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Microplastics are not important for the cycling and bioaccumulation of organic pollutants in the oceans – but should microplastics be considered POPs themselves?

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Microplastics are not important for the cycling and bioaccumulation of organic pollutants in the oceans – but should microplastics be considered POPs themselves?

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Background

This commentary discusses the current evidence about current prevailing themes on the relationship between marine microplastics and organic pollutants. In this context, microplastics can be defined as particles < 5 mm in size [*Thompson et al.*, 2004]. This plastic debris, mostly from anthropogenic land-based sources, fragments into smaller pieces over time [*Jambeck et al.*, 2015].

Do microplastics accumulate high concentrations of organic pollutants.

The current body of evidence suggests that this is true, as microplastics act – as do polymers in general - as passive samplers of organic pollutants. The specific affinity of a given organic pollutant for a polymer dictates its overall enrichment factor (partitioning constant) in the microplastic [*Rusina et al.*, 2007]. The specific affinity for various hydrophobic organic contaminants (HOCs) for polymers has been determined in numerous laboratory and field calibrations in which the partitioning constants between passive samplers and water or air were measured [*Adams et al.*, 2007; *Rusina et al.*, 2007; *Smedes et al.*, 2009; *Lohmann*, 2012;

Pintado-Herrera et al., 2016; *Ziccardi et al.*, 2016]. The polymers most commonly used as passive samplers in field experiments include polyethylene (PE), silicone rubber (SR) and polyoxymethylene (POM) sheets.

There is also plenty of field evidence showing that generic plastic debris accumulates organic pollutants [*Karapanagioti et al.*, 2011; *Rochman et al.*, 2012; *Endo et al.*, 2013]. A prominent example is the so-called 'pellet watch' global monitoring program, which relies on plastic pellets collected by volunteers from across the globe [*Hirai et al.*, 2011]. In these studies, strong enrichment of HOCs in the polymers, often exceeding 10^6 times relative to their dissolved concentrations was found.

How significantly will microplastics contribute to the dispersion and global cycling of POPs?

It has become common knowledge that microplastics are present around the globe, and have been found in all ocean gyres, coastal seas and beaches [*Jambeck et al.*, 2015; *Sebille et al.*, 2015]. It should therefore be no surprise that the concept of microplastics as being important for the global dispersion of organic pollutants, in particular persistent organic pollutants (POPs), a subgroup of persistent HOCs, has been suggested. Yet, numerous studies have refuted that idea [*Zarfl and Matthies*, 2010; *Gouin et al.*, 2011; *Koelmans et al.*, 2016; *Ziccardi et al.*, 2016]. There is simply not enough microplastic and plastic debris present in the oceans to outcompete the partitioning of POPs to water and natural organic matter (such as phytoplankton). In Koelman et al. [2016]'s analysis of a strongly HOC (concentrated 10^7 times from water), ocean water nonetheless contained 99% of the HOC, followed by DOC and colloids (0.4% each); microplastics captured ~ 10^{-4} % of the total mass present in the oceans.

In addition, diffusion of HOCs in and out of microplastics is slow. The time for various dissolved polychlorinated biphenyls (PCBs) to reach equilibrium with a 50 μm or 500 μm PE sheet ranges from days to decades [*Lohmann and Muir*, 2010; *Endo et al.*, 2013]. Thus the release of these contaminants from the microplastic present in the remote ocean will be strongly retarded [*Endo et al.*, 2013; *Bakir et al.*, 2014b] and only add a small contribution relative to already present POPs at any given place and time. Results by Zarfl and Matthies [2010] also implied that microplastics are not an efficient transport vector of HOCs in comparison to long range transport by ocean or atmosphere, except for very high log K_{ow} chemicals, which have otherwise limited transport potential in air and water.

Lastly, a comparison of microplastic particle density in the Pacific Ocean as detected by the Sea Education Association (SEA; Lavender-Law, personal communication) and measured concentrations of PCBs in surface seawater in the region [*Zhang and Lohmann*, 2010] found little correlation between both.

To what extent to microplastics contribute to the bioaccumulation and foodweb transfer of POPs?

