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Adsorption of organic pollutants to microplastics:
The effects of dissolved organic matter

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Abstract

Microplastics in the marine environment sorb persistent organic pollutants and transfer these compounds to marine organisms upon ingestion. However, few studies have examined the effects of dissolved organic matter (DOM) on these sorption processes. Here we examine differential sorption for matrices of surface water from a New England estuary and the Sargasso Sea, which contain a high and moderate quantity of DOM respectively, as well as for an artificial seawater control containing no DOM. Microplastics were prepared from aged plastics collected from a beach in St. George's, Bermuda, and the sorption characteristics of polyethylene and polypropylene were examined separately. Sorption of tonalide, 4-methylbenzylidene camphor (4-MBC), triclosan, and β-estradiol, were examined at concentrations of 20 and 100 μg/L. Compound hydrophobicity was found to be the primary factor influencing sorption. However, matrix composition and polymer type also affected sorption processes. A moderate concentration of DOM was found to generally increase sorption, but the overall effects varied amongst the examined compounds. For example, DOM enhanced sorption of 4-MBC but inhibited sorption of tonalide. Polypropylene sorbed a greater quantity of pollutants than polyethylene; however, this sorption was weaker suggesting that organic pollutants on polypropylene microplastics could be more bioavailable to marine life.

Introduction

Plastic has fueled technological advancement and become an integral part of modern life. Due to improper disposal and transport via wind and surface runoff, large quantities of these materials enter aquatic ecosystems, and it is predicted that by 2050 the world's oceans will contain a greater mass of plastic than fish (World Economic Forum, 2016; Derraik, 2002). Weathering, primarily by photo-oxidative and thermooxidative pathways, fragments these plastics into increasingly smaller pieces (Andrady, 2011). Pieces < 5 mm in diameter are coined "microplastic", and the term "nanoplastic" has recently been established to specify those particles with a diameter < 100 nm (Klaine et al., 2012). Additional sources of microplastics include microbeads included in cosmetics and fibers from synthetic fabrics such as polyester which freely pass through most water treatment facilities (Browne et al., 2011). Microplastics found in aquatic ecosystems are primarily polyethylene (PE) and polypropylene (PP), and these polymers respectively comprise 38% and 24% of global plastic production in 2007 (Andrady, 2011). Composing a similarly large 19% of 2007's global production, polyvinyl chloride (PVC) also commonly enters aquatic ecosystems and is concentrated in the benthos due to its negative buoyancy (Andrady, 2011; Wright et al., 2013).

Microplastics pose an immense threat to aquatic life due to their increasing abundance (Ng, 2006), long residence times (Arthur, 2009), and aptness to be consumed by aquatic organisms (Andrady, 2011). Commercially important fish (Lusher, 2013), crustaceans (Murray and Cowie, 2011), bivalves (Van Cauwenberghe and Janssen, 2014), and 44% of marine bird species (Rios and Moore, 2007) are known to consume microplastics. These particles cause physical harm by impeding digestion and respiration, and the presence of PVC microplastics in an experimental setting has been found to reduce filtering rates and increase mortality of the Asian green mussel *Perna viridis* (Rist et al., 2016). Some microplastic pieces are sufficiently small that they may enter and impair an organism's circulatory system (Browne, 2008). In addition to causing physical harm, microplastics may also release harmful chemicals upon being consumed by marine organisms. During production, plasticizers, most commonly phthalates, are incorporated into the polymer structure to provide flexibility and durability. However, these endocrine-disrupting compounds are not held in place by covalent bonds and are readily leached from the plastic (Latini, 2009).

Microplastics also expose aquatic organisms to dangerous concentrations of persistent organic pollutants (POPs), and this is likely the greatest threat that microplastics pose to marine life. Microplastics have hydrophobic surfaces upon which similarly hydrophobic organic pollutants are readily adsorbed. The resulting concentrations of hydrophobic pollutants on microplastics may be several orders of magnitude greater than in the surrounding water. For example, plastic resin pellets in Japanese waters were found to have concentrations of polychlorinated biphenyl compounds (PCBs) and dichlorodiphenyldichloroethylene (DDE) 10^5-10^6 times greater than the surrounding seawater (Mato, 2001). When marine organisms consume these contaminated microplastics, their digestion increases desorption rates. Simulated digestive conditions with biologically relevant pH and temperature along with sodium taurocholate, a major component of mammalian bile, found desorption rates 30 times greater than in seawater alone (Teuten, 2007). Feeding experiments of streaked shearwaters (*Calonectris leucomelas*) confirmed that organic pollutants from ingested plastics may be incorporated into animal tissue (Teuten, 2009). However, further work is necessary to determine the significance of microplastics as a vector of HOCs to marine organisms relative to other exposure pathways (Browne et al., 2013).

Important unanswered questions also remain regarding the adsorption of organic pollutants to microplastics. Previous work has examined the role of compound hydrophobicity (Wu et al., 2016), matrix salinity (Bakir et al., 2014), and polymer type (Lee et al., 2014) on the adsorption of organic pollutants to microplastics. Studies have additionally examined the competitive sorption of multiple organic pollutants (Bakir et al., 2012), however, little work has investigated the influence of dissolved organic matter (DOM) on the adsorption of organic pollutants to microplastics. DOM may adsorb to the plastic surface thus reducing the available surface area for organic pollutants to sorb and altering the surface polarity of the plastic. DOM may also modify the surface polarity and sorption capacity of organic pollutants via hydrophobic interaction and complexation (Nelson et al., 2000). Important work by Wu et al. (2016) has examined the effects of varying concentrations of humic acid on the adsorption of organic pollutants to microplastics, however, natural waters contain a great diversity of organic compounds dissolved within them. Understanding pollutant adsorption in environmentally relevant conditions requires natural water matrices, and the work reported here takes this approach.

The present study examined how adsorption of organic pollutants to polyethylene and polypropylene microplastics differed between water matrices consisting of DOC-free artificial seawater (ASW), filtered open ocean surface water from the Sargasso Sea (SS) and estuarine water from West Falmouth Harbor (WFH) in Falmouth, MA. SS water has a relatively low dissolved organic carbon (DOC) content of 0.8 ppm (Hansell and Carlson, 2001), and water from WFH has a much higher DOC content of 2.0 ppm (Oestreich et al., 2016) and receives significant inputs from terrestrial organic sources. This work presents the first time of which we are aware that such an experiment has been performed using aged microplastics and natural water matrices.

Materials and Methods

Four common organic pollutants classified as pharmaceuticals and personal care products (PPCPs) were chosen for study: tonalide, 4-methylbenylidene camphor (4-MBC), triclosan, and β-estradiol. The selected compounds range in hydrophobicity, as measured by the octanol/water partitioning (Log K_{ow}), and also in structural characteristics (Fig. 1). Tonalide is a polycyclic musk included as a fragrance in many detergents, soaps, and cosmetics. It is known to bioaccumulate in marine organisms and is an endocrine disruptor (Schnell et al., 2009). 4-MBC is a UV filter incorporated into sunscreens and other cosmetic products, and it is also a bioaccumulating endocrine disruptor. While it is banned in the US and Japan, its use is legal in Europe and Canada (Buser et al., 2006; Ekowati et al., 2016). Triclosan is an anti-bacterial agent found in products such as toothpaste and soaps. It is an environmental danger as it is both toxic to bacteria and promotes bacterial resistance to this widely used antibiotic (Carey and McNamara, 2015). Additionally, some of the degradation products of triclosan are carcinogenic, and these concerns along with studies questioning its efficacy in relevant concentrations resulted in the FDA ban of triclosan use in soaps this past year (Tohidi et al., 2014; U.S. FDA, 2016). β-estradiol is a hormone included in hormone replacement medications and it readily enters the environment as it is excreted in urine (Wright et al., 1979). These compounds are commonly detected in aquatic ecosystems, and are categorized as pollutants of emerging concern (Caliman and Gavrilescu, 2009).

