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Seasonal variations in the occurrence of perfluoroalkyl substances in water, sediment and fish samples from Ebro Delta (Catalonia, Spain)

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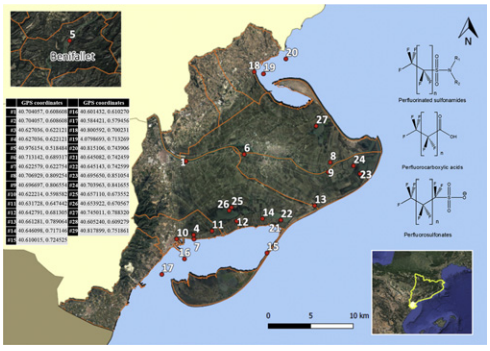
HIGHLIGHTS

- Seasonal variations of perfluoroalkyl substances in the Ebro Delta Area were studied.
- PFOA was the most frequently detected in water and sediments.
- Levels of PFASs in waters were characterised by a slight decrease during winter.
- Levels of PFASs in sediments showed a progressive decrease from autumn to summer.

GRAPHICAL ABSTRACT



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ABSTRACT

The main objective of this study was to assess the concentration levels and the seasonal variations of 13 poly- and perfluoroalkyl substances (PFASs) in different compartments (water, sediments and fish) of the Ebro Delta (NE Spain) and surrounding coastal areas. Perfluorooctanoic acid (PFOA) was the most frequently detected compound in waters and sediments. Perfluorocarboxylic acids (PFCAs) were the compounds found at the highest concentrations in water samples. On the other hand, sediments were more enriched in perfluorooctanesulfonate (PFOS) (range < 1.02–22.6 ng/g dw). Waters and sediments showed a different seasonal trend. While waters were characterised by a substantial constant level of PFASs over the year, sediments showed a progressive decrease from autumn to summer, revealing the great influence that environmental conditions exert on PFAS distribution in sediments. As regards fish samples, in spite of the ban of its production, PFOS was the most frequently detected compound in seawater fishes, in agreement with its high persistency, bioaccumulation and biomagnification. Moreover, PFASs showed to be more distributed in the skin rather than in muscle tissues. In addition, river fishes were characterised by very high PFAS levels (∑PFAS range from 63.8 ng/g ww to 938 ng/g ww), with perfluoroalkyl carboxylic acids being more concentrated than sulfonates. The PFASs concentrations in water, sediment, and biota revealed that one of the studied sites, Isla de Buda was the most contaminated site of the Ebro Delta. These results are consistent with its location at the final part of the estuary, where many irrigation channels are collected together.

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1. Introduction

Poly- and perfluoroalkyl substances (PFASs) are a wide group of synthetic substances with multiple industrial and domestic applications, such as stain repellents coatings for textiles and fire-fighting foams among many others (Arvaniti and Stasinakis, 2015; Zareitalabad et al., 2013). Because of the strong carbon-fluorine bond, these compounds are characterised by high thermal, chemical and biological stability. However, due to this high stability, they have been found to be persistent in the environment, with compounds such as the perfluorooctanesulfonate (PFOS) having a half-life of more than two months in waters and over six months in soils and sediments (Renzi et al., 2013). Moreover, PFASs show a tendency to bioaccumulate and biomagnify through the food chain (Ahrens et al., 2011; Naile et al., 2010), potentially causing adverse effects on organisms, such as hepatotoxicity reduction of the immune function among others (Lau et al., 2007; Zhang et al., 2013). Therefore, due to their persistence, accumulation in living organisms, the toxicity of some compounds and their wide distribution in the environment, the occurrence of PFASs is a cause for concern, and nowadays they are considered as emerging organic contaminants. For these reasons, the European Commission (EC) has set PFOS and its derivatives in the list of priority hazardous substances and has identified water and fish threshold concentrations for environmental quality assessment under the Water Framework Directive (WFD) (WFD, 2012). However, there is still a lack of legislation concerning most of these compounds in drinking water and food. Moreover, the Directive 2013/39/EC (EU Commission, 2013) laid down environmental quality standards (EQS) for priority substances in water and biota. The EQSs set for PFOS are 0.65 ng/l in inland surface waters (annual average concentration), 36 μg/l as maximum allowable concentration, and 9.1 μg/kg in biota. In the US Environmental Protection Agency (US EPA, 2016) has proposed a provisional threshold (between 0.01 and 0.09 μg/l) for drinking water with respect to only 7 compounds, including PFOS and perfluorooctanoic acid (PFOA).