There has been a long-standing assumption in many articles and studies that microplastics are efficient carriers of organic pollutants into biota and the foodweb [*Teuten et al.*, 2009; *Rochman et al.*, 2013; *Chua et al.*, 2014; *Batel et al.*, 2016; *Wardrop et al.*, 2016]. Such arguments have been based on the notion that microplastics enrich various POPs (correct, see above), coupled with the assumption that inside an animal, these pollutants are stripped off or leach out of the microplastic and are taken up by the organism (e.g.,[*Teuten et al.*, 2007; *Bakir et al.*, 2014a]). It is worth recalling that chemicals diffuse to achieve the same chemical activity in the

environment, be that water, microplastic or biota [*Schwarzenbach et al.*, 2003]. Just because microplastics display greater concentrations of POPs than present in water does not mean that there is a greater tendency for these pollutants to diffuse out of the plastic particles. The potential importance of microplastics as carriers of POPs into animals remains a strong theme in discussion on microplastics, though, seemingly corroborated by empirical evidence [*Teuten et al.*, 2009], it requires deeper examination. This will be addressed in more detail below using the three scenarios outlined in Figure 1, in which (a) a naturally contaminated fish ingests a naturally contaminated microplastic (e.g., both collected in the wild); (b) a clean fish consumes a contaminated microplastic particle (e.g., in laboratory experiments), and (c) a reverse set-up, where a contaminated fish consumes a pollutant-free microplastic particle. Examples from the literature supporting these different scenarios are listed in Table 1. At a very basic level, equilibrium partitioning thinking can be used to define simple expectations in which way organic pollutants will move in a bioaccumulation thought experiment.

Scenario A

As outlined in scenario a) (Figure 1) a fish and piece of microplastic both contain POPs already, simply from occurring in the environment. The presence of POPs in the fish, and a microplastic residing in the same environment, are driven by the contaminants' chemical activity and ought to be the same in both fish and microplastic particles. The ingestion of the microplastic by the fish does not change the contaminant burden by the fish or the microplastic, as they are both already in equilibrium [*Gouin et al.*, 2011]. This should be the most prevalent interaction of biota, microplastics, and POPs in the natural environment, as animals are constantly taking up POPs from the environment via their diet and respiration. There are neither

clean (i.e., POPs-free) oceans nor animals present, which means that they will bioaccumulate POPs regardless of whether they ingest microplastics or not.

In the South Atlantic Ocean, there was generally no correlation between HOCs in microplastics and amphipods [*Rochman et al.*, 2014]. Of the targeted HOCs (bisphenol A (BPA), alkylphenols, alkylphenol ethoxylates, PCBs, and polybrominated diphenyl ethers (PBDEs)), only PBDEs displayed increased body burdens in regions where more microplastics were present. The presence of PBDEs in tissues could be due to the presence of small microplastic particles during the extraction (see below). Another good example of scenario of (a) is the recent study in which birds and the microplastics in their gut were analyzed for PCBs [*Herzke et al.*, 2016]. The authors concluded that the presence of PCBs in the fulmars due to the ingestion of plastics was negligible relative to the uptake of PCBs via their prey.

Similar conclusions were reached earlier by Gouin et al. (2011) based on theoretical considerations based on a bioaccumulation food web model. Lastly, Koelmans et al. (2016) also concluded that there is no experimental or theoretical evidence for an important role of microplastics in the transfer of POPs into animals.

Scenario B

This scenario consists of exposing clean animals from a reference site to microplastics containing a high concentration of POPs, either from laboratory dosing or from microplastics exposed to contaminants at urban/industrialized sites. Most reported bioaccumulation studies with microplastics are based on this scenario, such as the ingestion of PBDE-spiked particles by amphipods in the laboratory [*Chua et al.*, 2014]. Interestingly, the experiment actually resulted in decreased PBDE bioaccumulation uptake relative to control animals. Other experiments used

116 field-contaminated microplastic particles. For example, Teuten et al. (2009) described the
117 feeding of microplastics naturally contaminated by PCBs from Tokyo Bay to shearwater chicks
118 hidden in a fish diet. Initially, some uptake of lower chlorinated PCBs was observed, but the
119 PCBs ingested from the bird's prey fish outweighed the birds' body burden over time [*Teuten et*
120 *al.*, 2009].
121 In general, an efficient transfer of POPs from the microplastic to the animals is observed. This is
122 due to the experimental design, and shows that microplastic can be used as a vector for POPs
123 into animals. ***It does not demonstrate, however, that this pathway is relevant in the field.*** As
124 noted above, animals in the wild are typically as 'contaminated' with respect to POPs as the
125 microplastic particles they might consume. The conclusion that microplastics is not an important
126 transfer process was also reached in a study exposing lugworms to sediments enriched with field-
127 contaminated polystyrene particles [*Besseling et al.*, 2013]. The observed increase in PCB
128 bioaccumulation (1.1 – 1.5 times relative to controls) was only observed at low concentrations of
129 polystyrene particles.
130
131 Scenario C
132 This scenario is the reverse of scenario b) in which a POP-contaminated fish is fed clean
133 microplastic to determine if this will lower its body burden with respect to the POP. The idea is
134 based on research that olestra, a non-digestible fat, can be used to remove POPs from
135 contaminated animals [*Moser and McLachlan*, 1999]. Gouin et al. (2011) picked up this idea in
136 their bioaccumulation model, suggesting that the ingestion of clean microplastic could indeed
137 cause a decreased body burden in animals. Recently, Rummel et al. (2016), did not observe a

