500 and 1000 hrs). This milled PE was originally brown in color (although was multi-colored as received in larger pieces), but became lighter following UV weathering.

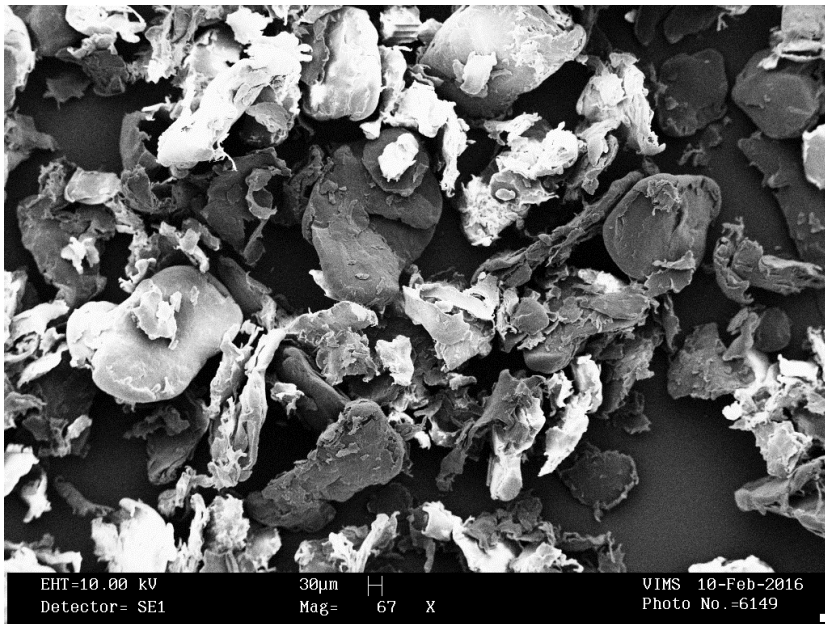


Fig. 13. SEM of regrind PE (nominally 53-300 µm). This material took a longer time to mill than other polymers. Many of the particles appear to be shredded versus being fractured. The surface texture appears less porous than the UHMW PE. This likely contributed to its lower BET surface area.

Additive composition of polymers tested: PUF contained a number of flame retardant additives, these ranged from quite water soluble to extremely hydrophobic.

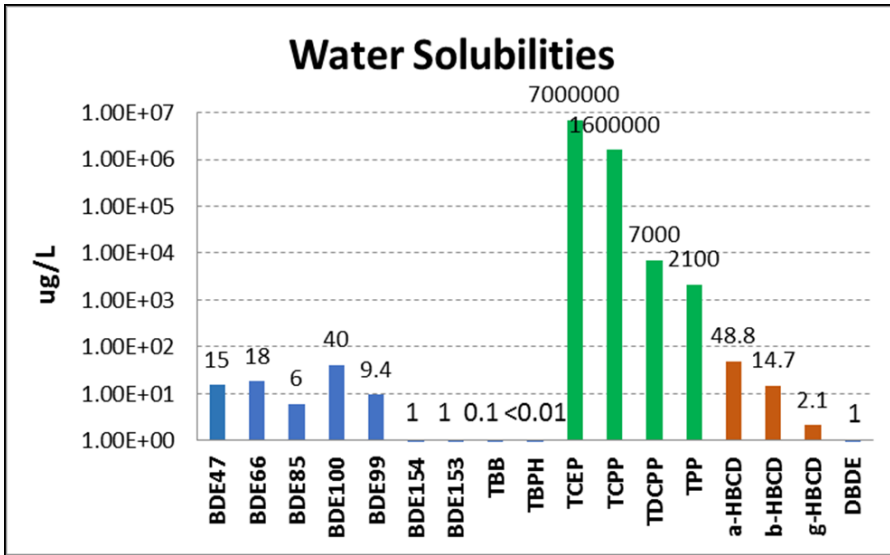


Fig. 14. Water solubilities of several of the flame retardants (FRs) in the PUF studied. The phosphate-containing FRs exhibited much greater water solubilities than the BFRs. Note that the HBCD isomers exhibited similar water solubilities to the PentaBDE constituents (BDE47 – BDE153).

The PUF material tested was transitional in terms of FR content, i.e. it contained Penta-BDE. U.S. manufacture of Penta-BDE was discontinued in 2004. However, substantial amounts remain in in-use & discarded products, as well as environmental debris. It also contained additives consistent with Firemaster® 550 (2-ethylhexyl 2, 3, 4, 5-tetrabromobenzoate (TBB); 2-ethylhexyl 2, 3, 4, 5-tetrabromophthalate (TBPH)) and several phosphate FRs: tris (1,3-dichloro-2-propyl) phosphate (TDCPP) and triphenyl phosphate (TPP)). Interestingly, (tris (2-chloroethyl) phosphate (TCEP) and tris (1-chloro-2-propyl) phosphate (TCPP) were not detected in the PUF, but were later detected in the aqueous leachates. These were apparently present as trace components in the PUF, but at levels below the limits of quantitation.

PUF: Concentration (mg/g)		
	mean	std dev
BDE-47	10.9	5.4
BDE-100	3.1	1.0
BDE-99	10.3	2.1
BDE-154	1.5	1.1
BDE-153	1.9	1.1
PentaBDE Total	27.8	
TBB	2.4	0.5
TBPH	0.8	0.3
TCEP	ND	
TCPP	ND	
TDCPP	0.5	0.1

Table 1. FR concentrations in the PUF studied. Note that TCEP and TCPP were not detected in the analysis of the PUF itself, but were detected in the leachates. This suggests that they were present at trace levels in the PUF and were at detectable levels in the water due to their relatively high water solubilities. This is important as it is evidence that analysis of original polymers may fail to reveal chemicals that might be important in leachates.

The expanded PS was purchased from a large home hardware chain. The product name was Perma R foam board insulation. It was white in color. In texture, it was similar to PS used in insulated cups and coolers.

PS: Concentration of HBCD (ug/g)		
	mean	std dev
α-HBCD	58.1	6.6
β-HBCD	34.1	2.6
γ-HBCD	342	58.1
TOTAL	434	

Table 2. The expanded PS contained hexabromocyclododecane (HBCD), totaling 434 µg/g, with the Y isomer being dominant.

The flexible PVC was received as a yellow pellet and the product name was Teknor Apex® 716. Based on GC/MS analysis we determined it contained dioctyl phthalate at 794 µg/g. We also detected TPP in it by GC/MS and are in the process of quantifying it by LC/MS.

Based on GC/MS analysis, the PE exhibited low levels of fragrance chemicals, perhaps original bottle contents, versus structural polymer additives. We anticipated the detection and subsequent leaching of colorants and other additives. However, we did not detect their presence. We concluded that additives that might have been extractable were perhaps reduced below detection by the hot water wash steps employed by the regrinder to cleanse the recycled plastics. They market the material as food grad plastic. However, as we saw in the case of the organophosphates in PUF, we pursued leachate tests of the regrind PE as we felt it was possible that we might detect additives in the aqueous leachates.

Results of 10 day consecutive leaching of PUF: An initial experiment was conducted to examine the pattern of additive release over time. PUF microplastics were leached for 10 consecutive days. Conditions chosen were fairly rigorous: 40°C, salinity 0 ppt, and 100 mg/L HA. One liter water samples were collected daily and analyzed by LC/MS to determine concentrations of FRs. Our initial hypothesis was that levels of additives in leachates would sharply decrease after one to two days of leaching as additives near the surface were depleted. Leaching of additives deeper within the particles would be inhibited by the viscosity of the polymer.

The x-intercept denotes the days required for the additive concentration leached into the water to reach 0 ng/L, assuming a consistent trajectory of release. The intercept will be determined by both the rate of chemical release and the concentration in the polymer. X-intercepts were calculated using equations of the lines describing decreasing PBDE leaching over time. This assumes that the 10-day concentration trend will continue until leaching ceases, however this trajectory remains unproven. BDE100, 153, 154 and TBB showed very similar x-intercepts: 19-22 days. BDE47 and 99, although more water soluble than the hexa-BDEs, exhibited larger x-intercepts: 85 and 38 days, respectively. This may relate to their higher initial levels in the PUF.

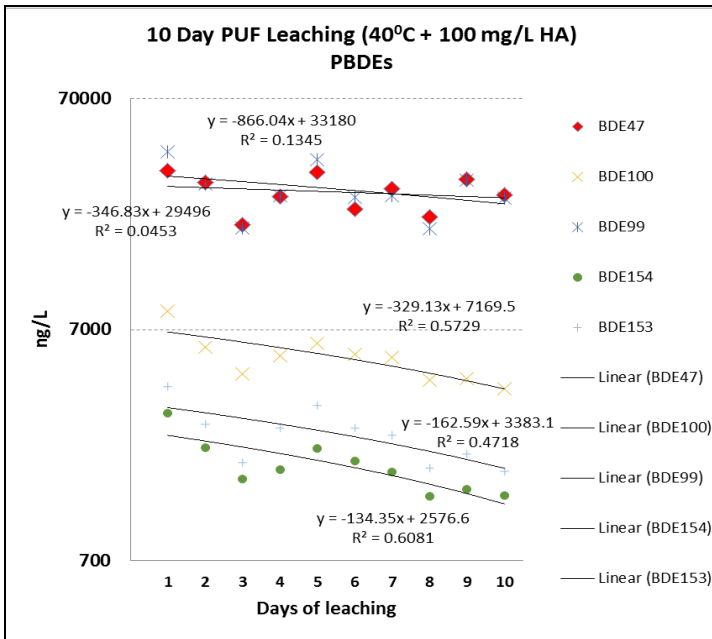


Fig. 15. Concentrations of PBDEs (BFRs) detected in water on each day of leaching. Note concentrations are in ng/L (parts per trillion) and scale is on a log basis. Highest levels were for the major constituents of the PentaBDE formulation. PBDEs continued to be leached from the 53-300 μm PUF microplastics even after 10 days, although concentrations decreased over time, as denoted by the negative slopes of the lines.

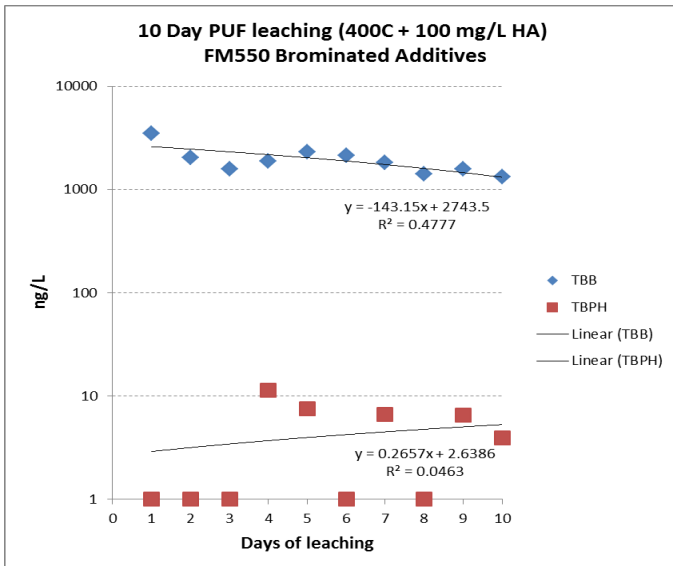


Fig. 16. Concentrations of TBB and TBPH (BFR replacements for PBDEs) detected in leachates of the 53-300 μm PUF microplastics over 10 days. Concentrations are in ng/L (parts per trillion) and scale is on a log basis. TBB has a water solubility (25°C and 0 mg/L DOM) of about 100 ng/L. Hence, TBB is ~10-fold less water soluble than either BDE153 or 154. The solubility of TBPH is <10 ng/L and was barely detectable in the leachates. No trend in leachate concentrations over time was observed for TBPH.

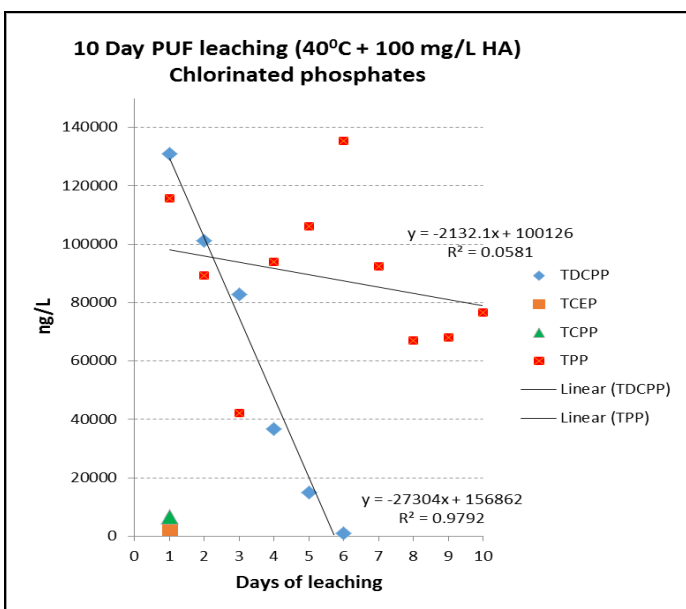


Fig. 17. Concentrations of phosphate FRs detected in water on each day of consecutive leaching. Note concentrations are in ng/L (parts per trillion). TDCPP concentration was the highest on day 1, but levels in the leachate decreased rapidly thereafter. In contrast, substantial release of TPP continued throughout the 10 days. TDCPP has a water solubility 3 to 4 times that of TPP. TCEP and TCPP were not detected in the original PUF, but were detected in the Day 1 leachates and not thereafter. These phosphate FRs exhibit water solubilities >10 fold that of TDCPP and TPP, so might be expected to be rapidly depleted.

