



## Levels and fate of perfluoroalkyl substances in beached plastic pellets and sediments collected from Greece



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### ABSTRACT

Plastic debris damages marine wildlife and ecosystems becoming an important source of marine pollution. In addition, they can sorb, concentrate and stabilise contaminants acting as toxic carriers to the marine food web. In this context, the presence of 18 perfluoroalkyl substances (PFASs) in plastic pellets ( $n = 5$ ) and beach sediment ( $n = 9$ ) samples widely distributed around Greek coastal areas was assessed.

The results, mainly, showed the sorption of PFASs onto pellet surface from surrounding water with concentrations from method limit of quantification to 115 ng/kg for C5, C7, C8 and C10 carboxylic acids and C8 sulfonate acid. A similar pattern was found by comparing plastic pellets and sediment for the same sampling locations that could indicate a common origin of contamination in both types of samples. However, since the number of analysed samples is limited, a more comprehensive study with a higher number of samples should be performed in future research.

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### 1. Introduction

The development of the plastics industry during the 20th Century has played a key role in the improvement of the quality of life. However, nowadays, the unsustainable disposal of these residues is a relevant environmental problem. The European plastics production in 2010 was about 57 million tonnes (Mt), covering various types of materials such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) (PlasticsEurope, 2011). The most used resin types are polyolefins (PE and PP), which account for around 50% of all plastics demand (PlasticsEurope, 2011). In 2010, 24.7 Mt residues were generated from the use of plastics and 42% was not recovered. This is an increasing cause of water pollution and marine debris (US\_EPA, 2002).

As a consequence of the massive use of plastic and their resistance to degradation, large areas of the oceans are covered by plastic debris (NOAA-NationalOceanProgram, xxxx). For example, in the North Pacific Ocean the “Great Pacific Garbage Patch” (NOAA-NationalOceanProgram, xxxx) of large floating plastic is an environmental problem. It covers approximately 8 million km<sup>2</sup>,

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more than the total extension of the United States (CenterForOceanSolutions, xxxx). Plastic debris can directly produce damage to the ocean wildlife by entrapment and entanglement of animals, or when marine faunas ingest the plastics (NOAA-NationalOceanProgram, xxxx). In addition, resin pellets of about 2–6 mm in diameter, made of PP or PE and used for the manufacture of plastic products (Derraik, 2002), are present in most of the world’s oceans (US\_EPA, xxxx; Gregory, 2009). Some of these plastics debris are buoyant, whilst others are suspended or deposited (Coe and Rogers, 1997; Redford et al., 1997; Gregory, 2009). Besides the direct harms on marine fauna, plastic marine debris can absorb and concentrate other contaminants, thus, acting as toxic carriers (Ivar do Sul and Costa, 2014). Recent evidence prompts scientists to suggest the characterisation of plastic debris as hazardous waste (Rochman et al., 2013a). In March 2011, the European plastics industry signed up with the “Joint Declaration for Solutions on Marine Litter”, announced at the 5th International Marine Debris Conference in Hawaii (The\_Plastics\_Portal, 2011).

Persistent Organic Pollutants (POPs) present in seawater can be concentrated onto the surface of plastic pellets (Mato et al., 2000; Hirai et al., 2011; Ivar do Sul and Costa, 2014), being ingested by animals (e.g. fishes and seabirds), and enter in the marine food chain (USEPA, xxxx; Gregory, 2009; Rochman et al., 2013c; Ivar do Sul and Costa, 2014). For example, Colabuono et al. (2010)

detected polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in plastics ingested by seabirds from Southern Brazil. PCBs and OCPs were detected in plastic pellets at concentrations ranging from 68 to 491 ng/g, and in plastic fragments at concentrations from 68 to 418 ng/g.

Because of their resistance to degradation under environmental conditions, PFASs can accumulate and biomagnify in marine biota (Kelly et al., 2009; Kantiani et al., 2010; Pico et al., 2010). They show moderate acute toxicity to mammals (Trudel et al., 2008) and are globally distributed (Shoeb et al., 2006; Dietz et al., 2008; Llorca et al., 2012). PFASs are hydrophilic and hydrophobic, being sorbed onto marine debris surface. For example, longer chain compounds and sulfonate PFASs are detected in water and sorbed onto sediments (Ellefson, 2001; Higgins and Luthy, 2006; Higgins and Luthy, 2007; Giesy et al., 2010; Ahrens, 2011). Stability studies of PFASs in water have shown that they are sorbed onto PP walls (Loveless et al., 2006; Berger et al., 2011). For example, Berger et al. (2011), found that the sorption of PFASs onto PP container walls after 28 days varied between 10% and 20%. These laboratory study showed that PFASs (Bakir et al., 2014), as well as other legacy POPs (Colabuono et al., 2010; Rochman et al., 2013b; Bakir et al., 2014; Lee et al., 2014), can be sorbed onto marine debris from the surrounding waters.

In this context, the main objective of this study was to assess the occurrence of 18 perfluoroalkyl substances (PFASs) including perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS) in 5 different beach samples of plastic pellet and 9 sediments collected from different coastal sites in Greece.

## 2. Experimental section

### 2.1. Standards and reagents

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 (PFDDA), perfluorotridecanoic (PFTrA), perfluorotetradecanoic (PFTeA), perfluorohexadecanoic (PFHxDA) and perfluorooctadecanoic (PFODA) acids; and ii) perfluorobutanesulfonate (PFBS), perfluorohexasulfonate (PFHxS), perfluorooctanesulfonate (PFOS) and perfluorodecane sulfonate (PFDS) was mixed with the sulfonamide perfluorooctanesulfonamide (PFOSA), >99%. The resulting mixture was used for recovery purposes and calibration curves.