Preparation of Microplastics

Pieces of plastic litter ranging in the longest dimension from 1-15 mm were collected from St. Catherine's beach in St. George's, Bermuda in October 2016. White pieces were separated from colored plastics and typed and sorted by polymer using an Agiltron Peakseeker Raman spectrometer coupled with an AmScope optical microscope. The plastics were ground in a cutter mill, and those particles that passed through a 420 µm mesh were obtained. As the pulverization altered the naturally weathered surfaces, the particles were subsequently exposed to a 30 W low pressure Hg lamp at a distance of ~15 cm for 30 hours at 50-70 °C to simulate weathering via photo-oxidation and thermo-oxidation. Particles were then sieved to obtain a particle size range of 250-300 µm for the experimental treatments. To remove any sorbed compounds, particles were solvent rinsed by sequentially rinsing 0.5 g batches with 25 mL of 1 M HCl in methanol and 6 mL each of acetone and hexane. The surface characteristics of both types of aged microplastics were examined using Scanning Electron Microscopy (SEM).

Preparation of Water Matrices

Surface water from West Falmouth Harbor (33 ppt salinity) was collected during an incoming tide and filtered by sequentially passing through a combusted GF/F filter (0.7 µm), a 0.4 µm Isopore HTTP filter, and a 0.2 µm cellulose nitrate filter. Sargasso Sea surface water (39 ppt salinity) was collected in 2000 about 75km SE of Bermuda, filtered through a 0.45 µm cartridge and refrigerated prior to use. For the experiments, the Sargasso Seawater was diluted using Milli-Q$^+$ water to obtain a salinity matching the estuarine water and filtered through a 0.2 µm cellulose nitrate filter. Artificial seawater was prepared in Milli-Q^+ water to a salinity of 33 ppt.

Sorption Experiments

30 mg of the cleaned and weathered microplastic polyethylene particles were transferred to 40 mL sample tubes and then filled with 30 mL of the appropriate water matrix. Due to a relative shortage of available material, the experiments for polypropylene particles used half of the particle mass and matrix volume in the same particle:water ratio. The sample tubes were then placed on a reciprocal shaker in the dark for 40 hours to acclimate DOM sorption before the PPCP mixture (tonalide, 4-methylbenzylidene camphor (4-MBC), triclosan, and β-estradiol) was added. Two concentrations of PPCP mixtures of 20 or 100 µg/L were used (low and high PPCP treatments, respectively). The experimental tubes were left to equilibrate for 48 hrs before analysis in the dark at 23 °C. (Note that ibuprofen and clofibric acid were also present in the PPCP mixture but due to difficulties in quantitatively extracting these hydrophilic compounds, they were not considered in this study).

Extraction of Microplastics

The water and microplastics from each sample treatment were separated by passing the samples through a 53µm stainless-steel filter under vacuum, rinsing each sample tube with 6 mL Milli-Q^+ water to ensure complete transfer. The water was collected in clean 40 mL PFA test tubes for later extraction. For the first particle extraction, 20 µL of the internal standard heneicosanol in methanol (3.6 µg) was added directly to the particles on the filter. The particles were then rinsed sequentially with 4 mL of 1 M HCl in methanol, 8 mL (2x 4 mL) of methanol (non-acidic), 12 mL (3x 4mL) of acetone, and 12 mL (3x 4 mL) of hexane, at a drip rate of approximately 6 mL/min. The combined solvent extracts were collected in a pear flask. A low vacuum was applied between solvents. The extracted particles and filters were then transferred to petri slides and stored until a second extraction to recover more tightly sorbed compounds.

The particle extracts were evaporated in vacuo to near dryness (~1 mL residual volume) and resuspended in 1 mL of 2:1 Dichloromethane (DCM):Methanol. The contents of the pear flasks were transferred to clean 13 mm Pyrex test tubes, rinsing with 3 x 1 mL 2:1 DCM:methanol. The extracts were then evaporated in a Savant SC110 SpeedVac (1-2 torr) leaving a residual aqueous layer on top of a lower DCM layer. The lower layer DCM layer was removed by pipet to a fresh test tube. The rinse/transfer process was repeated 3 x 1 mL DCM. The remaining aqueous layer was then evaporated to dryness using heat (1-2 torr vacuum, 60°C), resuspended in 0.5 mL of DCM and passed through combusted Na_2SO_4 into the test tubes containing the extracts. Finally, the combined particle extracts were evaporated to just dryness in the Savant SpeedVac (1-2 torr vacuum, no heat), resuspended in DCM and transferred to sample vials for GCMS analysis

To extract the more tightly sorbed organics, the extracted particles from the first extraction were transferred to Pyrex centrifuge tubes, 0.5 mL DCM was added, and the samples were ultrasonicated using a cup horn (100W) at room temperature for 5 min. The extract was transferred to a 40 mL test tube by vacuum filtering through a stainless-steel filter to prevent the transfer of any particles. The tubes were rinsed with DCM (2 x 1 mL) to aid the transfer. Extracts were then transferred to 13 mm centrifuge tubes, evaporated to just dryness in the Savant SpeedVac (1-2 torr vacuum, no heat), and resuspended in 0.5mL DCM for BF3-methylation and TMS-derivitization.

To check for sorption of target compounds to walls of the PFA sample tubes, the walls were subsequently rinsed with 1 mL of anhydrous methanol (10%), 1 mL of methanol, and 2 x 1 mL each of acetone and hexane. This extract was evaporated to just dryness under vacuum and resuspended in 0.5 mL DCM. Rinses were passed through Na_2SO_4 columns into a 13 mm centrifuge tube, washed with additional DCM (2 x 0.5 mL), and then evaporated to just dryness in the Savant SpeedVac (1-2 torr vacuum, no heat). Extracts were resuspended in 0.5mL DCM pending BF3-methylation and TMS derivatization before gas chromatography-mass spectrometry (GCMS) analysis.

Extraction of Water Matrix

The water phase was acidified to pH 2 using trace-metal clean 12 M HCl and 20 µL of the heneicosanol internal standard (3.6µg) was added. Samples were loaded onto Hypersep C18 cartridges (500mg, 3mL bed) which had been preconditioned by rinsing with 10mL methanol and 10mL Milli-Q$^+$ water. The acidic components were first eluted with 5 mL acetone:0.1 M $NaHCO_{3,}$ (40:60 v:v) and the nonacidic components with 6 mL of acetone. A flow rate of ~3 mL/min was obtained for both sample loading and eluting. The acidic components were then extracted with ethyl acetate (2x 2 mL), and this extract was passed through Na_2SO_4 and combined with the nonacidic extract. The combined extracts were then evaporated to just dryness in the Savant SpeedVac (1-2 torr vacuum, no heat), resuspended in 0.5mL DCM in preparation for BF3-methylation and TMS-derivitization.