Chemical	Days
BDE 47	85
BDE 99	38
BDE 100	22
BDE 153	21
BDE 154	19
TBB	19
TBPH	NA
TDCPP	6
TPP	27 ²

Table 3. Calculated x-intercepts of the lines describing the change in analyte concentration leached from the PUF over 10 consecutive days of leaching (water at 40°C and humic acid content of 100 mg/L).¹

¹TBPH did not show a clear trend, perhaps as concentrations in the leachate were near or below the detection limit. ²TPP estimate made after excluding Day 3 and Day 6 points. The numbers of bromines in the PBDE congeners are provided.

Leaching of additives from different microplastics under varying water conditions: A series of experiments were performed evaluating the influence of polymer type, particle surface area/size, temperature, salinity, humic acid content and the presence of two surrogate gut fluids on leaching of additives over a 24 hr period.

PUF: Salinity

Increasing salinity was expected to either have no effect of leaching or to decrease it by reducing the water solubilities of hydrophobic additives. We also desired to use 0 ppt as a default condition versus 35 ppt, as high salt content was expected to cause precipitation of HA. Three salinities were tested here, in concert with the 53-300 μm fraction of PUF microplastics. Reagent grade NaCl was used as the source of the salt versus artificial and natural seawater due to the potential for these latter materials to contain variable amounts of organic matter and other materials. Leaching fluid HA content was 0 mg/L and temperature 40°C. Leaching of hydrophobic brominated FR additives from PUF decreased with increasing salinities. Note: the BDE153, 15 ppt level was at the method detection limit.

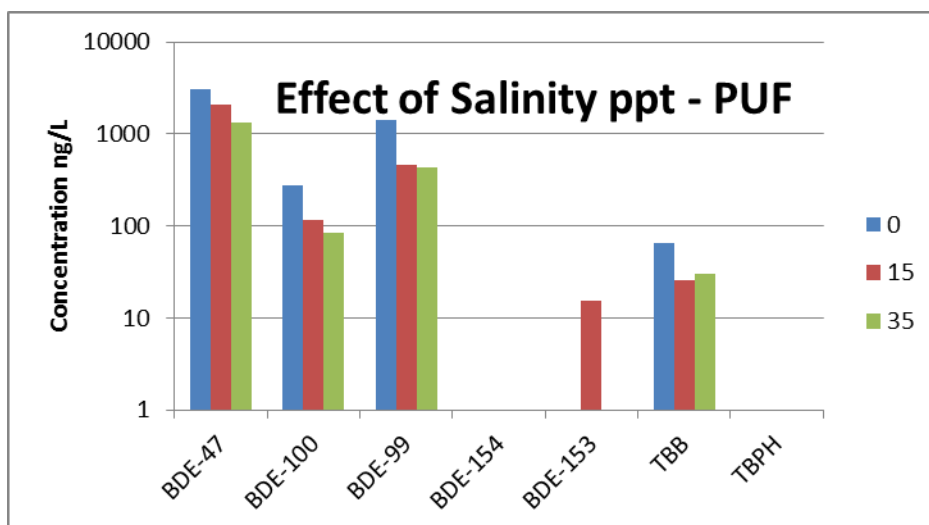


Fig. 18. Increasing salinity typically reduced the levels of hydrophobic BFR additives in the leachates. BDE153 was at the limit of detection. BDE154 and TBPH were not detected in the leachates in these experiments.

A less obvious picture was observed for the relatively water soluble phosphate FRs. However, concentrations were generally lowest at 35 ppt, except for TPP.

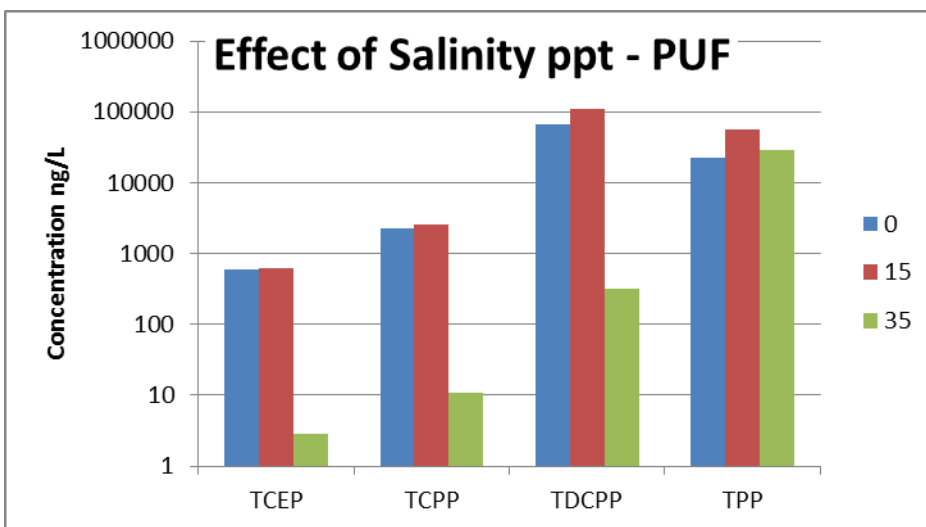


Fig. 19. Salinity had a less obvious impact on the leaching of phosphate FRs than for hydrophobic BFRs. This is not unexpected due to the high water solubilities of these chemicals.

PUF: Microplastic surface areas

We hypothesized that increasing particle surface area would increase the extent of additive leaching from microplastics. Here, three microplastic size fractions were assessed. We originally planned to examine three discrete sizes that differed by orders of magnitude (i.e. 1000 μm , 100 μm and 10 μm). We also wanted to produce small particles to maximize surface areas and hence migration potential of the more hydrophobic additives. Unfortunately, we found that to get adequate microplastic material for experiments we needed to widen the size ranges selected for each test size. Also, that is was quite difficult to produce adequate amounts of the smallest particle size for all experiments. As a result, our size ranges in the end were contiguous, versus narrow and differing by orders of magnitude. We believe this decreased the effect of surface area observed in our experiments. Leaching water conditions for the size/surface area experiments were: salinity 0 ppt, temperature 40°C, HA 0 mg/L. Although there appears to be an increasing trend for some analytes (e.g. BE47, BDE100, BDE99), we did not see as substantial increase in the release of additives with increasing surface areas as we initially hypothesized.

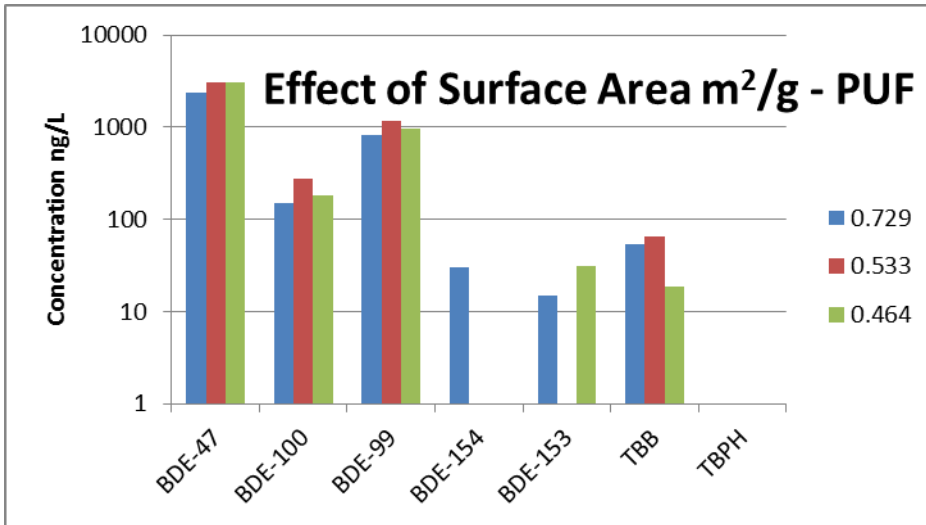


Fig. 20. Increasing microplastic surface area had a modest effect on BFR concentrations in leachates. BDE153, BDE154 and TBPH were at or below the detection limit in leachates in these experiments.

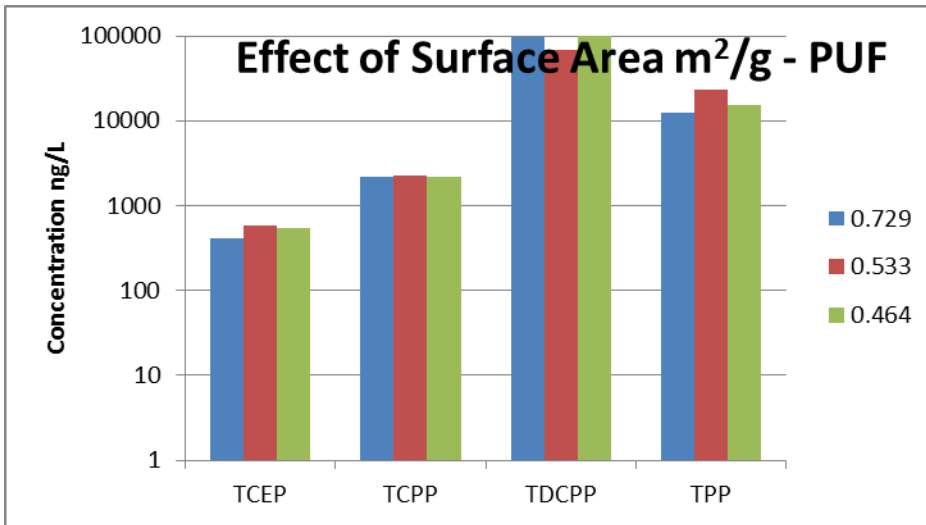


Fig. 21. Increasing microplastic surface area had no or a modest effect on phosphate FR concentrations in leachates.

PUF: Water temperature

We evaluated the effect of three water temperatures (4, 20 and 40°C) on additive leaching potential. Again salinity was held at 0 ppt and HA 0 mg/L. The microplastic size evaluated was 53-300 µm. Here, a clear trend in increasing BFR concentrations with increasing temperature was apparent. Note that elevated temperatures are present in landfills (18-55°C, average of 35°C: Bjorn et al, 2007) and the digestive tracts of organisms. For example, body temperatures of mammals may range from 35 to 40°C, while that of birds may range from 39 to 44°C (Prinzinger et al, 1991).

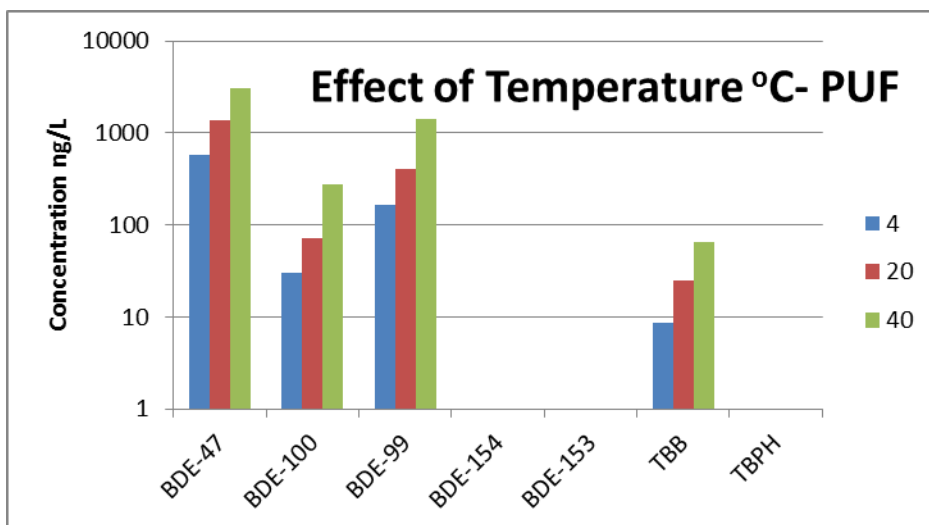


Fig. 22. BFRs exhibited greater leachability from PUF microplastics (53-300 μm) at higher water temperatures. BDE154, BDE153 and TBPH were below quantitation.

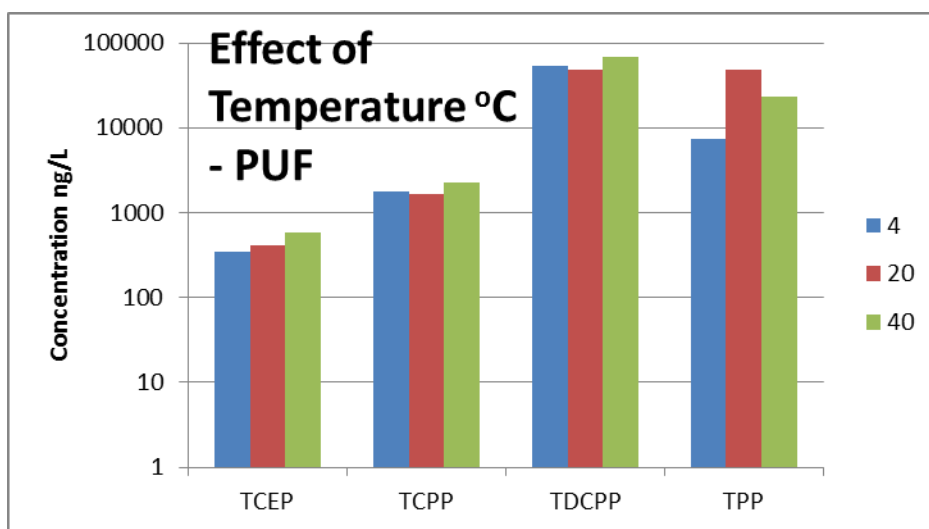


Fig. 23. Phosphate FRs were generally more leachable from PUF microplastics (53-300 μm) at higher water temperatures.