A mixture of labelled PFASs [MXA; >98%] in methanol containing: [ $^{13}\text{C}_4$ ]-perfluorobutanoic acid (MPFBA ( $^{13}\text{C}_4$ )), ion [ $^{18}\text{O}_2$ ]-perfluorohexanesulfonate (MPFHxS ( $^{18}\text{O}_2$ )), [ $^{13}\text{C}_2$ ]-perfluorohexanoic acid (MPFHxA ( $^{13}\text{C}_2$ )), ion [ $^{13}\text{C}_4$ ]-perfluorooctanesulfonate (MPFOS ( $^{13}\text{C}_4$ )), [ $^{13}\text{C}_4$ ]-perfluorooctanoic acid (MPFOA ( $^{13}\text{C}_4$ )), [ $^{13}\text{C}_5$ ]-perfluorononanoic acid (MPFNA ( $^{13}\text{C}_5$ )), [ $^{13}\text{C}_2$ ]-perfluorododecanoic acid (MPFDDA ( $^{13}\text{C}_2$ )), [ $^{13}\text{C}_2$ ]-perfluorodecanoic acid (MPFDA ( $^{13}\text{C}_2$ )), [ $^{13}\text{C}_2$ ]-perfluoroundecanoic acid (MPFUDA ( $^{13}\text{C}_2$ )), added before extraction procedure, was used as a surrogate in order to normalise all the analytical process.

Labelled PFASs: [1,2- $^{13}\text{C}_2$ ]-perfluorooctanoic acid (M2PFOA ( $^{13}\text{C}_2$ ); >98%) and ion [ $^{13}\text{C}_8$ ]-perfluorooctanesulfonate (M8PFOS ( $^{13}\text{C}_8$ ); >98%), added just before LC injection, were used as internal standards in order to normalise the instrumental analysis response.

All analytical standards, and labelled standards, were purchased from Wellington Laboratories Inc., Canada. Water and Methanol (MeOH) CHROMASOLV<sup>plus</sup>, for HPLC grade, ammonium acetate salt (AcNH<sub>4</sub>: 77.08 g/mol; 98%), ammonium hydroxide (NH<sub>4</sub>OH:

33.05 g/mol; 99.9%) and sodium hydroxide (NaOH: 44 g/mol; ≥97%) were obtained from Sigma–Aldrich, Steinheim, Germany.

### 2.2. Sample collection

Plastic pellets from 2 to 6 mm diameter and sediments were collected from the beach surface of coastal areas around Greece during 2008. The samples were collected at Corfu Island, Lavrio beach, Kato Achaia beach, Leros Island and Loutropyrgos beach, from the high-tide line to the berm or terrace of the beach. Immediately after sampling, the plastic pellets were separated from the sand using tweezers. They were then stored in aluminium foil and preserved at 4 °C for their transportation to the laboratory. Plastics pellets that had sand adhered to them, or those covered by algae or tar were discarded. The samples were preserved at –4 °C in the University of Patras (Greece) before their shipment to the IDAEA–CSIC laboratories (Barcelona, Spain). The samples were finally kept at –20 °C until their analysis.

The pellets were all cylindrical or disk-shaped pre-production pellets with diameters ranging from 4 to 5 mm and they were identified visually since they were all collected by tweezers. None of the pellets used in the present study contained visually appreciable dyes. The yellow colour of beached pellets is due to erosion and not due to dyes (Ogata et al., 2009; Fotopoulou and Karapanagiotti, 2012). According to previously published monitoring studies in Greece that included some of the batches of pellets used in the present study, the pellets collected were mainly (60–90%) polyethylene and (40–10%) polypropylene (Karapanagiotti and Klontza, 2007; Karapanagiotti et al., 2011).

Sediment samples were collected at the beach face from Corfu Island, Kato Achaia beach, Leros Island, Pagasitikos Gulf, and Lavrio using glass jars; at the near shore zone from Loutropyrgos using a shovel; and at the bottom of the sea using a core sampler from a boat in Amvrakikos Gulf and Aliveri. As in the case of plastic pellets, the sediment samples were transported at 4 °C to the laboratory of the University of Patras (Greece) and frozen at –4 °C before their shipment to the IDAEA–CSIC laboratories (Barcelona, Spain). The samples were finally kept at –20 °C until their analysis.

In all cases, the handling personnel wore latex gloves, free of PFASs.

In order to rule out any possible source of cross contamination, blank samples were processed in parallel with the samples of beached plastic pellets and sea sediments. The blanks were carried with the samples during shipment, preservation, and analyses. Blank samples were composed of three samples of blank virgin plastic pellets (2 made of polypropylene (PP) and 1 made of polyethylene (PE)), which were obtained from a local manufacturer. The material of the virgin plastic pellets was verified by Dr. H. Takada's group from the Laboratory of Organic Geochemistry, Tokyo University of Agriculture and Technology, Japan using near-infrared spectroscopy (PlaScan-SH, OPT Research Inc. Tokyo, Japan) (Fotopoulou and Karapanagiotti, 2012). A blank sample of sea sand (SiO<sub>2</sub>) was obtained through a commercial provider (Panreac Quimica SA, Barcelona, Spain), which was washed and thin grain, of particle size 0.25–0.30 mm, preserved in a PE bottle. Finally, blanks of solvents were also analysed in parallel with the samples.

### 2.3. Sample pre-treatments and extraction procedures

#### 2.3.1. Sediment sample pre-treatment

The sample pre-treatment for sediments was based on a previous procedure (Llorca et al., 2012). 1 g of dry sediment was weighed and introduced into a 50 mL PP centrifuge tube. Then, labelled surrogates standards were added (10 µL at 50 pg/µL, in methanol) and left to reach the equilibrium during 20 min at room temperature. After this time, the sediment was extracted by ultra-

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