GC-MS Analysis

Sample extracts were evaporated to dryness, resuspended in 50 µL of toluene and then methylated under N_2 using 200 µL of BF_3 in methanol (60 °C, 20 min). The methylated extract was extracted with hexane (2 mL, then 2x 1 mL), passed through Na_2SO_4, and evaporated to just-dryness. Samples were transferred using DCM to GCMS autosampler v-vials, evaporated under a stream of N_2 and TMS-derivitized under N_2 using 25 µL of pyridine and 25 µL of N,O-Bis(trimethylsilyl)trifluoroacetamide + 1% Trimethylchlorosilane (BSTFA + 1% TMCS) (55 °C, 1 hr). Samples were then dried under N_2 and resuspended in 50 µL of DCM for analysis by gas chromatography-mass spectrometry (GC-MS).

GCMS analysis was done using an Agilent 7890A GC with a 5975C inert MSD with triple-axis detector and a Varian CPSil 5CB low bleed MS column (60 m x 0.25 mm diameter x 0.25 µm film thickness) at a temperature program of 50°C (5 min hold) ramped 5°C/min to 320°C and held for 20 minutes. The Agilent GCMS system has a splitter post-column allowing for identification using the MS detector and quantification using the GC Flame Ionizing Detector (FID).

PPCP compounds were quantified using both a prepared standard curve for the PPCP compounds and the heneicosanol internal standard.

Results

Sorption Isotherms: Sorption isotherms for treatments using polyethylene particles were prepared to compare the differential adsorption of the organic pollutants, following the methods described in Bakir et al, 2012 (Fig. 2). The concentration of PPCP on the microplastics (C_s) is plotted against the concentration in the sample matrix (C_w). The slope of the linear trendline yields the linear sorption coefficient (K_d). As K_d increases, the proportion of the pollutant adsorbed to the plastic increases. The log K_d values of the compounds were positively correlated ($r^2 = 0.930$) with the log of their octanol/water partition coefficients (log K_{ow}) (Fig. 3).

Effects of DOM on sorption: The partitioning, or the mass percent of each compound sorbed to the microplastics relative to the total recovered mass, was plotted for experimental treatments using polyethylene particles (Fig. 4). Matrices correspond to West Falmouth Harbor (WFH) water, Sargasso Seawater (SS), and artificial seawater (ASW), which contain a high, an intermidate, and no concentration of DOM respectively. At the lower spike concentrations (20 µg/L), tonalide was completely adsorbed to the particles while at the higher spike concentration (100 µg/L) there was a greater adsorption of tonalide only when no DOM was present. For 4-MBC, sorption was greater when DOM was present for both low and high spike concentrations. The effects of DOM on triclosan sorption were concentration dependent. At the lower spike concentration triclosan sorption was greater when DOM was present while at the higher spike concentration triclosan sorption was greater when DOM was not present. The more polar β-estradiol did not sorb substantially in either spike concentration; however, it is notable that at the lower spike concentration some adsorption occurred when DOM was present but not when it was absent.

Differential sorption was observed between the two water matrices which contained DOM. For the low PPCP spike, sorption was greatest for the SS matrices which contain a moderate quantity of DOM. However, for the high spike concentration, sorption was usually greater for the WFH matrices which contain a large quantity of DOM. Spike concentration, in addition to the affects outlined thus far, also dictated the magnitude of partitioning. For each compound and sample matrix, partitioning for the 20 µg/L spike was greater or equal to that found for the 100 µg/L spike, and this indicates a saturation of the microplastic surface.

Effect of plastic composition on sorption: Differences in the partitioning of polyethylene (PE) and polypropylene (PP) in the WFH water matrix (DOC conc. 2.0 ppm) are shown in Fig. 5. At the low spike concentration, both PE and PP readily adsorbed tonalide. PP preferentially sorbed 4-MBC while triclosan was sorbed to PE to a greater degree. For the high spike concentration, sorption to PP was greater than PE for all three of these pollutants. While a small quantity of β-estradiol sorbed to PE at both spike concentrations, no sorption was observed for PP. Scanning Electron Microscopy (SEM) indicated that the PP microplastics used here had considerably rougher surfaces than PE (Fig. 7), and suggests that the differential sorption observed could be related to differences in surface area.

To assess the strength of PPCP adsorption among the sample conditions, we computed the relative contributions of the first and second extractions (Fig. 6). The first extract corresponds to loosely sorbed pollutants obtained by sequentially rinsing the particles with HCl in methanol, acetone, and hexane, and the second extract comprises those more tightly bound compounds which were removed via a subsequent extraction with dichloromethane. For polyethylene, results indicate a much higher fraction of tightly sorbed PPCPs at the lower spike concentration than at the high spike concentration, suggesting that there is a limited surface area in which strong sorption may occur. For polypropylene particles, the ultrasonic DCM extraction did not yield any additional PPCPs, indication that sorption to this polymer is weaker.

Our results also suggest that DOM influences extraction efficiency. Tonalide sorbed entirely on the microplastic surface for each water matrix at the low spike concentration, and therefore DOM does not significantly affect partitioning. However, as DOM content increased the efficiency of the first extraction decreased from 78% to 71% and then 62%, indicating that the presence of DOM likely inhibits the solvation of PPCPs.

Discussion

Sorption Isotherms

Sorption isotherms indicate sorption is greatest for hydrophobic compounds, and polarity is the dominant factor influencing the adsorption of these organic pollutants to microplastics. However, the linear sorption coefficients reported here are significantly lower than those found by Wu et al. (2016) and others (Teuten et al. 2007, Lee et al. 2014), who measured sorption in single compound matrices without the presence of DOM. Possible reasons for the lower sorption under the experimental conditions of our study are discussed below.

Influence of DOM on Partitioning

DOM is known to affect pollutant sorption by a variety of mechanisms which vary in strength depending on the pollutant, the DOM composition, and the polymer type. DOM may both enhance and inhibit adsorption by interacting with the pollutant. Complexation of DOM with pollutants may facilitate adsorption via a process named “cosorption” (Ling et al., 2006). However, these complexes may also inhibit adsorption, and whether enhancement or inhibition is favored varies depending on the pollutant and DOM composition. DOM may also affect adsorption by interacting with the polymer surface. The adsorption of DOM to the polymer surface may increase the total hydrophobic surface area thus enhancing total adsorption. However, DOM adsorption may occupy surface area, and thus reduce the area available for pollutant adsorption. Adsorption to the plastic surface is not evenly distributed across the polymer surface, but is instead concentrated in the amorphous regions which are characterized by a randomized molecular arrangement and a flexible and free-flowing structure (Teuten et al., 2009). Therefore, DOM may only need to occupy these preferential sorption sites to significantly decrease pollutant sorption. Additionally, this adsorption could alter the surface chemistry of the polymer. Sorption by molecules which have distinct hydrophilic and hydrophobic regions, such as fatty acids and alcohols which form a major proportion of DOM in natural waters, may decrease surface hydrophobicity and thus decrease pollutant adsorption.

The overall effects of DOM on pollutant sorption are therefore a balance of these various mechanisms, and previous studies have identified that optimal adsorption occurs when a moderate amount of DOM is present (Ling et al., 2006). As DOM concentration increases, adsorption eventually decreases until it is less than that found when no DOM is present. These studies examined the adsorption of organic pollutants to soils; however, as adsorption to soils primarily occurs at the surface of hydrophobic organic material, this process is comparable to adsorption to microplastics and may thus follow similar patterns (Chiou et al., 1979). The partitioning for the lower concentration PPCP spike followed this pattern excellently (Fig. 4). Except for tonalide, which adsorbed completely to the particles in all matrix conditions, the moderate DOM concentration (SS) resulted in the greatest sorption while a lesser sorption was found for the higher DOM concentration (WFH). DOM concentrations for the high DOM matrix were not sufficiently great to decrease sorption relative to the matrix lacking DOM (ASW).