PUF: humic acid concentration

We evaluated the effect of four Aldrich humic acid (HA) concentrations: nominally 0, 5, 10 and 100 mg/L. Dissolved organic carbon (DOC) content of water is typically reported for field samples. DOC values we measured for the 0, 5 and 100 mg/L HA solutions (using combustion catalytic oxidation: Shimadzu TOC-5000 Carbon analyzer) and were (mean/std dev): 0.070/0.014, 2.23/0.037 and 29.6/1.07 mg/L, respectively. Krom and Sholkovitz (1977) reported DOC levels varying between 8.3 and 15.8 mg/L for oxic marine sediments and 55.9 to 70.5 mg/L for anoxic pore waters. Katsoyiannis

and Samara (2007) reported DOC values of 70 mg/L raw wastewater and primary sedimentation effluent, decreasing to 19 mg/L in secondary sedimentation effluent. Christensen et al (2001) reported dissolved organic carbon contents of landfill leachate-polluted groundwater ranging from 30 to 29,000 mg/L.

The 53-300 μm particle fraction was studied, using water of 0 ppt salinity and 40°C. A trend in increasing BFR concentrations in leachates with increasing HA concentration was observed. Note that Aldrich HA is more hydrophobic than most HAs extracted from natural waters and thus likely facilitated greater leaching for a given concentration. However, Aldrich HA is also commercially available and thus is a readily accessible material for comparative studies.

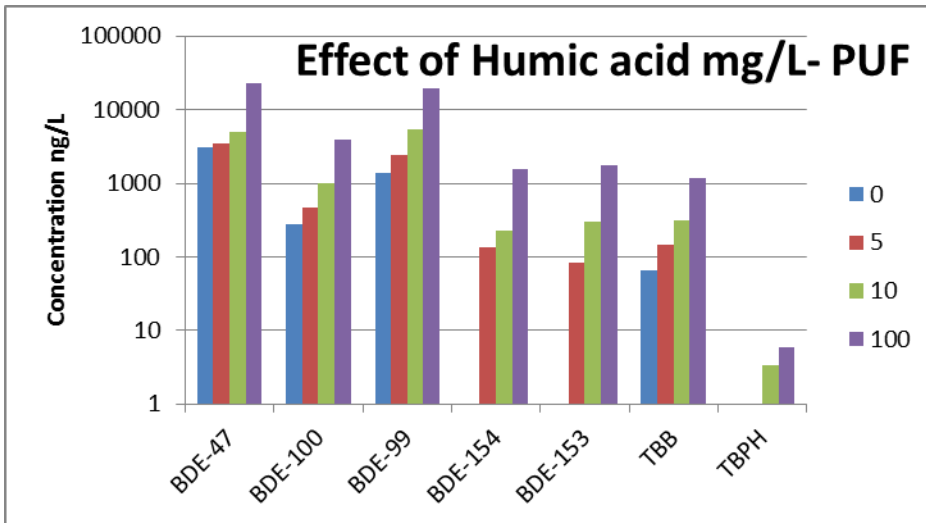


Fig. 24. Effect of increasing HA level in leaching fluid on BFR concentrations. The presence of 100 mg/L HA (nominal; measured DOC 29.6 mg/L) substantially increased BFR concentrations. The presence of HA resulted in leaching of even the extremely hydrophobic TBPH.

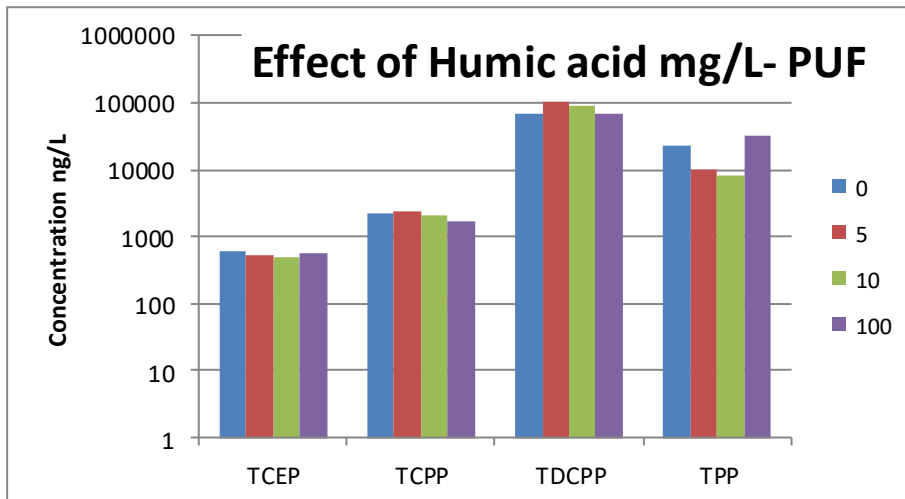


Fig. 25. Unlike the more hydrophobic BFRs, increasing HA concentration did not increase leaching of more water soluble phosphate FRs.

PUF: Digestive fluid addition

The impacts of two synthetic digestive fluids (sodium taurocholate (STC) and sodium dodecyl sulfate (SDS) at 10 mM) on leaching of PUF additives were investigated. The concentrations were those suggested by Voparil et al. (2004) as comparable to the lipid solubilizing power of the gut fluid of the benthic lugworm and deposit feeder *Arenicola marina*. Note that 10 mM is considerably more concentrated than the 100 mg/L HA solution previously evaluated. The salinity of the water was 0 ppt and temperature 40°C. As in previous experiments the 53-300 µm fraction was used. The presence of either synthetic fluid greatly increased leaching of the hydrophobic BFRs. These two digestive fluid surrogates appeared to be similarly effective here.

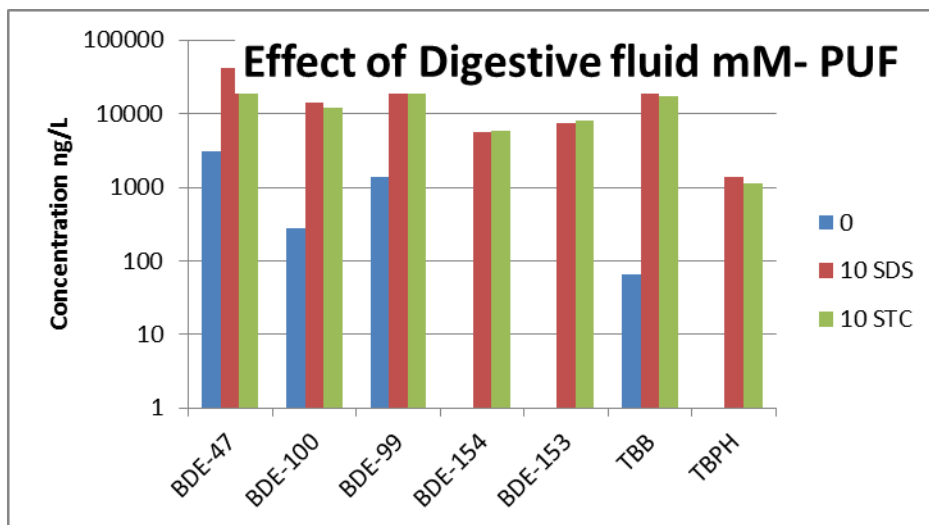


Fig. 26. The presence of 10 mM synthetic gut fluids greatly enhanced leaching of hydrophobic BFRs from the 53-300 µm PUF microplastics. The two fluids increased leaching to a similar extent. Note that BDE153, BDE154 and TBPH were below detection in leachates in the absence of the digestive fluids.

In contrast, an effect of the two synthetic fluids on leaching of the phosphate FRs was not apparent. Concentrations of these additives were similar to the no digestive fluid control. This is not surprising considering their substantial water solubilities.

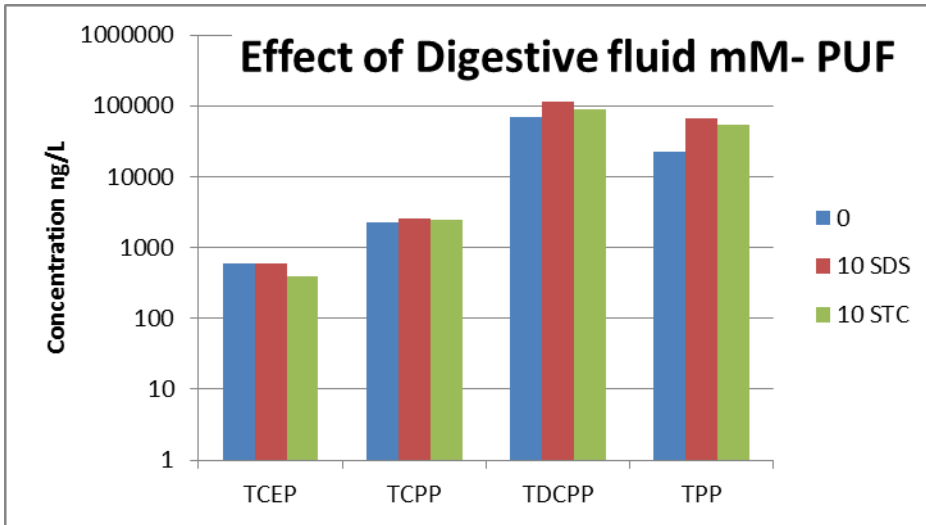


Fig. 27. The two synthetic digestive fluids (sodium taurocholate (STC) and sodium dodecyl sulfate (SDS)) had minimal effects on leaching of the relatively hydrophilic phosphate FRs from the 53-300 μ M PUF microplastics.

PUF: Weathering by UV exposure

The 53-300 μ m fraction of microplastics was subjected to 0, 500 (~ 6 months natural light) or 1000 hrs (~1 year natural light) of artificial UV irradiation. Column leaching conditions were: 0 ppt salinity, 0 mg/L HA and 40°C. BET analyses indicated a decrease in the surface area of the PUF following 500 hrs of UV irradiation. The PUF was also yellowed. A pattern towards lower release of hydrophobic BFRs was observed with UV irradiation. The weathered PUF microplastics also were more brittle, but were not subjected to frictional forces in this experiment, which would have decreased their particle sizes.

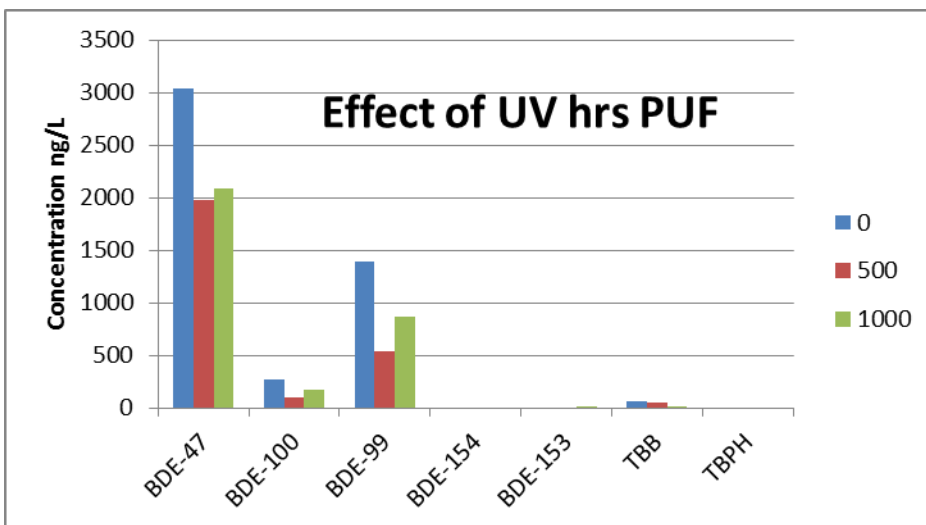


Fig. 28. PUF microplastics that were irradiated by UV showed both a decrease in BET surface area and lower concentrations in the aqueous leachates.