Manufacturing facilities are considered to be one of the main sources of contamination by PFASs (Prevedouros et al., 2006; Pistocchi and Loos, 2009), along with wastewater treatment plants (WWTPs), which have been found to be inefficient in the removal of these compounds from wastewater influents (Ahrens et al., 2009; Boulanger et al., 2005; Schultz et al., 2006). Once released into the aquatic environment, they can easily be transferred into different environmental compartments, reaching groundwater (Houtz et al., 2013), soils (Houtz et al., 2013), sediments (Gao et al., 2015) and biota (Campo et al., 2016). Furthermore, these compounds have been found in remote environments, such as the Antarctica region (Llorca et al., 2012a). Once in the aquatic environment, PFASs are accumulated and biomagnified through the aquatic food chain whereby they reach human food (Pérez et al., 2014) and drinking water (Llorca et al., 2012b; Schwanz et al., 2016). The partitioning mechanism and their fate in the environment, though, are still not well-known (Ahrens, 2011). In addition, most studies have been mainly focused on more persistent and accumulative compounds such as PFOS and PFOA, while less information has been reported regarding the use of short-chain PFAS in the substitution of the 8-carbon chain compounds.

Different studies have already investigated the occurrence of PFASs in the aquatic environment, mainly focusing on their distribution in fresh waters, particularly rivers (Ahrens, 2011; Loos et al., 2013a; Munoz et al., 2015; Valsecchi et al., 2015; Lorenzo et al., 2016). But, up until now, scarce information is available about their seasonal fluctuation in coastal and highly productive areas, such as estuarine habitats. Those are fragile ecosystems that can be highly affected by human activities since they receive urban sewages and other by-products of human activities (Jiang et al., 2014).

Within this context, the main aim of this study was to assess the occurrence and environmental fate of 13 PFASs in the Ebro Delta (NE of Spain), as well as the surrounding coast: 8 perfluorocarboxylic acids, 4 perfluorosulfonates and 1 sulfonamide in a total number of 213 samples (87 waters, 71 sediments and 55 fishes). These compounds were analysed in the water, sediment and fish samples during three different seasons.

2. Materials and methods

2.1. Chemicals and reagents

Perfluoroalkyl compounds standards were provided by Wellington Laboratories Inc. (Canada) and were composed of: (i) a mixture of PFASs (PFAC-MXB, 2 μg/ml in methanol, purity >98%) containing perfluoropentanoic (PFPeA), perfluorohexanoic (PFHxA), perfluoroheptanoic (PFHpA), perfluorooctanoic (PFOA), perfluorononanoic (PFNA), perfluorodecanoic (PFDA), perfluoroundecanoic (PFUdA) and perfluorododecanoic (PFDoA) acids, and perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), perfluorodecane sulfonate (PFDS); and (ii) the perfluoroctanesulfonamide (PFOSA). Surrogate internal standards used for quantification normalisation were supplied by Wellington Laboratories Inc. (Canada), and included: (i) a mixture of labelled PFASs (MPFAC-MXA, 2 μg/ml in methanol, purity > 98%), composed of $^{18}O_2$-perfluorohexanesulfonate (MPFHxS-18O2), $^{13}C_2$-perfluorohexanoic acid (MPFHxA 13C2), $^{13}C_4$-perlfuorooctanesulfonate (MPFOS-13C4), $^{13}C_4$-perfluorooctanoic acid (MPFOA-13C4), $^{13}C_5$-perfluorononanoic acid (MPFNA-13C5), $^{13}C_2$-perfluorodecanoic acid (MPFDA-13C2), $^{13}C_2$-perfluorododecanoic acid (MPFDoA-13C2); and (ii) $^{13}C_8$-perfluorooctanesulfonamide (M8FOSA, >99%).

All solvents and reagents were of analytical grade. Water and methanol (CHROMASOLV® Plus), ammonium acetate (MW: 77.08, purity > 98%), and ammonium hydroxide (MW: 35.05, purity > 98%) were purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Area of study

The Ebro Delta is the third largest delta in the Mediterranean Sea. It is a wetland area of 320 km^2, highly relevant for conservation, which is included in the Ramsar Convention list. This estuarine habitat is characterised by a high biological productivity, thanks to the nutrients that are provided by the Ebro River (Lloret et al., 2004). The climate in the middle and lowland reaches of the River Ebro is typically Mediterranean, with rainfall concentrated in autumn and spring (200–300 mm) and intense summer drought (<50 mm). Flow regime is pluvio-nival because of the left-margin tributaries from the Pyrenees. The average annual temperature is between 10 and 15 °C. The lowest temperatures occur in winter (down to −5 °C) and the highest in summer (>40 °C). Substratum in the area is mainly calcareous, with Cenozoic limestones, gypsum and alluvial sediments. Aquatic vegetation consists of macrophytes such as water crowfoot *Ranunculus* spp. and *Scirpus* spp. The land use is mainly for agriculture and cattle rearing approximately 13% of its total surface is composed of natural lagoons, bays and marshes, whereas the major part (77%) is dedicated mainly to agricultural activity such as rice and orchards. For this reason, since the 1960s, different dams and irrigation channels have been built in order to control Ebro River water and sediment inputs and to fulfil the surrounding water demand (Cardoch et al., 2002).

Amposta, Deltebre, Sant Jaume d'Enveja and Sant Carles de la Ràpita are the main towns that are located in this area, and they can potentially affect estuary environmental quality with the discharge of their treated sewages into the Ebro River. Chemical industries and a nuclear power plant on the northern side of the area (province of Tarragona) may be additional sources of contamination.