While the trend is not as explicit, some aspects of the pattern describing sorption in the lower PPCP concentration are also observed for the higher PPCP spike concentration (Fig. 4). For two of the three significantly-adsorbing pollutants, adsorption is greater in the higher DOC matrix (WFH) than the moderate one (SS). This suggests that what constitutes a "moderate" DOC concentration varies with pollutant concentration. Therefore, as PPCP spike concentration increases, the DOC concentration in which pollutants optimally adsorb may similarly increase. Tonalide, however, adsorbs preferentially when no DOM is present, and this is indicative of the immense adsorption strength of this compound. As it sorbs completely without DOM, the presence of DOM decreases the sorption of this compound. Surprisingly, sorption was greater for the high DOC condition than the moderate, and this suggests that sorption enhancement due to DOM increases at high concentrations. Additionally, the DOM composition could impact the sorption of this compound as the high and moderate DOM matrices were obtained from vastly different marine ecosystems (esturaine New England harbor and open ocean Sargasso Sea, respectively). Sorption of triclosan shows decreasing sorption with increasing DOM, and this is surprising as the matrix with a moderate DOM content resutled in a substantial increase in triclosan sorption for the lower spike concentration. The higher spike will increase competitive sorption, and as triclosan is significantly less polar than tonalide and 4-MBC, its sorption is higher when there is less DOM also competing for space on the polymer surface.

Influence of Polymer Type on Sorption

Pollutant adsorption was found to be generally greater to polypropylene (PP) than polyethylene (PE) (Fig. 6). This result is contrary to much of the studies in the literature, which have found greater sorption to PE (Endo et al., 2005; Karapanagioti and Klontza, 2008). Laboratory studies have found that PE sorbs polycyclic aromatic hydrocarbons (PAHs) and chlorinated benzene (CB) compounds to a greater extent than PP (Lee et al., 2014). It has been proposed that PE's superior sorption stems from its enhanced capabilities for diffusion, and although greater sorption was found for PP, this explanation aligns with our findings that sorption to PE was stronger than to PP (Pascall et al., 2005). The amorphous regions of a plastic polymer, where sorption primarily occurs, may be in a glassy or rubbery phase depending primarily on the type of polymer and the temperature. The rubbery phase consists of polymer segments which are flexible and may allow other molecules to penetrate the polymer surface. In the glassy phase, however, these polymer segments are in a more rigid and condensed state, and thus diffusion into the polymer is largely inhibited. The glass transition temperature, T_g, corresponds to the temperature at which a polymer transitions between these two phases. For polyethylene and polypropylene, T_g is approximately -100 and 0 °C respectively, and therefore both polymers are rubbery at room temperature (Gupta and Gupta, 1982). PP is much closer to its T_g, however, and its structure will therefore have more of a glassy character than PE. The second ultrasonic DCM extractions of the PP microplastics did not yield any additonal PPCPs for any of the samples, while the yields for PE were substantial (Fig. 6). Therefore, the second extract likely yields those pollutants which have begun to diffuse into the polymer surface.

However, if sorption to PE occurs via multiple mechanisms and results in stronger sorption, our data suggest additional factors can favor sorption of PPCPs to PP. One possibility is that the surface interactions of PP with the pollutants examined here are substantially stronger than for PE. Additionally, aged PP microplastics used here may also have had a greater surface area than those of PE. Others have found that virgin and weathered PE microplastics have a greater surface area than similar PP particles both quantitatively using the Brunauer—Emmett—Teller (BET) method and qualitatively using scanning electron microscopy (SEM). (Fotopoulou and Karapagioti, 2012; Brunauer, Emmett, and Teller, 1938) However, SEM images of the aged microplastics used here indicated that PP had a much greater surface roughness than PE and thus likely a greater surface area as well (Fig. 7). A higher surface area for the PP particles would also explain the observed partitioning data (Fig. 5). As spike concentration increases, saturation of the polymer surface is increasingly responsible for inhibiting sorption, and surface area exerts a greater influence on total sorption. This explanation rationalizes why at the lower spike concentration, sorption is roughly equivalent for the two polymers, while at the high spike concentration sorption to PP dominates. Lastly, few if any other studies have examined the effects of DOM in natural waters on sorption processes, and differential interactions between PE or PP and DOM could influence sorption. It is likely some combination of these factors is involved, and such a conclusion is not unprecedented as Lee et al. (2014) found that sorption of hexachlorocyclohexanes was greater to PP than PE.

Influence of DOM on Sorption Strength

In addition to polymer type, spike concentration and DOM content also significantly affected sorption strength. There is a limited available surface area to which strong sorption may occur via a combination of surface adsorption at or diffusion into the amorphous regions of the polymer. Therefore, as spike concentration increases, a greater proportion of the pollutants may be loosely sorbed, as observed here. Also, DOM may compete with pollutants for the plastic surface and decreases sorption strength, likely by reducing the area of the amorphous regions available for sorption. DOM could also interact with the sorbed pollutant molecules to decrease the extraction efficiency, as observed here. However, at the lower spike concentration the percentage of PPCPs yielded from the second particle extraction is greater for the matrices which contain DOC. This may be due to a reduced efficiency for the first sequential solvent extraction as DOM will form a greater proportion of the total material sorbed to the plastic and thus be more effective at decreasing extraction efficiency. However, the effect of DOM on the sorption strength of pollutants may also vary with pollutant concentration.

Conclusions and Suggestion for Further Work

This study indicates that the sorption of organic pollutants to microplastics in natural waters is influenced by dissolved organic matter. Compound hydrophobicity was found to be the primary factor influencing sorption, and sorption was enhanced as hydrophobicity increased. An intermediate concentration of DOM was found to generally increase sorption, but the overall effects of DOM on sorption were compound specific. A greater fraction of PPCPs sorbed to polypropylene than polyethylene, however, the novel dual extraction procedure implemented here determined that sorption to polyethylene was stronger. The quantity of sorbed pollutants is likely dictated by surface area, and sorption strength is influenced by the capacity for pollutants to diffuse within the microplastic.

Our results suggest that sorption of pollutants to microplastics will be greatest in regions, such as the open ocean, where there is a moderate concentration of DOM. The presence of DOM also increased the strength of sorption suggesting that DOM may also influence the bioavailability of sorbed pollutants. Further work is necessary to determine how DOM affects the extraction of sorbed pollutants via digestive processes, and this information coupled with the findings of this work can determine in which ecosystems microplastics serve as the most significant vector of POPs to marine life.