An effect of PUF microplastic UV irradiation duration was not apparent for the more water soluble phosphate FRs

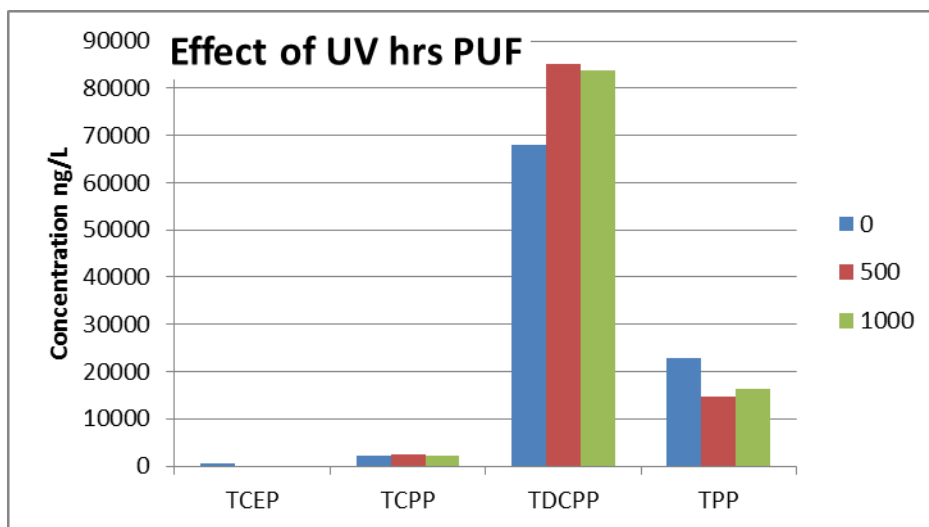


Fig. 29. UV irradiation did not appear to substantially affect leaching of the relatively water soluble phosphate FRs from the 53-300 μm fraction of PUF.

PS: Leaching of HBCD

As previously noted, HBCD was found to be present at 434 $\mu\text{g/g}$ in the expanded PS studied. The summed mean concentration of the three HBCD isomers reported by Rani et al (2014) for expanded PS samples was 475 $\mu\text{g/g}$. Jang et al (2016) found HBCD levels ranging from 0.15 to 5220 $\mu\text{g/g}$ (mean 17.2 $\mu\text{g/g}$) in styrofoam samples taken from South Korean aquaculture buoys. The water solubilities of the three major isomers of HBCD are: 2.1 (Y-HBCD), 14.7 (β -HBCD) and 48.8 (α -HBCD) $\mu\text{g/L}$. This is in the same range of solubilities as the PBDE congeners in PentaBDE. The surface area of the 53-300 μm PS was over two-fold higher than the PUF. These factors suggest that HBCD might be readily detectable in aqueous leachates that were comparable in strength to those resulting in substantial PBDE concentrations. However, this was not the case here. In only one treatment was HBCD detected in substantial concentrations in PS leachates, i.e. the 10 mM STC synthetic digestive fluid treatment. Therein, Y-HBCD was quantitated at 3610 and 4420 ng/L. The other isomers (α - and β -HBCD) in this leachate were below quantitation. Y-HBCD constituted 78.8% of total HBCD in the PS, but also exhibits the lowest water solubility. SDS at 10 mM failed to leach out HBCD from PS at detectable levels.

Rani et al (2013) reported quite different results from ours; i.e. leaching of 4000 to 14,500 ng/L of HBCD (equivalent to 16-20% of the original PS additive burden) in a beaker design, wherein PS and water were equilibrated over 1 to 96 hrs. The PS loading was 3 g of “detached spherules” to 3 L of water. The leachate water was filtered through 0.4 μm glass fiber filter paper before extraction. They reported an increase in HBCD leaching with higher water temperature (15 and 28°C); but greater leaching at 32 ppt versus 25 ppt salinity. They indicated no increase in leaching in the presence of shaking.

We conducted additional HBCD standard addition spiking column studies with sand alone and with PS in an attempt to determine the factors limiting the leaching of HBCD from expanded PS. HBCD was quantitatively (mean 60.8%) leached from a sand column (no PS present) at 40°C and 100 mg/L HA, but leaching of α -HBCD (the most water soluble isomer and lowest in commercial HBCD) spiked onto a column containing PS were only 1% and 0.2% of the added dosage (10,000 ng) at 40°C and 0 mg/L HA. This may be related to an interaction of the HBCD with the PS or possibly residual toluene used to spike the HBCD. The low recovery of HBCD in the second case may also relate to the leaching power of the 0 mg/L HA solution for the hydrophobic HBCD. More investigations are in order.

PVC: Leaching of additives.

We encountered low level phthalate contamination in most water blanks analyzed, typically 200-300 ng/L. This is not surprising as phthalates are ubiquitous indoor contaminants, used at high levels in PVC plastics for decades. Diisooctyl phthalate was identified as the phthalate present in the PVC itself, concentration 794 ug/kg. Phthalates have been reported in PVC products up to 40% by weight (Kastner et al, 2012). Additional smaller chromatographic peaks were observed by GC/MS that also exhibited the phthalate diagnostic mass/charge ratio (m/z) 149. However, these peaks were not observed in the aqueous leachates.

Kaster et al (2012) measured diethylhexylphthalate (DEHP) leaching from lab-prepared PVC discs. They estimated a leaching of <1% of the phthalate load in the PVC itself after 1 week, using deionized water at room temperature (assumed to be ~20°C). This would be equivalent to about 400 ng/L, considering the phthalate load measured in our study material. Our experiments were ~24 hrs in duration. Only the 10 mM sodium taurocholate (STC) synthetic digestive fluid set of aqueous leaching conditions resulted in the apparent release of diisooctyl phthalate beyond what we observed in the blanks. Therein, diisooctyl phthalate was detected at 42,000 and 26,000 ng/L in replicate experiments. Levels of this phthalate in the PVC leachate using the SDS synthetic digestive fluid, as well as the Aldrich HA treatment, were similar to reagent water blanks. A water blank spiked with STC at 10 mM will be analyzed to determine if the STC itself might be the source of the diisooctyl phthalate, rather than the PVC.

TCPP and TPP were also detected in several PVC leachate treatments. An apparent effect of particle size/surface area (40°C, 0 ppt salinity and 0 mg/L HA) was observed for PVC for these analytes. Unfortunately, the 300-1000 μm particles presented too small a surface area for the Micromeritics Gemini V series surface area analyzer to measure. For the purposes of the below figure a default PVC surface area value for the 300-1000 μm particles of 0.04 m^2/g was used. The surface area data available does suggest that these differed more than those observed for PUF and this might have contributed to the greater effect of particle size on leaching we observe with PVC. TCPP was only present at 46.3 ng/L and below detection in the leachate replicates.

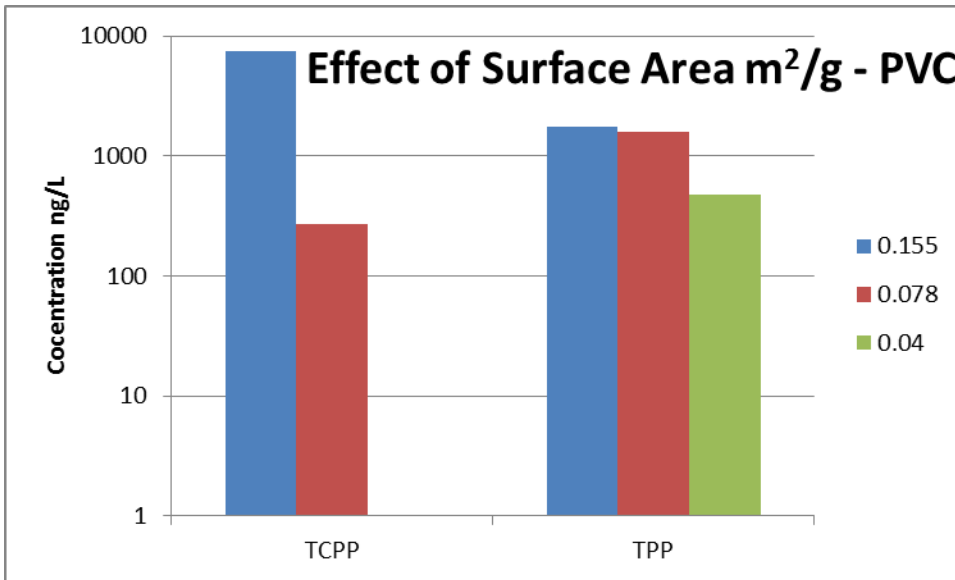


Fig. 30. Effect of PVC surface area on leaching of TCPP and TPP.

Data were also available for the impact of salinity on leaching of TCPP and TPP from PVC of nominal 53-300 μm size. Again TCPP concentrations were lower than TPP. Salinity appeared to have a modest negative impact on TPP leaching. No trend was apparent for TCPP, but concentrations detected were quite low.

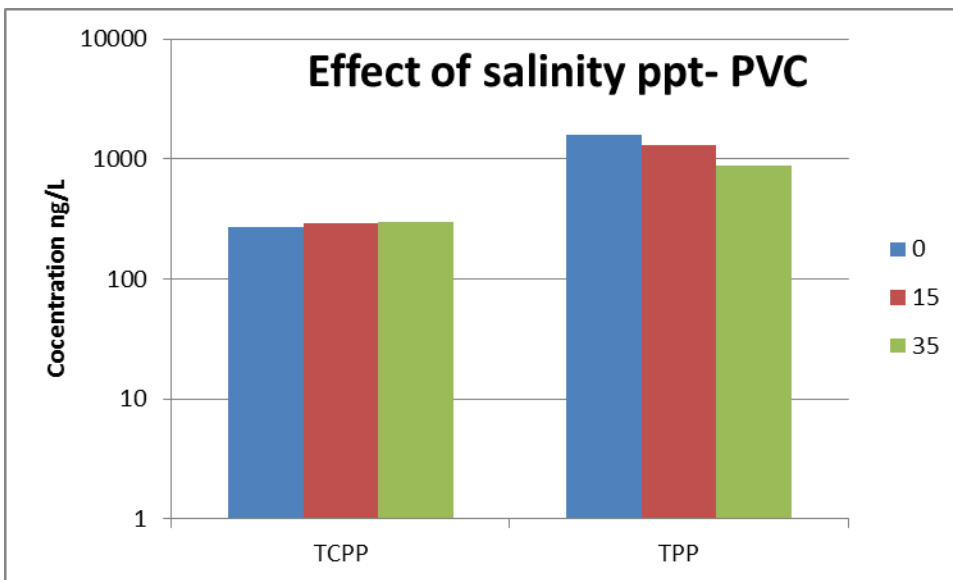


Fig. 31. Effect of salinity on leaching of TCPP and TPP from PVC. Particle sizes were 53-300 μm . Experiment temperature was 40°C and 0 mg/L HA.

UV exposure appeared to increase TPP leaching somewhat, i.e. 0 to 500 hrs, but not thereafter (1000 hrs). UV exposure did increase BET surface areas of 53-1000 μm PVC particles. Areas increased from 500 to 1000 hrs of exposure as well. TCPP levels appeared to decrease with UV exposure, but all were quite low and hence the reliability of concentration estimates is diminished.

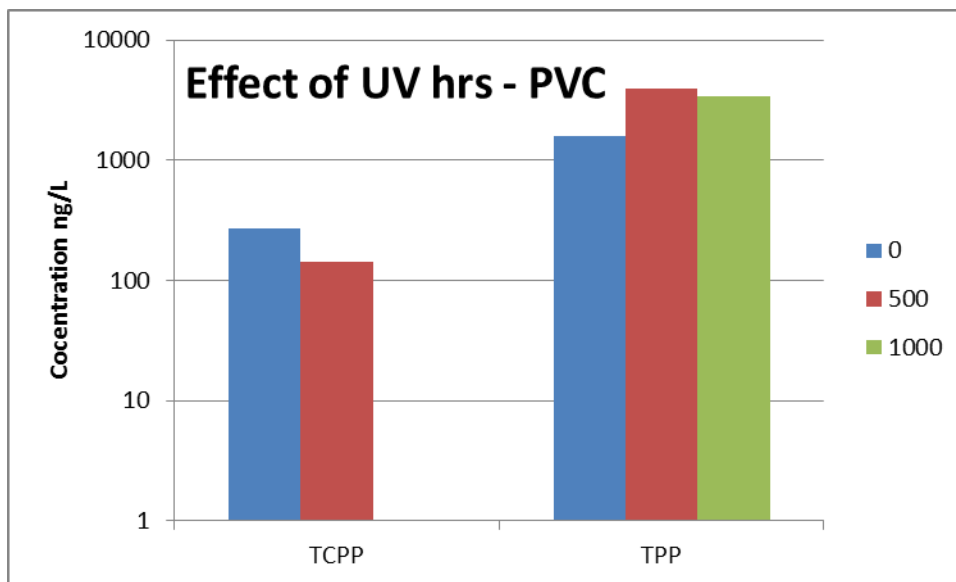


Fig. 32. A modest increase in TPP levels was apparent following UV weathering, although concentrations did not increase with increased duration (500 versus 1000 hrs). TCPP levels appeared to decrease with weathering, but were near the limit of quantitation.

We are further investigating the impact of temperature and humic acid content on PVC leaching as well. Preliminary data from 4°C and 40°C trials indicates increases in leachate concentrations of both TCPP and TPP.

PE: Leaching studies

No additives were detected in any of the PE column studies. As noted previously, this may be due to exhaustive cleaning procedures used by the recycler. In retrospect, milling of new bottles or PE suspected to contain additives such as the antimicrobial agent triclosan might have been more insightful.

Conclusions:

The conceptual approach of using column elution of additives from microplastics, permitting evaluation of a matrix of leaching conditions, was validated. The column leaching system could be constructed such that multiple columns could be leached simultaneously, permitting more rapid replication. Alternatively, the leachates could be used in toxicological assays. Our initial expectation was that additives would leach to their greatest extent initially and then leachate concentrations would drop drastically as the additive was depleted from the microplastic surface. This pattern was observed, especially for some hydrophilic additives, but release of hydrophobic BFRs continued at a substantial rate for an extended period (e.g. throughout the 10 day leaching study).

