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Adsorption of perfluoroalkyl substances on microplastics under environmental conditions[☆]

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ABSTRACT

Plastic debris has become an environmental problem during recent years. Among the plastic debris, microplastics (<5 mm; MPLs) imply an extra problem due to their capacity to enter into the fauna through ingestion. In this work, we study the capacity of three MPLs, that include high-density polyethylene (HDPE), polystyrene (PS) and polystyrene carboxylate (PS-COOH), to sorb 18 perfluoroalkyl substances (PFASs; including carboxylic acids, sulphonates and one sulphonamide) from the surrounding waters (freshwater and seawater).

Conclusions drawn from the results are that perfluoro sulphonates and sulphonamides have more tendency to be sorbed onto MPLs. In addition, PS and PS-COOH have more affinity for PFASs than HDPE. Finally, the increment of conductivity and pH of the water decreases the exposure time that is necessary to reach equilibrium. However, the presence of salts decreases the tendency of PFASs to be sorbed onto plastic surfaces. These results highlight the problem associated with the presence of MPLs in inland and marine waters since toxic compounds can be sorbed onto surrounding plastics that could be ingested by aquatic fauna.

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1. Introduction

Nowadays, the unsustainable disposal of plastic residues is an emerging environmental problem for surface water (Mani et al., 2015; Van Sebille et al., 2015) and the ocean is presented as final sink (Avio et al., 2016; Llorca et al., 2014; PlasticsEurope, 2011). Plastic debris represents an aesthetic problem but also implies harmful damages for coastal areas and socio-economic activities that are linked to contaminated regions (Cole et al., 2011; Harrison et al., 2011; US_EPA, 2002). The low degradability of these materials and the presence of low-density polymers in upper layers of aquatic systems hamper oxygen exchange and obstruct light, which leads to eutrophication processes (Harrison et al., 2011). Recent studies have demonstrated that zooplankton (Setälä et al., 2014), fish (Romeo et al., 2015) and birds (Holland et al., 2016) can ingest

microplastics (MPLs <5 mm). The ingestion of MPLs can alter different functions on aquatic biota, for example, polystyrene can significantly change the feeding capacity of zooplankton, and prolonged exposure significantly decreases their reproductive output (Cole et al., 2015). In addition, ingestion by zooplankton may assist in the marine food web transfer of MPLs. However, their impact has not yet been fully evaluated (Bouwmeester et al., 2015; Cole et al., 2011; Lusher, 2015). On the other hand, MPLs can accumulate persistent organic contaminants and pathogens, that are also an additional transport vector for these contaminants (Bakir et al., 2014a; Lusher, 2015; Rios et al., 2007). Therefore, the effects that MPLs may cause to the marine food web are not only associated with the consequences of their direct ingestion, but they are also associated with the release of compounds adsorbed onto surfaces of MPLs (Deudero and Alomar, 2015; Engler, 2012).

Perfluoroalkyl substances (PFASs) are a large group of chemicals that have been synthesised for more than 60 years. These are used in industrial and commercial applications due to their inertia and resistance to physical, chemical and biological degradation (Llorca

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et al., 2012). In addition, these compounds have been related to different toxicological effects (e.g., disruption of the thyroid hormones and the metabolism of high-density lipoproteins, cholesterol and triglycerides (Lau et al., 2007; Peden-Adams et al., 2008)). The high stability of PFASs and their wide distribution around the environment make them considered as being emerging persistent organic pollutants (POPs). Their presence in surface waters varies from few to hundred ng/L, even µg/L. For example, recently, average concentrations of 162 ng/l have been reported in the Qiantang River in China (Lu et al., 2017), while in other areas only few ng-pg/L levels have been reported (Sammut et al., 2017). But their occurrence is in general confirmed even in pristine areas (Casal et al., 2017) and open oceans waters (González-Gaya et al., 2014). Their environmental transport has been related to geophysical phenomena (Lohmann et al., 2007) as well as other vectors, such as sorption, onto marine plastic debris (Bakir et al., 2014b; Llorca et al., 2014). Sorption is also an additional vector for the entrance of PFASs in marine biota. That phenomenon has been previously identified for other POPs such as polychlorinated biphenyls (PCBs) (Colabuono et al., 2009; Rochman et al., 2013) and personal care products (Wardrop et al., 2016). Recently, different authors highlighted the limited evidence or the low role of MPLs as a vector to the biota of persistent organic pollutant (POPs) (Koelmans et al., 2016; Lohmann, 2017) while the importance of the study of some additives used in plastic manufacture is pointed out (Kwon et al., 2017). However, some controversy arises at the light of some other studies. Hartmann et al. indicated the need to improve the estimations of the role of MPs as vectors for hydrophobic organic compounds transfer into biota under environmental conditions (Hartmann et al., 2017). Bakir et al. (2014b) studied the desorption of organic contaminants such as phenanthrene, dichlorodiphenyl-trichloroethane (DDT), diethylhexyl phthalate (DEHP) and perfluorooctanoic acid (PFOA) from polyethylene (PE) and polyvinyl chloride (PVC) under simulated physiological conditions. The results of that study proved that desorption was enhanced in the physiological medium and induced a hypothesis that the presence of selected pollutants adsorbed onto MPLs could enhance their bioavailability via marine organisms (Bakir et al., 2014b). But, in the case of PFOA, the environmental transport was shown to be negligible.