Figures

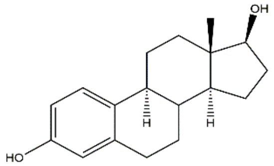
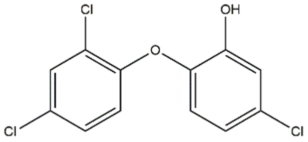
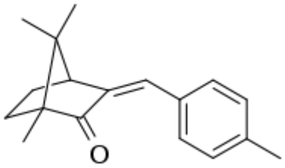
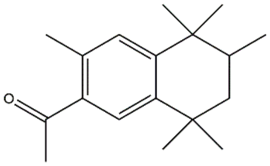
Chemical Structure	Compound	log K_{ow}	Description
	β-Estradiol	4.01[a]	Hormone
	Triclosan	4.76[b]	Anti-biotic
	4-methylbenzylidene camphor (4-MBC)	5.1[c]	UV Filter
	Tonalide	5.7[d]	Fragrance

Fig. 1 Summary Table of the PPCPs examined in this experiment. Log K_{ow} is the experimentally determined log of the octanol/water partition coefficient.

a) SRC PhysProp Database

b) Database value from the U.S. Env Pro Age EPI Suite Ver.4.11

c) Buser, 2006

d) Balk et al. (1999)

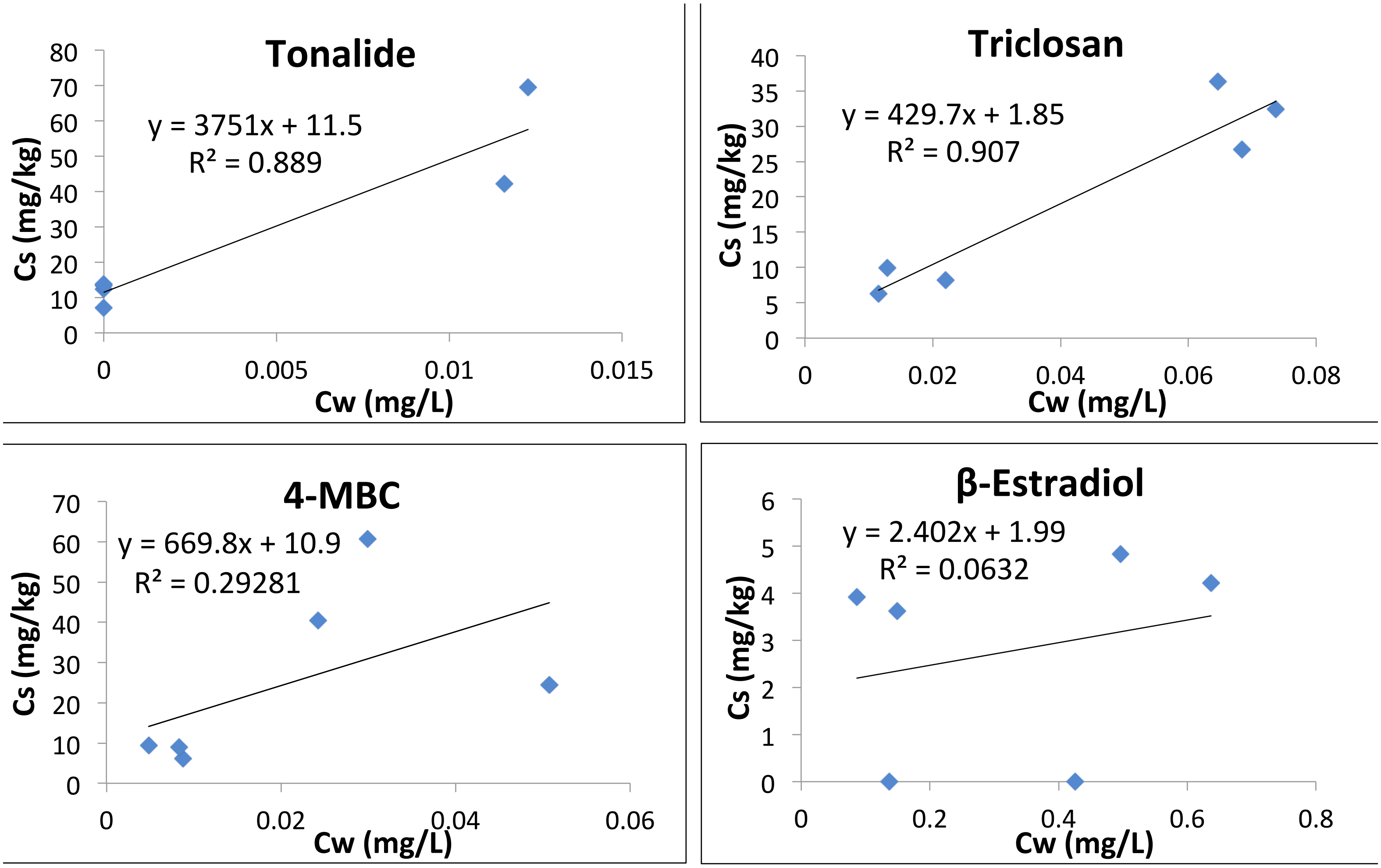


Fig. 2 The linear sorption isotherms of each PPCP to PE for all sample conditions. C_s is the concentration of PPCP sorbed to the microplastics, and C_w is the concetration in the water matrix.