PUF was observed to release substantial amounts of additives. DOM was much more impactful in liberating hydrophobic additives (e.g. BFRs) than hydrophilic ones (e.g. phosphate FRs).

Leaching results for PS/HBCD were intriguing. It appears that HBCD may associate with PS, perhaps limiting its environmental release. European studies have suggested that use of HBCD on textiles released greater amounts of HBCD to the environment than use in PS, despite greater usage in the former application (Swedish Chemicals Agency. 2008). Nonetheless, the synthetic digestive fluid STC appears to possibly release HBCD from PS (pending further analysis of STC-containing water blanks). Low release of phthalates from PVC followed a similar pattern. Again, we must evaluate further the possibility that STC itself contained phthalate contaminants. The take-home at this point is that consideration of polymer/additives pairing is more critical than initially supposed in evaluating the potential leaching of additives. This was the case regardless of whether the polymer was dense or cellular (i.e. PVC or PS, respectively).

Data obtained here suggest that organic content/composition of the leaching fluid was the most critical parameter influencing additive release from polymers. This indicates that substantial amounts of additives may be leached from microplastics under conditions where DOM is high, e.g. in digestive systems, interstitial sediment water, wastewaters and landfill fluids. Elevated temperature also increased leaching of some additives from microplastics. Warm-blooded organisms ingesting microplastics may thus be at greater exposure and subsequent risks from chemical additives. Beach water temperatures in tropical areas may surpass 30°C. Temperatures in landfills may exceed 50°C.

Interestingly, wastewater treatment plants (WWTPs) that utilize anaerobic digestion operate with a fluid stream high in DOM and with a targeted temperature of 40°C. Their goal here is to facilitate microorganisms in degrading polymeric structures in the sludge, reducing its volume by about half prior to subsequent disposal. About 60% of that sludge is then land applied as biosolids. In addition, some treatment plants are now preceding anaerobic digestion with an even more aggressive treatment, thermal hydrolysis (one version of which is known as the Cambi® process). Here the sludge is subjected to over 100°C and 6 bar of pressure. The pressure is then quickly dropped, resulting in a “steam-explosion” further disintegrating cells and fibers (e.g. <http://www.environmentindex.com/en/article/cambi-thermal-hydrolysis-sludge-treatment-medium-to-large-scale-application-677.aspx>). These processes may also further liberate PBT chemicals from plastics. These additives, in turn, will enter the liquid phase in the WWTP and may ultimately sorb to the surfaces of sludge particles, where they may exhibit greater bioavailability compared to additives residing within microplastics. In addition, a greater percentage of recalcitrant polymer additives may escape via the treated effluent to surface water.

In contrast to DOM and temperature, salinity did not have a substantial impact of leaching of additives. This was expected. UV weathering resulted in substantial changes in the appearance and some cases surface areas of some microplastics. The effect varied depending on polymer type. PUF was most embrittled by UV exposure, although changes in other polymers were visible. In the field these plastics would have more quickly fragmented, exposing new surfaces to the environment. Additional research on the consequences of weathering on sorption of PBTs and leaching of additives is indicated.

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Additional Information:

4. **Were any significant challenges encountered? If so, how were they resolved?** Yes. The first challenge related to difficulties in milling the polymers into the desired size classes. We had arranged for another institution to do this initially, but they were unable to accomplish it. We investigated commercial polymer companies, but none could do some economically. We ultimately investigated and obtained additional funding, purchased a lab scale cryomill and air jet sieve and did the milling of polymers in-house. This set us back time-wise, but has now given us that ability for future microplastic research. We also compressed the size ranges of the microplastics we used in experiments due to difficulties in producing adequate quantities of the smallest size fractions. We felt it was essential to work with the smallest sizes feasible. In retrospect, we could have used larger-sized particles. However, we wanted to maximize surface areas, as we were concerned that hydrophobic contaminants would be nondetectable in leachates (in some cases this proved true anyway) if surface areas were limited. Had we used larger particles we likely would have demonstrated a greater influence of particle size on leaching potential of additives. However, a greater share of hydrophobic chemicals might have not been detectable in the leachates.

The Q-Sun Xenon Test Chamber for accelerated UV weathering of plastics employed an internal fan to maintain temperature and humidity conditions. We sent the first batch of 53-300 μm microplastics to the Particle Technology Research Center (Western University; Ontario, Canada) for weathering treatments. These were subsequently lost due to the fan operation. We researched and found UV transparent glass plate, purchased these and had them shipped to the facility. We then had to ship replacement microplastics to Canada. Placement of these covers over the sample jars in the apparatus eliminated losses.

Another challenge was the actual selection of the polymer study materials themselves. Selection of these materials had to be completed before milling and any leaching experiments. Thus this step held up all subsequent experiments and polymer treatments (e.g. milling and UV weathering). As we were already delayed due to the unanticipated polymer milling issue, we felt we needed to move ahead. In retrospect, we should have invested even more time in selecting the polymers materials for experiments, especially PE. Unfortunately there is not a supplier of polymer/additive combinations with known compositions. Most polymer manufacturers will not divulge compositional information. Researchers must thus operate by trial and error. The PUF chosen proved to be highly informative. The PS selected gave unexpected but interesting results, as did the PVC. We are still evaluating the ramifications of some elements of the leaching experiments using those two materials. Our selection of regrind HD PE proved problematic. To date we have not identified additives within this particular material. In some

cases unknown, trace ingredients in polymers may prove to be important as well (e.g. some phosphates in the PUF). However, this has not proven to be the case with the regrind HD PE.

5. **Other issues/concerns – Are there things that we (the MDP) can do better to manage research projects in the future?** The staff was extremely patient as we attempted to overcome several unanticipated hurdles to completing the proposed research.
6. **Did you have any media inquiries due to your research? If so, please list them.** A) Interview with NIEHS Environmental Health Perspectives (Kellyn Betts). California Furniture Labels Shift Flame Retardant Debate. 2015. B) Interview with NIEHS Environmental Health Perspectives (Erin Dooley) for “New Link in the Food Chain? Marine Plastic Pollution and Seafood Safety” <http://ehp.niehs.nih.gov/123-A34/>. C) Interview for Medical Unit for ABC News: Danielle Krol, MD. Related to microplastics.
7. **Were any grad students/interns involved in project? If so, please indicate the number of grad students/interns involved in the project.** At VIMS graduate student (Kelley Uhlig-MS VIMS) was involved in the project, although received no direct funding from the grant.
8. **Did you participate in outreach/education events? Please list these events and estimate how many students and adults attended these events.** We participated in numerous such activities that to varying extents involved aspects of this research effort. These included:
 - A) *Microplastics in the Environment: It's Complicated*. VIMS Aquatic Health Sciences Departmental Seminar Series. 2016 (~45 students & faculty).
 - B) *Plastics: Potential effects on environmental & human health*. Hampton University, Hampton VA. 2015 (~50 students & faculty).
 - C) *Lab Tour: Microplastics* - York High School AP Environmental Science 2015 (~30 students).
 - D) Rappahannock Institute for Lifelong Learning. *Microplastics in the Environment*. 2015 (~10 adults).
 - E) *A Scientist Walks Into A Bar...* Park Lane Tavern, Hampton, VA. Presentation & discussion on health and environmental issues related to microplastics. 2014. (~30 attendees).
9. **Did you present your research at any scientific conferences? If so, what conference? Yes.** These were:
 - A) *Aqueous leaching of chemical additives from microplastics*. World Congress: Society of Environmental Toxicology & Chemistry (SETAC), Orlando, FL. November 2016.
 - B) *Technical Review of Microbeads/Microplastics in the Chesapeake Bay*. Chesapeake Bay Program Toxics Workgroup Meeting. 2016.
 - C) *Microplastics & Human Health: Searching for Links*. 2nd Virginia Marine Debris Summit.
 - D) *Microplastics: Vectors for chemical exposure & transport*. 1st International Conference on Environmental Pollution and Health, Jinan University, Guangzhou China. 2015.
 - E) *Comparison of the sorption of hydrophobic pollutants to polyethylene and two bio-based polymers*. North American Meeting of the Society of Environmental Toxicology and Chemistry. 2015. Salt Lake City.

F) *Plastic Marine Debris & Potential Human Health Risks Forum*. National Academy of Sciences. Washington DC. 2014.

G) *Ghosts in the machine: Releases of flame retardants from microplastics and recycled materials*. North American Meeting of the Society of Environmental Toxicology and Chemistry. 2014. Vancouver, Canada.

H) *Microplastics: Is smaller bigger?* Virginia Marine Debris Summit. Virginia Beach, VA. 2013.

Marine Debris Program Final Report

Part I. Research Project Information

Project Title: Influence of a suite of environmentally relevant conditions on PBT leaching from, and sorption to, marine microplastic debris

Submitted by: Da Chen, Assistant Professor

Date submitted: December 7, 2016

Project location: Southern Illinois University Carbondale, 1125 Lincoln Drive, Carbondale, IL 62901

Report:

10. Introduction & Research Question

Study Questions: Sorption of hydrophobic chemicals from water to microplastics has been reported previously. Thus microplastics may serve as a carrier to transport organic chemicals to organisms or other water regions. Sorption may be affected by a number of factors, including particle size, temperature, and presence of organic matters. Formation of biofilm on microplastics may also change the sorption kinetics. In the present sorption study, we focused on the effects of particle size and biofilm on the sorption of PCBs and halogenated flame retardants on two model polymers (PE and PVC).

11. Methods

Test materials: To study the effects of particle size on sorption, three different size classes (i.e. nominal size of <53, 53-300, and 300-1000 μm) of high density PE (HDPE) and PVC microplastics were tested. HDPE particles (nominal size of 300-1000 μm) were used to study the effect of biofilm formation on chemical sorption.

Test chemicals: Chemicals under test included polychlorinated biphenyls or PCBs (one congener of each degree of chlorination), polybrominated diphenyl ethers or PBDEs (one congener of each degree of bromination), α -hexabromocyclododecane (HBCD), and organophosphate flame retardants (OPFRs). The OPFR chemicals included isotopically labeled tris(2-chloroethyl)phosphate (TCEP), tris(1,3-dichloro-2-propyl)phosphate (TDCPP), tri-n-butyl phosphate (TBP), triphenyl phosphate (TPP), and tris(2-butoxy-ethyl)phosphate (TBEP).

Table 1. Chemicals tested for sorption experiments

PCB-3	BDE-3	Tris(2-chloroethyl)phosphate-d12
PCB-5	BDE-15	Tris(1,3-dichloro-2-propyl) phosphate-d15
PCB-28	BDE-28	Tri-n-butyl phosphate-d27
PCB-74	BDE-47	Triphenyl phosphate-d15
PCB-118	BDE-85	Tris(2-butoxy-[13C2]-ethyl)phosphate
PCB-138	BDE-99	
PCB-180	BDE-153	α -hexabromocyclododecane
PCB-203	BDE-183	
PCB-206	BDE-208	
PCB-209	BDE-209	

Experimental system:

Equilibrium time and sorption kinetics. HDPE particles with three different size classes (i.e. nominal size of <53, 53-300, and 300-1000 μm) were tested. A mixture of chemicals (100 ng each) was added to the simulated marine water system containing 25 mL salt water (35 ppt) and 50 mg of particles in a glass tube. Acetone was used as a vehicle (<0.5%) to expedite aqueous dissolution. Water bath shakers were running constantly at 100 rpm and 25°C. Three replicates of samples from each size of HPDE were collected at days 0, 1, 2, 4, 8, 14, and 20, respectively, since the beginning of experiments. Particles were filtered from water. Both particles and filtered water were stored at 4°C until analysis.

Effect of particle size on sorption. HDPE and PVC particles with three different size classes (i.e. nominal size of <53, 53-300, and 300-1000 μm) were tested to evaluate the effects of particle size on chemical sorption. Chemical mixtures at four concentrations (i.e. 10, 20, 50, and 100 ng each) were added to the simulated marine water system containing 40 mL of salt water (35 ppt) and 10 mg of microplastics in a glass tube. The ratio of microplastics weight to water volume used in this experiment was 10 mg/40 mL, different from the ratio (50 mg/25 mL) used earlier. This was utilized in an attempt to increase the likelihood of detection of some PCB and PBDE congeners in aqueous phase, required to determine their Freundlich constants. Acetone was used as a vehicle (<0.5%) to expedite aqueous dissolution. Water bath shakers were running constantly at 100 rpm and 25°C. Three replicates of samples from each size of HDPE or PVC particles were collected at day 6 after the beginning of experiments. Particles were filtered from water. Both particles and filtered water were stored at 4°C until analysis.

Effect of biofilm on sorption. HDPE particles with a nominal size of 300-1000 μm were tested in a freshwater system to understand the effect of biofilm on chemical sorption. Biofilm appeared on particles after they were placed in a freshwater fish tank with a circulated water flow system for 60 days. Approximately 50 mg of wet particles (~20 mg after moisture removal in oven) were transferred to each glass tube containing 40 mL water. Control groups included 20 mg of dry particles without biofilm placed into 40 mL water. Chemical mixtures at four concentrations (i.e. 10, 20, 50, and 100 ng each) were added to the simulated freshwater system. Three replicates of samples from each size range of HDPE particles were collected at day 6 after the beginning of experiments. Particles were filtered from water. Both particles and filtered water were stored at 4°C until analysis.