In addition, while the adsorption of highly hydrophobic compounds has been widely studied other groups of compounds with more hydrophilic properties have been much less considered as well as those with surfactant properties as PFASs. PFASs are a large group of industrial compounds with a plethora of uses. Moreover, currently, legacy PFASs, such as PFOA and perfluorooctanesulfonate (PFOS) have been substituted by shorter-chain compounds.

The main objectives of this work were to characterise the sorption capacity of 18 PFASs by three different types of microplastics (size between 3 and 12 µm) and to carry out the evaluation of a mixture of PFASs, as in real emissions. The selected MPLs were high-density polyethylene (HDPE), polystyrene (PS) and polystyrene carboxylic acid (PS-COOH) due to their high production and uses, low biodegradability in the environment and their increase as a litter in different water bodies (Kwon et al., 2014; PlasticsEurope, 2011). To assess the capabilities of these MPLs in the aquatic environment, the experimental setup was emulating realistic environmental conditions of freshwater and seawater ecosystems.

2. Materials and methods

2.1. Materials

The studied MPLs consisted of HDPE microspheres, ranging from 3 to 16 µm, which were supplied by Cospheric (Santa Barbara,

California, USA); and 10 µm PS and PS-COOH, which were supplied by Phosphorex (Hopkinton, Massachusetts, USA).

A mixture of PFASs [MXB; > 98%] in methanol containing: i) perfluorobutanoic (PFBA), perfluoropentanoic (PFPeA), perfluorohexanoic (PFHxA), perfluoroheptanoic (PFHpA), perfluorooctanoic (PFOA), perfluorononanoic (PFNA), perfluorodecanoic (PFDA), perfluoroundecanoic (PFUdA), perfluorododecanoic (PFDoA), perfluorotridecanoic (PFTrA), perfluorotetradecanoic (PFTeA), perfluorohexadecanoic (PFHxDA) and perfluorooctadecanoic (PFODA) acids; and ii) perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS) and perfluorodecanesulfonate (PFDS), was mixed with the sulphonamide perfluorooctanesulphonamide (PFOSA), >99%. A mixture of labelled PFASs [MXA; > 98%] in methanol containing: [¹³C₄]-perfluorobutanoic acid (MPFBA (¹³C₄)), ion [¹⁸O₂]-perfluorohexanesulfonate (MPFHxS (¹⁸O₂)), [¹³C₂]-perfluorohexanoic acid (MPFHxA (¹³C₂)), ion [¹³C₄]-perfluorooctanesulfonate (MPFOS (¹³C₄)), [¹³C₄]-perfluorooctanoic acid (MPFOA (¹³C₄)), [¹³C₅]-perfluorononanoic acid (MPFNA (¹³C₅)), [¹³C₂]-perfluorododecanoic acid (MPFDoA (¹³C₂)), [¹³C₂]-perfluorodecanoic acid (MPFDA (¹³C₂)), [¹³C₂]-perfluoroundecanoic acid (MPFUdA (¹³C₂)), was mixed with [¹³C₈]-perfluorooctane sulphonamide (M8FOSA (¹³C₈)), that was added before analysis, and they were used as internal standards in order to normalise the instrumental analysis results. All of the standards were supplied by Wellington Laboratories Inc., Canada. In Table S1 of the Supporting Information, the list of compounds and the carbon chain length of each one is presented.

Water and Methanol CHROMASOLV[®]Plus, for HPLC grade, ammonium acetate salt (AcNH₄: 77.08 g/mol; 98%) were provided by Sigma-Aldrich, Steinheim, Germany.

2.2. Freshwater and seawater sampling

The experiments were carried out using fortified real environmental waters at 10 µg/l with the 18 PFASs. For this purpose, in February 2016, 2.5 l of water from the Ebro River (40.976154,0.518484; NE of Spain) and 2.5 l of seawater from the Alfacs Bay (40.584421,0.579456; Ebro Delta, NE of Spain) were collected. The main physicochemical parameters including pH, dissolved oxygen, conductivity and total organic carbon (TOC) are shown in section S1 from supplementary material. Natural waters were transported to the laboratory under cool conditions. To assess the initial concentration of PFASs, 1 ml of each type of sample was directly analysed by liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS; according to the methodology described elsewhere (Llorca et al., 2014)). The samples were analysed in triplicates. The results showed that no PFASs were present at concentrations higher than limits of 10 ng/l.

2.3. Adsorption experiments

Adsorption experiments were conducted according to a batch method at room temperature (20 °C) using natural waters fortified with a mixture of PFASs. The experiments were designed as follows: 48 glass vials were filled with 10 ml of freshwater and a further set of 48 glass vials were filled with 10 ml of seawater. All of them were fortified with a mix of PFASs for a final concentration of 10 µg/l of each individual compound (180 µg/l ΣPFAS). This concentration was selected in consideration of background concentration of PFASs in the environment (Llorca et al., 2012). Then, 12 vials of each type of water were spiked with HDPE at 5 mg/l, PS at 2 mg/l and PS-COOH at the same concentration. Finally, the last 12 vials containing only PFASs were used as blanks in order to monitor the adsorption of PFASs onto the inner glass walls.

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