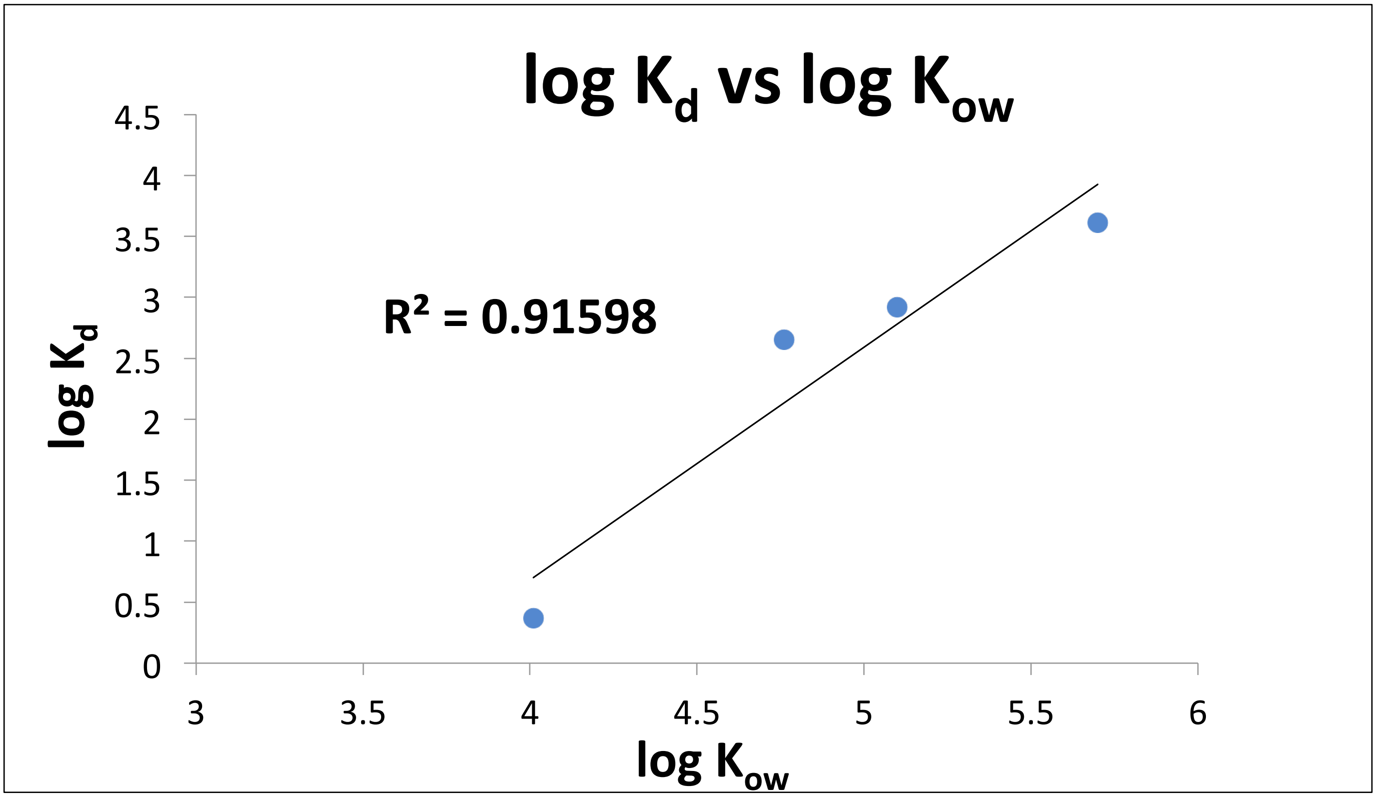
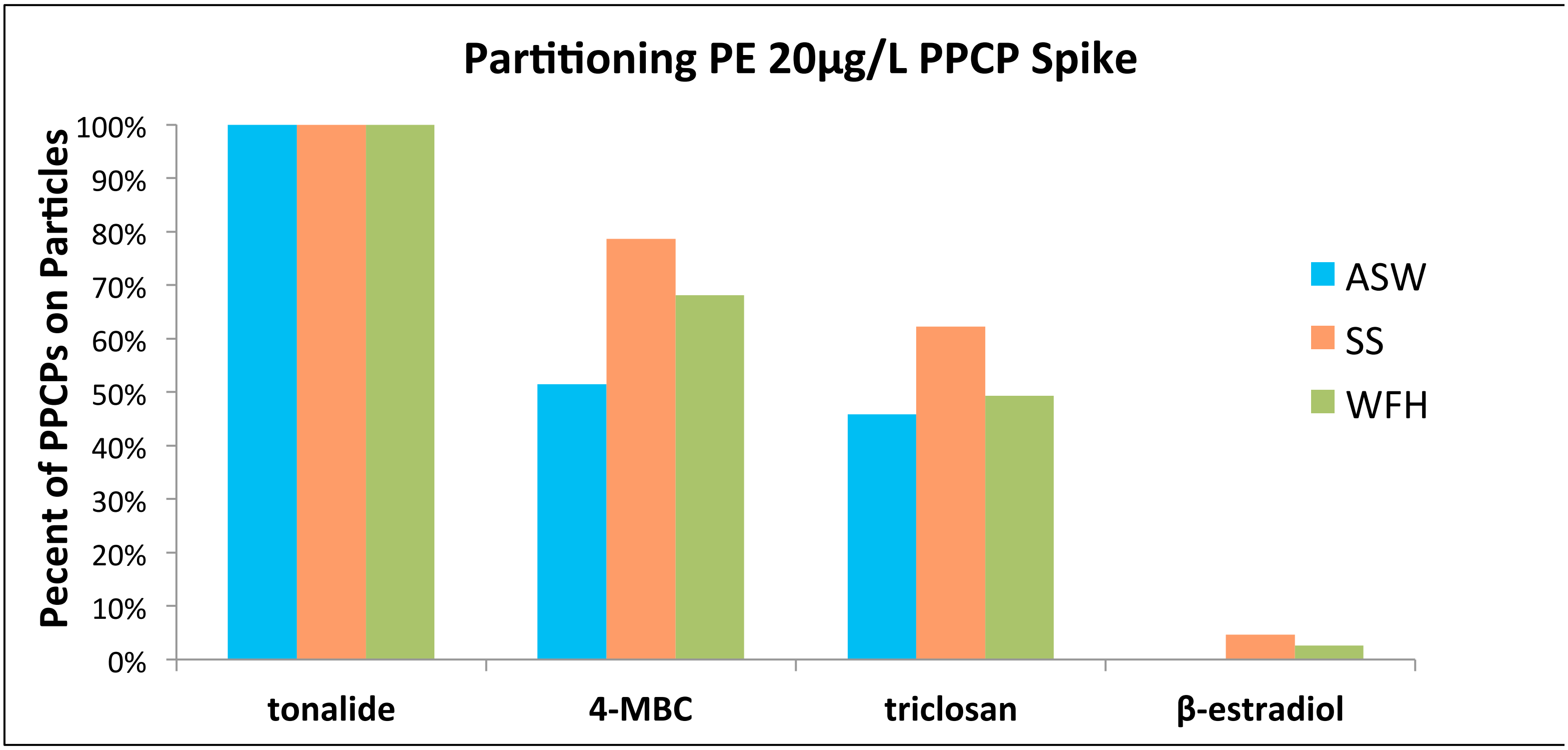


Fig. 3 The log of the linear sorption coefficient (K_d) versus the log of the octanol/water partition coefficient (log K_{ow}) which is an index of polarity.



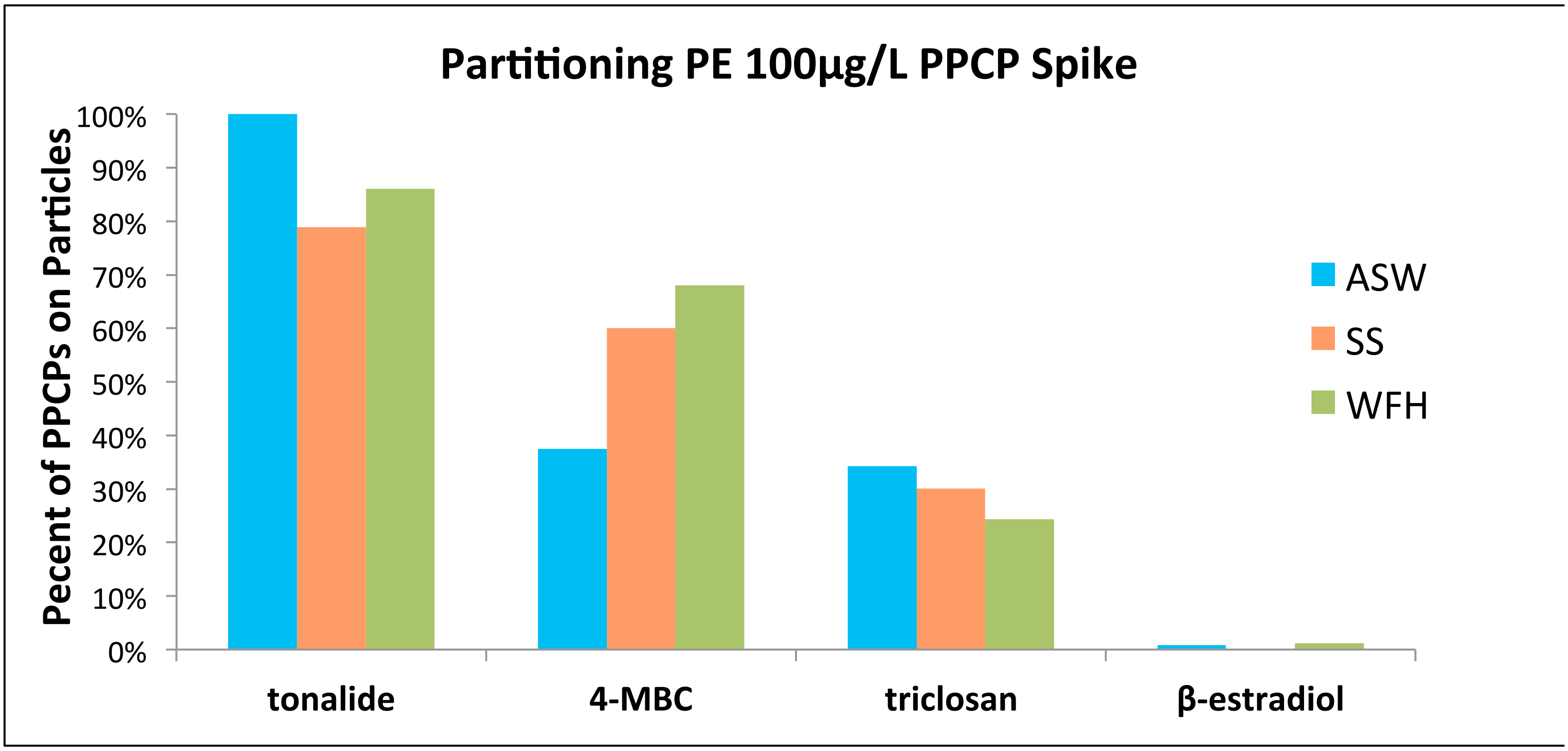


Fig. 4 The partitioning—mass percent of each compound sorbed to the microplastics relative to the total recovered mass—for sorption to polyethylene with three different water matrices. Matrices are artificial seawater (ASW), Sargasso Seawater (SS), and water from West Falmouth Harbor (WFH).