Sample treatment and extraction. Immediately following sample collection, water solution was filtered through a Whatman 0.45 μm filter. Microplastic particles were collected on the filter. As some particles were attached on the glass tube, HPLC water was used to wash particles off the tube as much as possible and then filtered through the filter. The filter containing particles was extracted to determine chemical residues on particles. All collected water was combined and extracted to determine chemical residues in water. After surrogate standard mixtures were added, the filter was extracted by the accelerated solvent extraction (ASE 350, Dionex, CA) with dichloromethane. Each extract was run through pre-washed sodium sulfate to remove moisture and then transferred to a GC vial. Internal standards were added to each extract prior to instrumental analysis. Filtered water was transferred to a 50 mL separatory funnel. After surrogate standard mixtures were added, each water sample was extracted three times with 20, 10, and 10 mL of dichloromethane, respectively. The extracts were combined and transferred to a GC vial. Internal standards were added prior to instrumental analysis.

Instrumental analysis. Detection of PBDE congeners was conducted on an Agilent 7890B gas chromatography (GC) coupled to a 5977A mass spectrometer (MS; Agilent Technologies, Palo Alto, CA). The GC was equipped with a 15-m DB-5HT column (0.18 mm i.d., 0.1 mm film thickness, J&W Scientific, Folsom, CA). The initial column temperature was held at 50 °C for 4 min and then ramped to 300 °C at 10 °C/min (held for 15 min). Identification and quantification of PBDE congeners were achieved via selected ion monitoring (SIM) of

characteristic ions in the electron capture negative ionization (ECNI) mode. Detection of PCB congeners was conducted on the same type of GC-MS equipped with a 30-m HP-5MS column (0.25 mm i.d., 0.25 mm film thickness, J&W Scientific, Folsom, CA). The initial column temperature was held at 110 °C for 1 min and then ramped to 200 °C at 10 °C/min, then to 250 °C at 4 °C/min, finally to 290 °C at 8 °C/min (held for 8 min). Analysis of OPFRs and HBCD was conducted on an Agilent 1260 HPLC equipped with a 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). The MS was equipped with a TurboIonSpray® electrospray ionization (ESI) probe operated in the multiple reaction monitoring (MRM) mode for quantitative measurement of OPFR or HBCD substances.

Doubling time and maximum sorption. Doubling time of sorption and the maximum sorption on microplastics were predicted by an exponential regression (Eq. 1).

$$Y = Y_0 + A \times \exp (R_0 \times X) \quad (\text{Eq. 1})$$

Where X is the sorption time (day); Y is the sorption amount at X; Y₀ is the predicted maximum sorption amount; R₀ is the sorption rate constant; and A is a constant.

Doubling time is a period of time required for a chemical to double in concentration. Doubling time of chemical sorption on particles was calculated using Eq. 2

$$t_2 = \ln(2) / R_0 \quad (\text{Eq. 2})$$

Where t₂ is doubling time and R₀ is the sorption rate constant.

Sorption isotherm. Sorption isotherms were generated via the Freundlich model:

$$\text{Log } C_s = \text{Log } K_F + n \text{ Log } C_{aq} \quad (\text{Eq. 3})$$

Where C_s is the solid phase concentration (ng chemical/g microplastics), C_{aq} is the aqueous concentration (ng chemical/mL simulated water), K_F is the Freundlich constant, and n is the Freundlich exponent.

12. Results

Equilibrium time and sorption kinetics

Figures 1-3 describe the sorption of PBDEs, PCBs, OPFRs, and α-HBCD on three different sizes of microplastics over time, as well as the change of chemical residues in the water phases. The data revealed that chemical residues on microplastics generally reached equilibrium 4-8 days after the beginning of sorption experiments, regardless of microplastic sizes. Very low masses (i.e. generally < 2 ng) of BDE-3, BDE-15, BDE-28, BDE-47, PCB-3, PCB-5, and PCB-28 were detected in water after day 0, whereas other PBDE or PCB congeners were generally non-detectable. By contrast, OPFRs were detectable in both microplastics and water throughout the experiments. This may be due to greater water solubility of OPFRs compared to that of PCBs and PBDEs. It is noted that the total mass of a chemical in plastics and water phases was generally 10 – 55% less than 100 ng. This may be due to the sorption of chemical on the wall of glass tubes and loss during extraction of residues from different phases.

Based on this pilot study, we chose to use day 6 as the time point for collecting particles and water samples in the subsequent investigations of the effects of particle size and biofilm on sorption. This would ensure the sorption of most target chemicals reaches or nearly reaches equilibrium at the time of collection.

The predicted maximum sorption and doubling time changed along with the logK_{ow} of individual chemicals. For example, on the HDPE (< 53 µm), the predicted maximum sorption and doubling time of sorption of PBDEs or PCBs increased with increasing logK_{ow} (octanol-water partition coefficient) of individual congeners,

but then declined when $\log K_{ow}$ was $>8.5 - 9$ for both groups of chemicals (Figure 4; $p < 0.01$ in both cases). The octanol/water partition coefficient (K_{ow}) is defined as the ratio of a chemical concentration in the octanol phase to that in the aqueous phase. This indicates that the sorption of hydrophobic compounds on microplastics is driven by their $\log K_{ow}$ within a range of $4 - 9$, while the sorption capacity may be suppressed for an extremely hydrophobic compound.

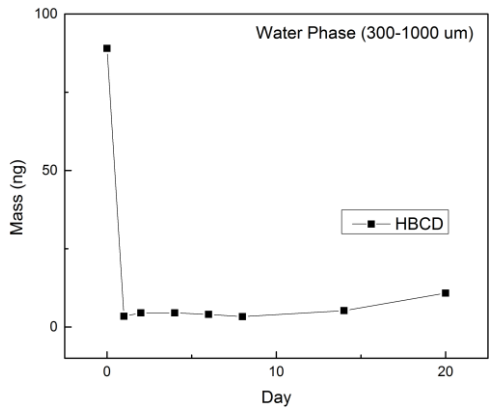
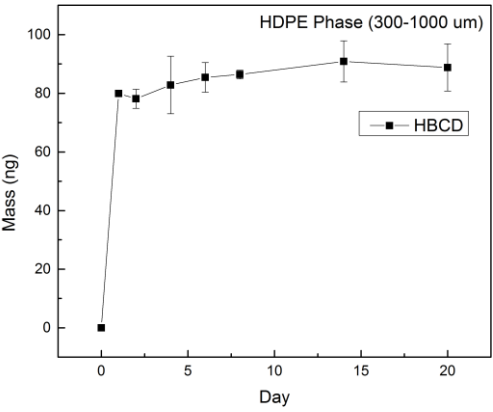
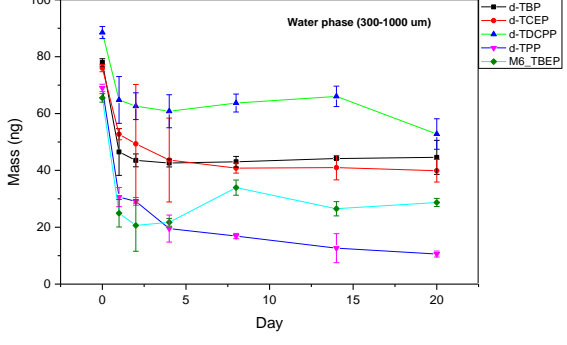
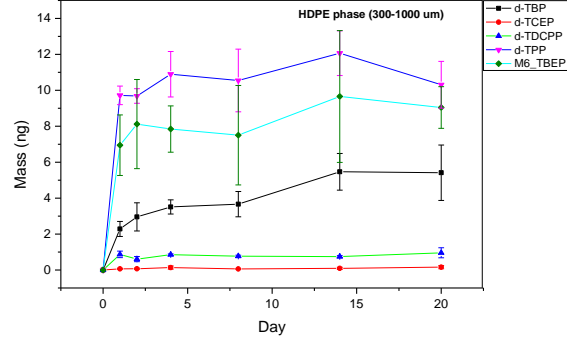
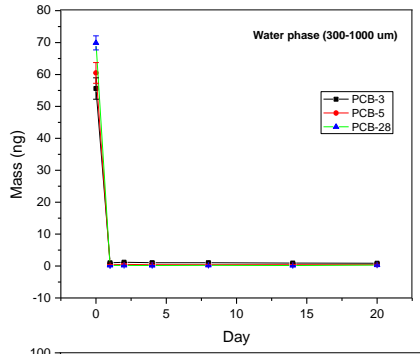
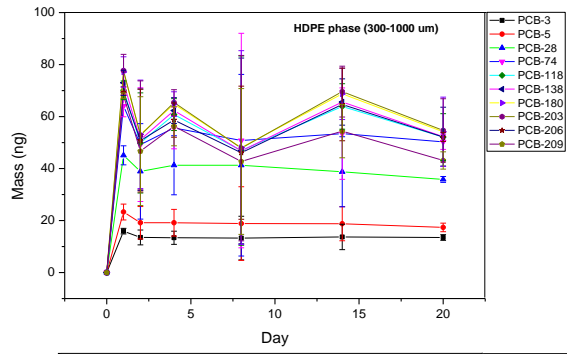
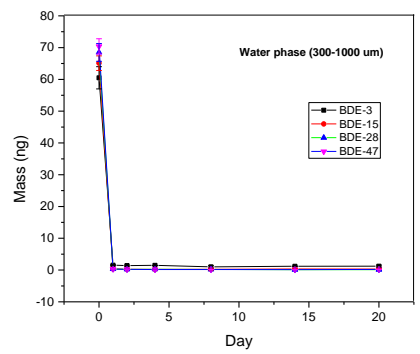
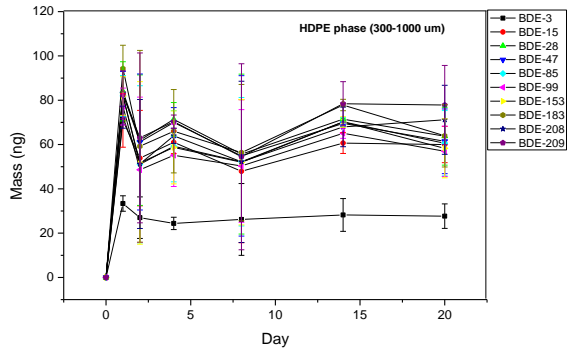
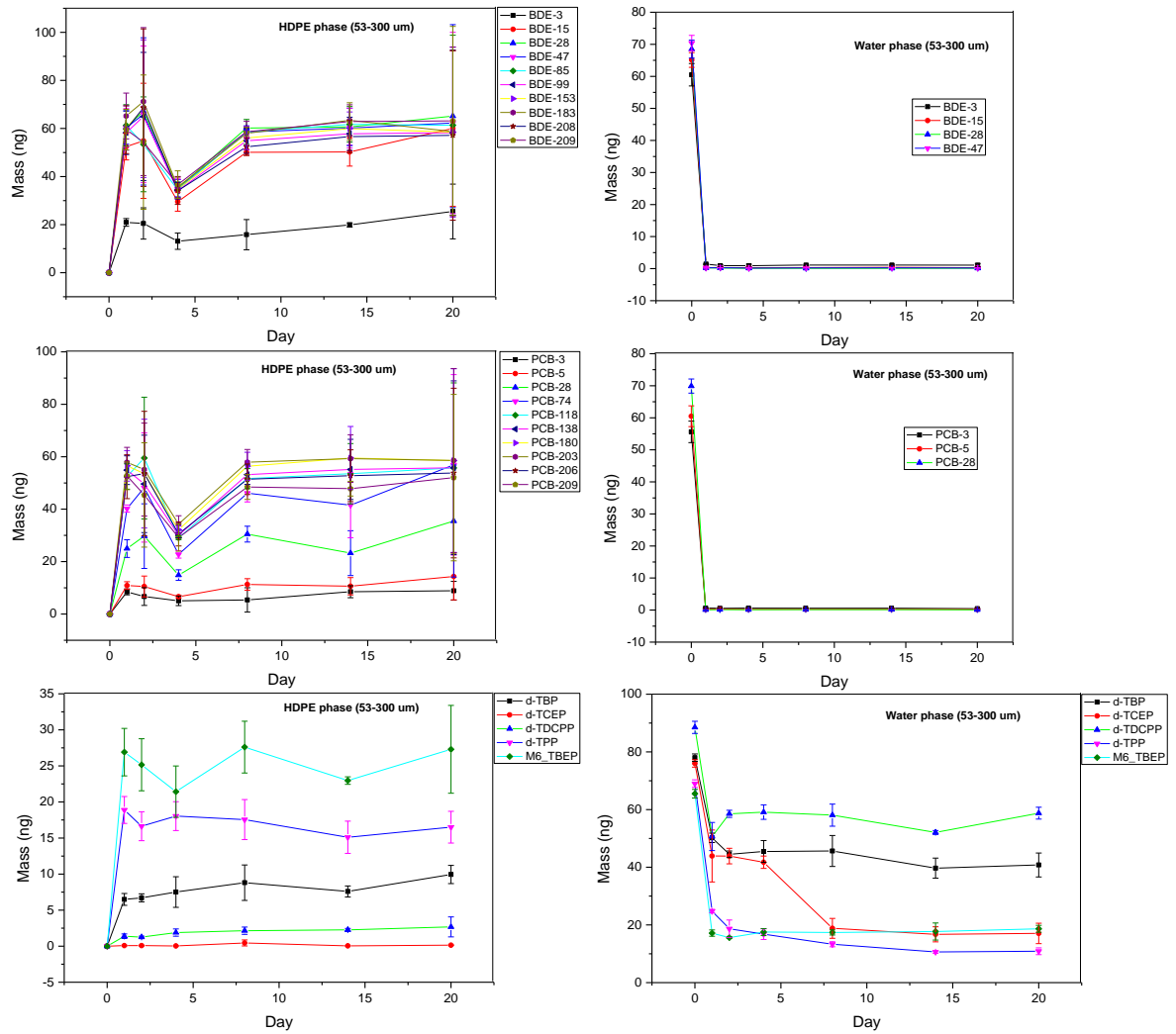


Figure 1. Changes in the residues of PBDEs, PCBs, OPFRs, and α -HBCD on HDPE particles (300-1000 μm) (left side) and in water (right side) over time.