138 significant decrease in bioaccumulation of PCBs in rainbow trout allowed to ingest clean
139 microplastics.
140
141 **Do microplastics transfer other organic contaminants into biota?**
142 As discussed above, there is little evidence that microplastics play a major role in the
143 bioaccumulation of POPs, when compared to the role of diet in nature. As already discussed by
144 [*Teuten et al.*, 2009] and [*Gouin et al.*, 2011], microplastics could become an important pathway
145 for polymer additives that otherwise would not be easily transferred into the marine environment.
146 In particular, [*Teuten et al.*, 2009] suggested research should focus on the release of phenolic
147 additive-derived chemicals (i.e., alkylphenols and BPA) from microplastics in the food web. Yet
148 neither a modeling study by [*Koelmans et al.*, 2014] nor the field study by [*Rochman et al.*,
149 2014] found evidence that the ingestion of microplastics is relevant for the uptake of these
150 compounds by biota.

151 Several recent studies highlighted that certain chemicals, likely originating from plastic particles,
152 can indeed be transferred into animals. The presence of highly brominated BDEs 183 and 209 in
153 seabirds was linked to their ingestion of marine plastics [*Tanaka et al.*, 2013]. The birds' prey
154 items had no detectable BDE 183 and 109 concentrations but these contaminants were observed
155 in both the birds and ingested plastic debris particles. Similarly, the presence of
156 hexabromocyclododecanes (HBCDs) in Styrofoam and blue mussels from coastal South Korea
157 were linked [*Jang et al.*, 2016]. Elevated concentrations, and a α/γHBCD ratio closer to that of
158 Styrofoam were detected in mussels colonizing Styrofoam buoys, when compared to mussels
159 collected from other substrates and regions along the coast. Overall, strong evidence was

presented for a direct pathway of HBCD from the Styrofoam buoy into the mussel, including the detection of Styrofoam particles in the mussels themselves.

As there is good evidence that brominated compounds can be metabolized in animals [*Stapleton et al.*, 2004], the presence of several low solubility brominated compounds (highly brominated BDEs, HBCD) in biota, linked to the ingestion of microplastics, seems surprising at first. Yet it might actually indicate that these compounds are not properly dissolved in the animals, but rather part of nanoplastic particles dispersed within the animals' tissue and organs.

Should microplastics be considered POPs?

While the preceding discussion highlighted that microplastics in the oceans do little to affect the presence and transfer of most organic pollutants at this point, there is still plenty of evidence that microplastics are harmful and their impact should be minimized, as far as possible. This be could be seen as a contribution towards a sustainable use of resources.

One approach would be to consider classifying microplastics as potential pollutants under the Stockholm Convention on POPs [*UNEP*, 2001]. Four criteria, namely persistence, bioaccumulation, long-range transport and adverse effects (Table 2), must be met for a compound to be listed as a POP. There is strong evidence that microplastics are persistent, as a result of their industrial polymer properties and additives [*Gewert et al.*, 2015], and that they undergo long-range transport, as documented by their widespread presence in remote oceans [*Lavender Law et al.*, 2010; *Sebille et al.*, 2015]. Several ecotoxicologial studies highlight adverse effects, though these experiments are often performed at unrealistically high doses of microplastic exposure. The classical concept of bioaccumulation and biomagnification on a

molecular level is not met, but there is evidence that microplastics are present in top predators and are transferred up the food chain.

In summary, there is little evidence that marine microplastics affect the global transport or bioaccumulation of POPs in the oceans. In terms of bioaccumulation, experimental designs can be manipulated to show that microplastics are a vector of POPs into organisms in the laboratory. Yet, there is scant evidence from field studies that the ingestion of microplastics affects the bioaccumulation of POPs. While there are some studies that show several low-solubility compounds increase in animals that have ingested more microplastics, this might in fact be from the presence of micro- and nanoplastic particles in those animals. Just because microplastics are not relevant for the transport of POPs does not take away from their potential for detrimental impacts on the environment. A possibility to address these concerns could be to consider marine (micro)plastics as POPs, and rely on the Stockholm Convention to reduce their sources.

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