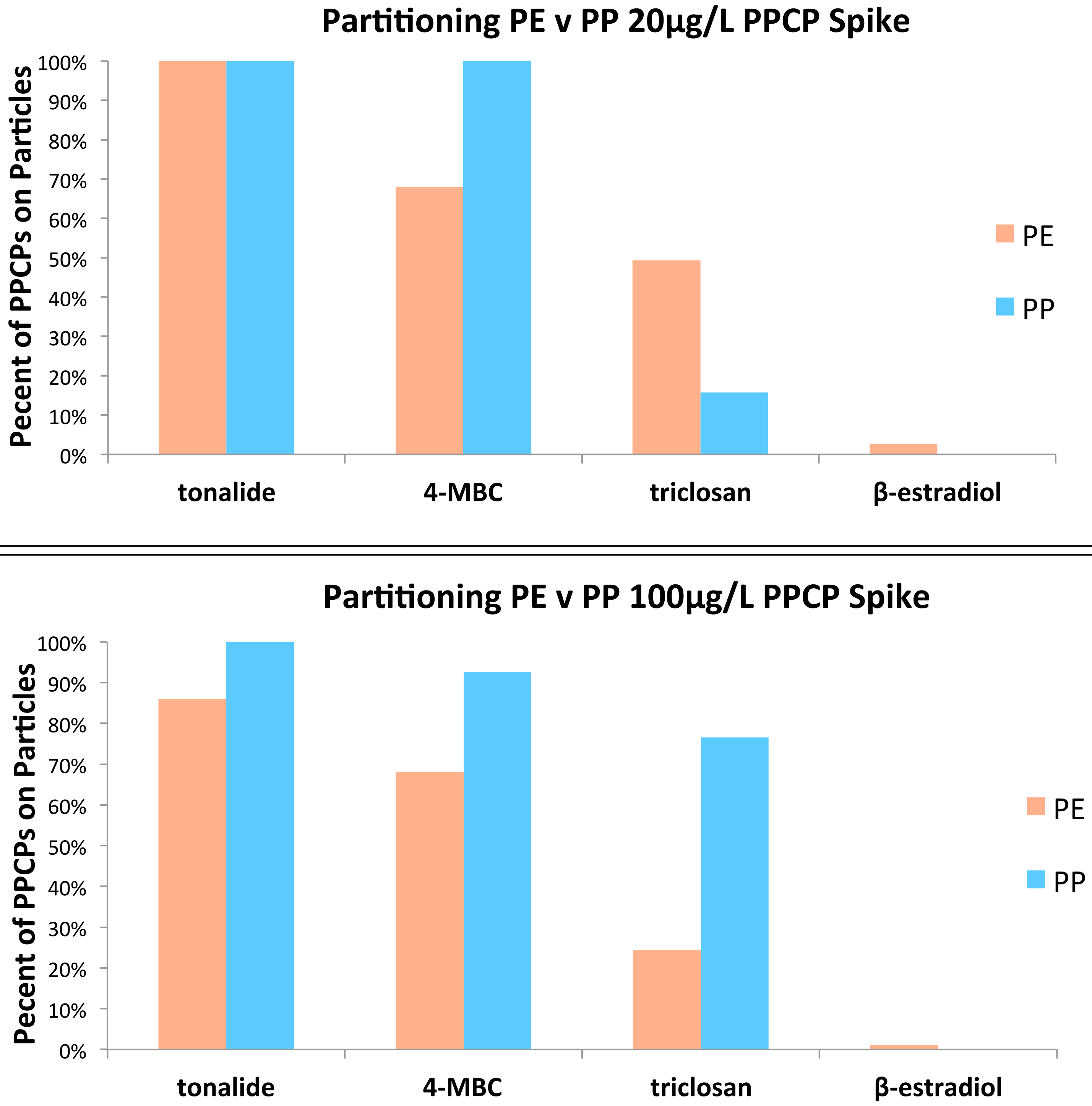


Fig. 5 The partitioning for sorption to polyethylene and polypropylene. For all samples the matrix is West Falmouth Harbor, the high DOC condition.