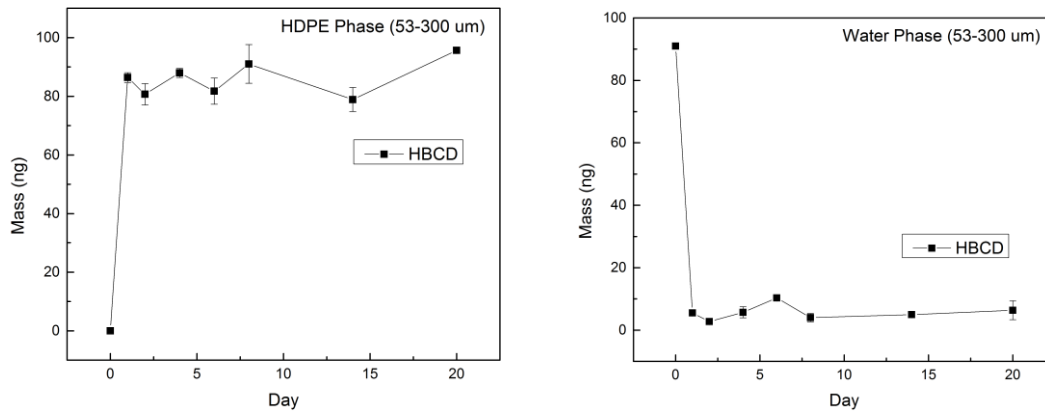


Figure 2. Changes in the residues of PBDEs, PCBs, OPFRs, and α -HBCD on HDPE particles (53-300 μm) (left side) and in water (right side) over time.

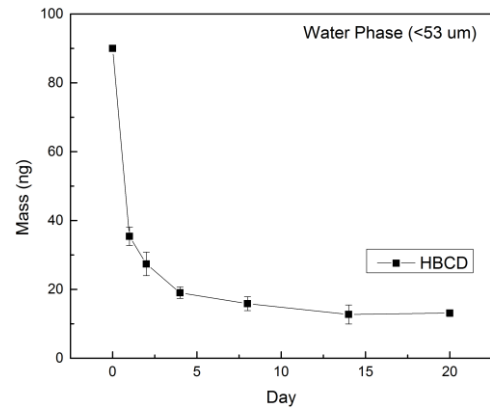
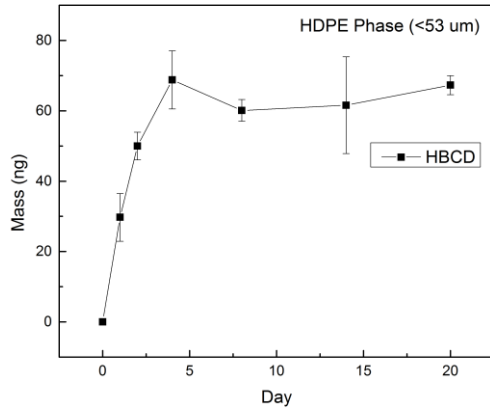
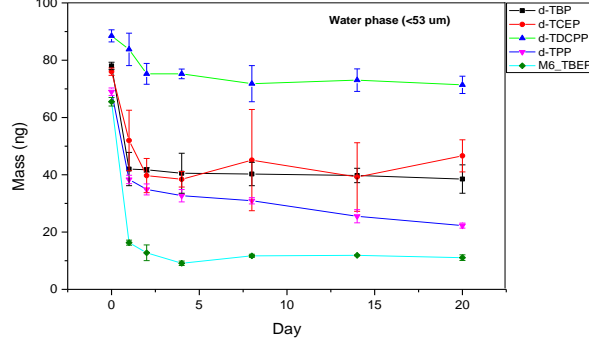
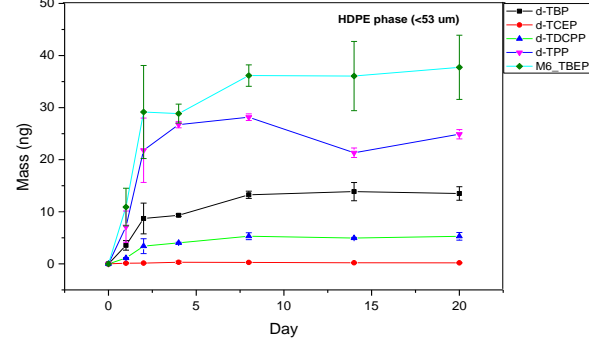
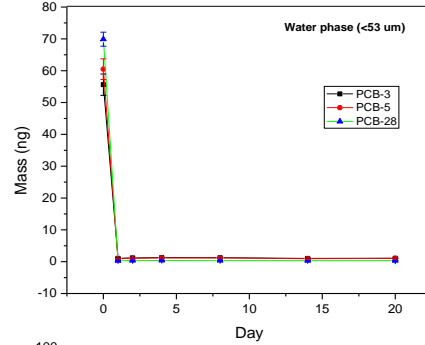
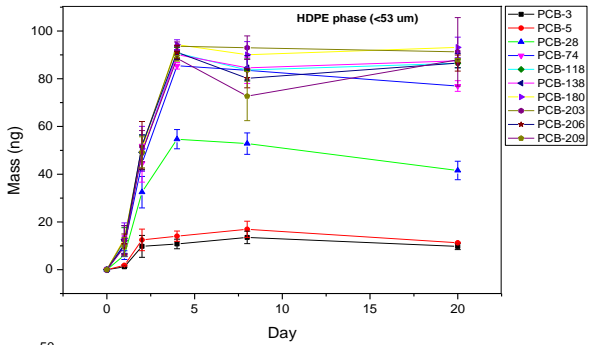
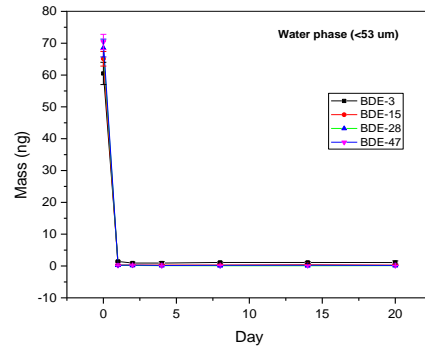
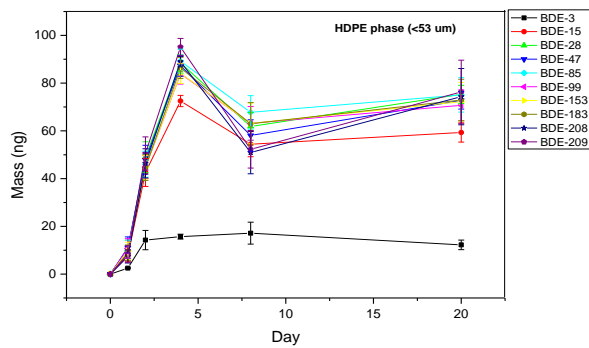


Figure 3. Changes in the residues of PBDEs, PCBs, OPFRs, and α -HBCD on HDPE particles (<53 μm) (left side) and in water (right side) over time.

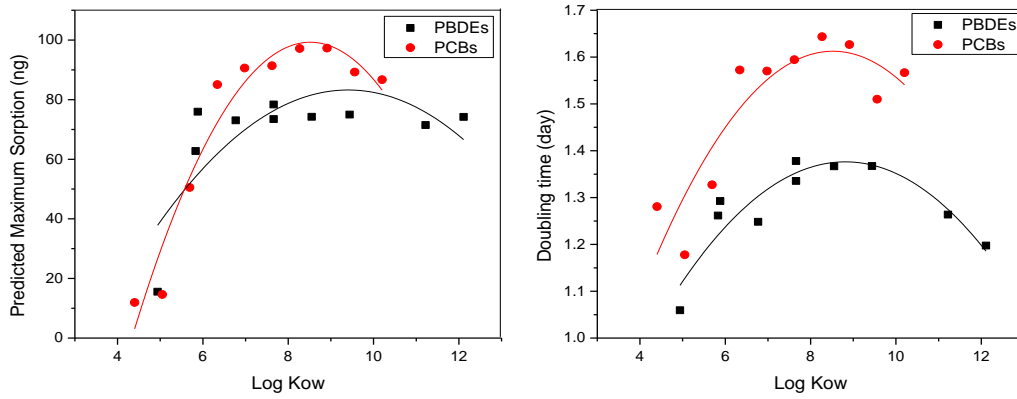


Figure 4. Changes of the predicted maximum sorption (left) and doubling time of sorption (right) along with $\log K_{ow}$.

Particle size affected the predicted maximum sorption (Figure 5). The smallest size of HDPE particles appeared to have the capacity of absorbing greater amounts of PBDEs, PCBs, or OPFRs than other two sizes of HDPE. This may result from a greater surface area of the < 53 μm HDPE particles than those of the bigger sizes of pellets (Figure 6); however in the figure it appeared that surface areas for 53-300 and 300-1000 μm HDPE were similar.

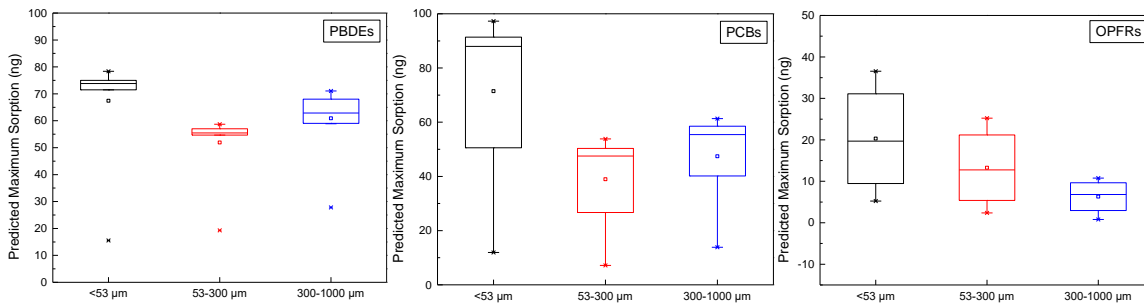


Figure 5. Comparison of the predicted maximum sorption of PBDEs ($p = 0.07$), PCBs ($p = 0.01$) and OPFRs ($p = 0.20$) on different sizes of HDPE particles.

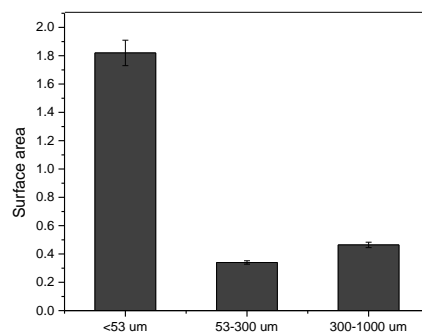


Figure 6. Surface areas of three different sizes of HDPE particles.

Effects of particle size on sorption

The Freundlich isotherms were investigated to assess the effects of particle size on sorption. As only a few chemicals were quantifiable in water (Table 2), the others were excluded from the determination of Freundlich constant (K_F). Table 3 summarizes the logarithmic K_F for the sorption of target chemicals on HDPE and PVC particles. For each size class of HDPE or PVC particles, the $\log K_F$ increased along with a chemical's $\log K_{ow}$ (Figures 7 and 8). These patterns strongly support the hypothesis that PBT sorption increases as a function of the chemical's hydrophobicity.

Table 2. Chemicals tested for Freundlich isotherm experiments

PCB-3	BDE-3	Tris(1,3-dichloro-2-propyl) phosphate-d15
PCB-5	BDE-15	Tri-n-butyl phosphate-d27
PCB-28	BDE-28	Triphenyl phosphate-d15
	BDE-47	Tris(2-butoxy-[13C2]-ethyl)phosphate
		α -hexabromocyclododecane

Table 3. The logarithmic Freundlich constant ($\log K_F$) of sorption of PCBs, PBDEs, OPFRs, and α -HBCD on HDPE and PVC particles with different nominal sizes.