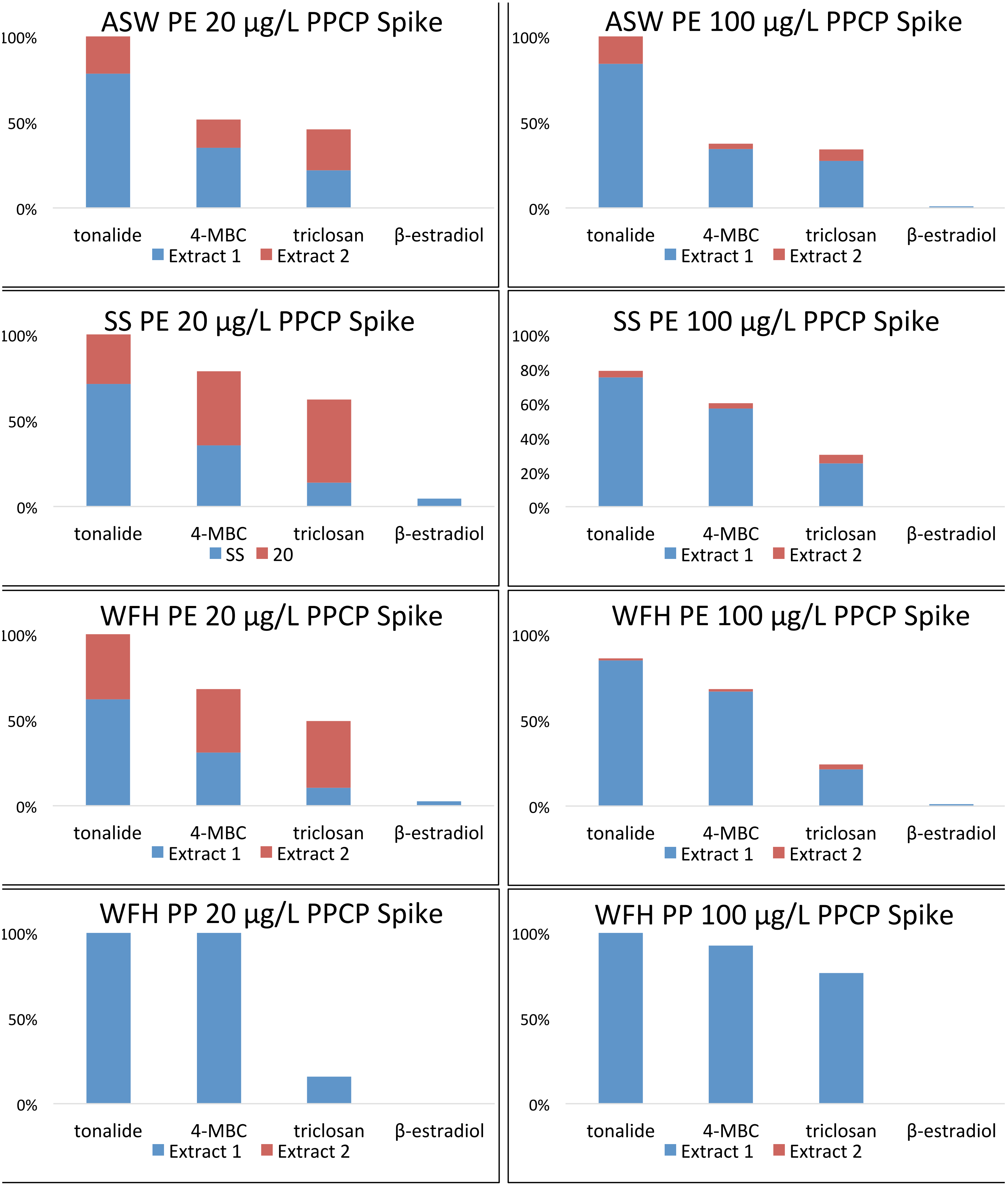


Fig. 6 The total partitioning contribution for each extract. Extract 1 corrersponds to easily extractable PPCPs (sequential solvent rinsing) while extract 2 corresponds to those pollutants that are more tightly bound (subsequent methylene choride ultrasonic extraction).

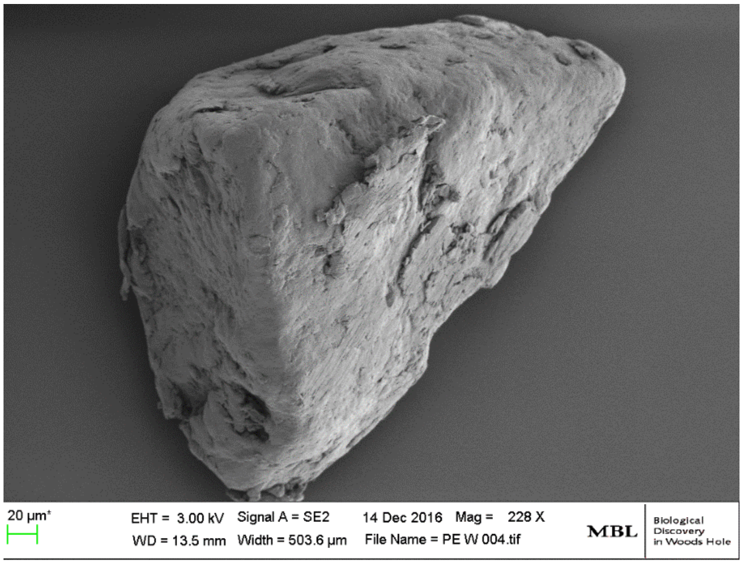


Fig. 6a – Polyethylene

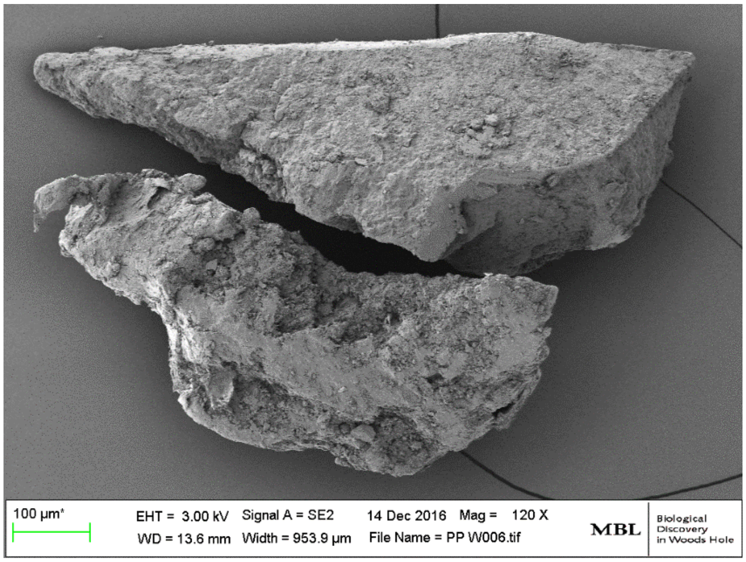


Fig. 6b – Polypropylene

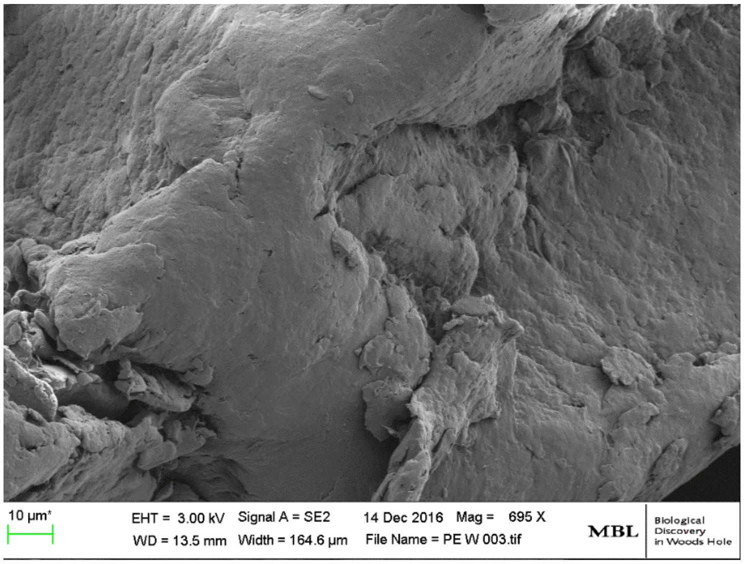


Fig. 6c – polyethylene

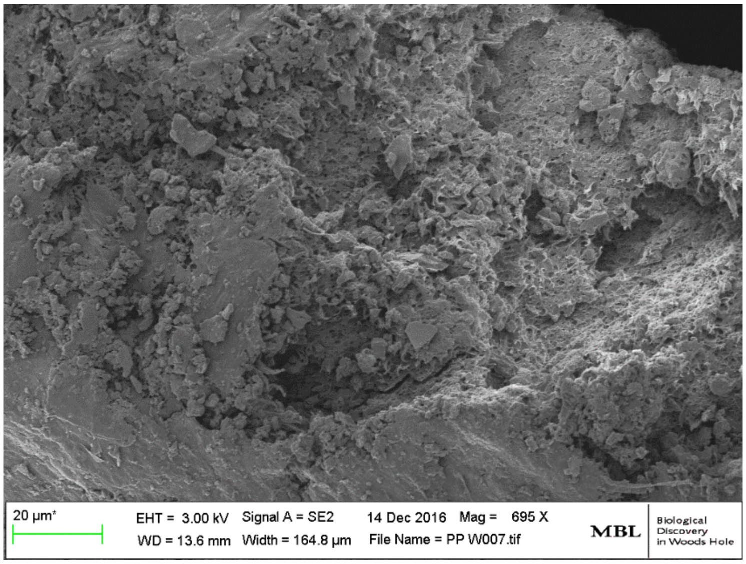


Fig. 6d – polypropylene

Fig. 7 SEM images taken of the plastic particles used in this experiment. Two magnifications are included for each compound, and it is apparent that PP has a much greater surface roughness than PE.

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