Log K_F	HDPE			PVC			Log K_{ow}
	300-1000 μ m	53-300 μ m	<53 μ m	300-1000 μ m	53-300 μ m	<53 μ m	
BDE3	3.60	3.63	3.56	6.38	5.76	4.89	4.94
BDE15	3.96	3.86	3.74	7.64	8.89	6.87	5.83
BDE28	4.48	4.18	4.00	5.98	6.80	7.52	5.88
BDE47	4.76	4.70	4.35	10.11	7.39	10.83	6.77
PCB3	4.06	4.44	4.15	5.82	5.04	4.18	4.40
PCB5	4.18	4.30	3.79	5.76	5.23	4.53	5.05
PCB28	4.92	5.27	4.72	5.08	5.78	4.72	5.69
d-TBP	2.53	2.53	2.70	2.90	2.93	2.70	3.82
d-TDCPP	2.01	2.03	2.04	3.32	3.47	3.15	3.65
d-TPP	2.60	2.79	3.06	4.85	4.33	4.32	4.70
M6-TBEP	3.20	3.21	3.49	3.06	3.00	2.84	3.00
α -HBCD	6.90	6.71	6.45	8.52	7.79	8.41	7.74

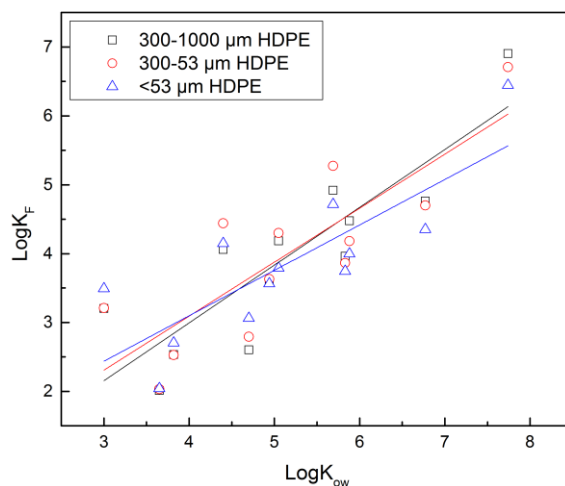


Figure 7. Linear regressions between $\log K_{ow}$ and $\log K_F$ for chemical sorption on HDPE particles with nominal sizes of 300 – 1000 ($p < 0.001$), 53 – 300 ($p < 0.001$), and $<53 \mu\text{m}$ ($p = 0.001$), respectively.

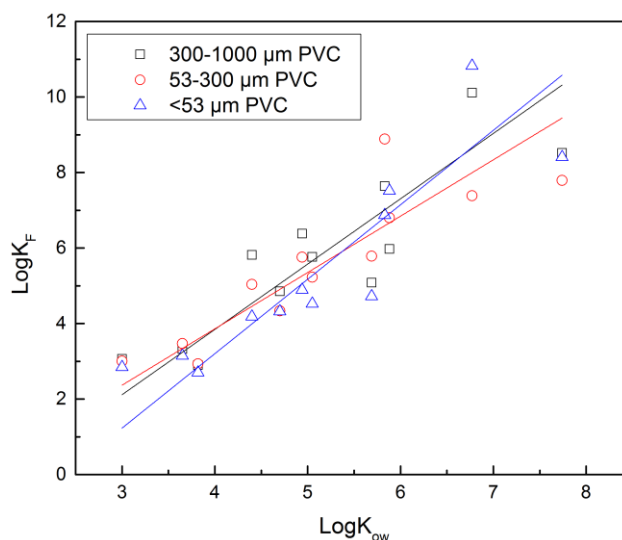


Figure 8. Linear regressions between $\log K_{ow}$ and $\log K_F$ for chemical sorption on HDPE particles with nominal sizes of 300 – 1000 ($p < 0.001$), 53 – 300 ($p < 0.001$), and $<53 \mu\text{m}$ ($p < 0.001$), respectively.

The $\log K_F$ did not differ significantly among different size classes of HDPE ($p = 0.899$) or PVC ($p = 0.916$) particles (Figure 9). According to our previous findings, particle size influences the predicted maximum sorption of hydrophobic chemicals (e.g. PBDEs and PCBs), which is likely due to elevated surface area when nominal size of particles is reduced. However, particle size or surface area seems to produce no significant impact on the Freundlich constant. It is noted that the particles used in our study are all at μm scale in nominal size. Future work may need to investigate nano-scale particles in order to better elucidate the effect of particle size on sorption.

The $\log K_F$ differed significantly between HDPE and PVC particles with the same nominal size (Figure 9). PVC appeared to result in greater K_F for the tested chemicals. HDPE particles generally exhibit a greater surface area compared to PVC particles with the same size (Figure 10). Thus the surface area may not significantly affect the sorption of organic chemicals on particles. Additional factors, such as the strong π - π -interactions between PVC

and chemicals, may enhance the sorption. By contrast, HDPE particles may mainly undergo non-specific vander Walls interactions.

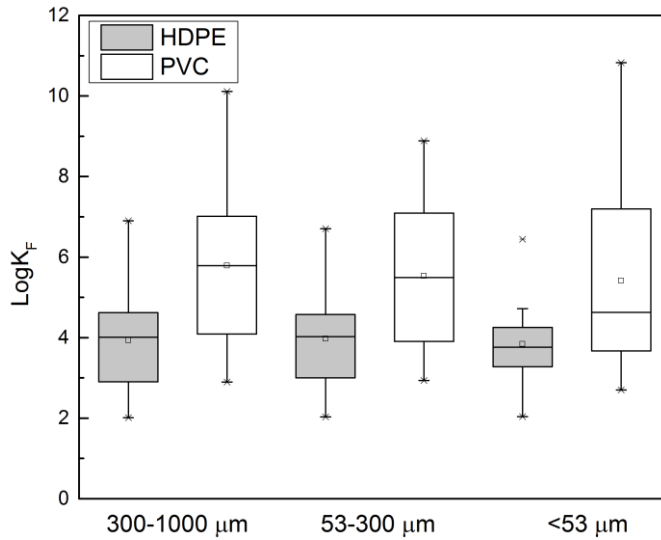


Figure 9. Statistically different $\log K_F$ values were observed between chemical sorption on HDPE and PVC particles with the same nominal size ($p \leq 0.001$ for all sizes).

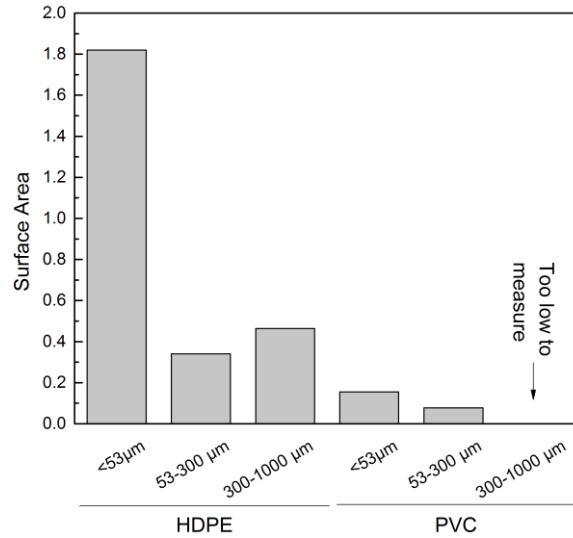


Figure 10. Surface areas of HDPE and PVC particles with different nominal sizes

Effects of biofilm on sorption

The formation of biofilm on HDPE particles did not significantly change the sorption isotherms compared to the control group ($p = 0.761$; Table 4 and Figure 11). However, the results may be influenced by a number of factors, such as the extent of biofilm formation on particles, the heterogeneity of biofilm among particles, and the possible shedding of biofilm from particles during shaking. Future research will aim to prevent or minimize the impacts of these uncertainties.

Table 4. The LogK_F of sorption on HDPE particles (300-1000 μm) with and without biofilm.

	Control	Biofilm
BDE3	3.71	3.81
BDE15	4.60	4.65
BDE28	5.05	5.00
BDE47	5.79	5.03
PCB3	3.88	3.97
PCB5	4.04	3.98
PCB28	4.75	5.18
d-TBP	2.40	2.58
d-TDCPP	1.85	1.36
d-TPP	3.23	2.41
M6-TBEP	2.75	2.80
α-HBCD	4.31	3.78

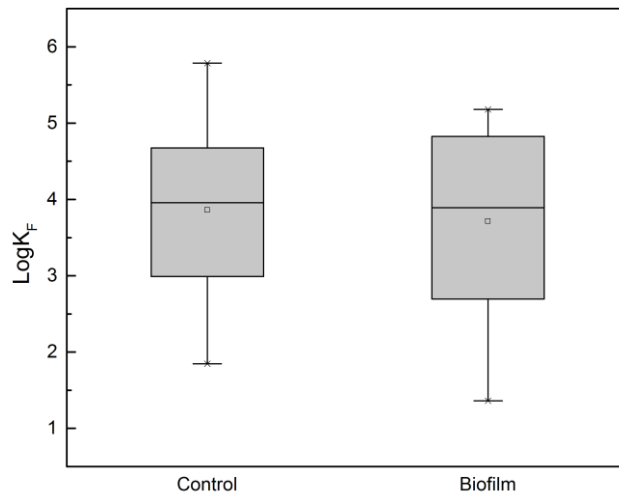


Figure 11. Comparison of the LogK_F values for a suite of target chemicals sorbed to particles with and without biofilm.

Conclusions:

There are several main conclusions from the sorption study.

- a. Particle size affects the maximum sorption of PCBs and flame retardant chemicals. Particles with smaller sizes tend to accumulate more of these organic chemicals from aqueous phases, likely due to elevated surface areas.
- b. The predicted maximum sorption of organic chemicals increases with $\log K_{ow}$ within a range of 4 – 9, but the sorption capacity may be suppressed for an extremely hydrophobic compound. This might be affected by other experimental factors such as low aqueous dissolution of extremely hydrophobic compounds.
- c. The Freundlich constant of sorption (K_F) derived from the isotherm determination increases along with a chemical's $\log K_{ow}$.
- d. The $\log K_F$ of organic chemicals did not differ between micro-sized HDPE or PVC particles. Surface areas of the tested particles may have been insufficiently different, relative to experimental error, to detect differences. Nano-sized particles may need to be investigated for the effect of particle size on sorption.
- e. The hydrophobicity of plastic particles affects the Freundlich constant.
- f. Current findings did not reveal a significant impact of biofilm formation on sorption. However, future studies are needed to re-evaluate this topic with some uncertainty factors are controlled.

Additional Information:

13. Were any significant challenges encountered? If so, how were they resolved?

Yes. There were several major challenges. (1) Recovery of plastic particles from water was difficult. Some particles were attached to the glass tubes and hard to wash out. We had to use a significant amount of HPLC water to collect particles for residue analysis. (2) Large variations in chemical residue concentrations were observed between some replicates during pilot studies. Therefore, triplicates samples were run for sorption studies. (3) Hydrophobic chemicals, such as PCBs and PBDEs, had very low water solubility, which resulted in non-detection or below detection limits in water. Sample extracts were thus concentrated to a very small volume (~50 µL) in order to increase the response on GC-MS.

14. Other issues/concerns – Are there things that we (the MDP) can do better to manage research projects in the future? No.

15. Did you have any media inquiries due to your research? If so, please list them. No.

16. Were any grad students/interns involved in project? If so, please indicate the number of grad students/interns involved in the project. Two graduate students (Hongli Tan and Changfeng Peng) were involved.

17. Did you participate in outreach/education events? Please list these events and estimate how many students and adults attended these events. We hosted a lab visit by undergraduate students of Southern Illinois University in April 2016 (~20 students).

18. Did you present your research at any scientific conferences? If so, what conference? No. But we will present the sorption work at the Society of Environmental Toxicology and Chemistry Annual North American Meeting in November 2017.

Part II. Budget Information

1. Provide an Itemized Budget Table according to the format below showing expenses incurred (in dollar amounts) throughout the project. Feel free to add rows as needed.

Budget Category	NOAA Funds (\$)	Matching Contributions (\$)	Match Contribution Description: Nature (cash or in-kind) and Source of Match	Total Expense (\$)
Personnel	70,535.41	80,890.80	Cash	151,426.21
Fringe	25,553.39	23,416.04	Cash	48,969.43
Supplies	8,354.63	0.00	-	8,354.63
Other direct costs/printing	375.53	0.00	-	375.53
Contractual	23,124.00	20,000.00	-	43,124.00
Travel	2,505.87	0.00	-	2,505.87
Indirect costs	43,048.17	62,588.06	Cash	105,636.23
Other	-	-	-	
Total	173,497.00	186,894.90		360,391.90

Note: to add rows and/or see updated totals you will need to update the formulas in each “total” cell. Click in the total cell, go to “Table Tools” on the top toolbar, click the “layout” tab, click “formula”, and add the new cell references.

2. Provide an updated budget table according to the format below showing funding expended throughout the project.

TOTALS	NOAA funds (\$)	Matching contributions (\$)	Total Expense (\$)
TOTAL amount of award	173,497.00	174,160.00	347,657.00
Cumulative amount expended from this award (<i>enter this as a negative number, e.g. -500</i>)	173,497.00	186,894.70	360,391.90
Amount of funds awaiting expenditure	0.00	0.00	

Note: to add rows and/or see updated totals you will need to update the formulas in each “total” cell. Click in the total cell, go to “Table Tools” on the top toolbar, click the “layout” tab, click “formula”, and add the new cell references.