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Occurrence, distribution and behavior of emerging persistent organic pollutants (POPs) in a Mediterranean wetland protected area

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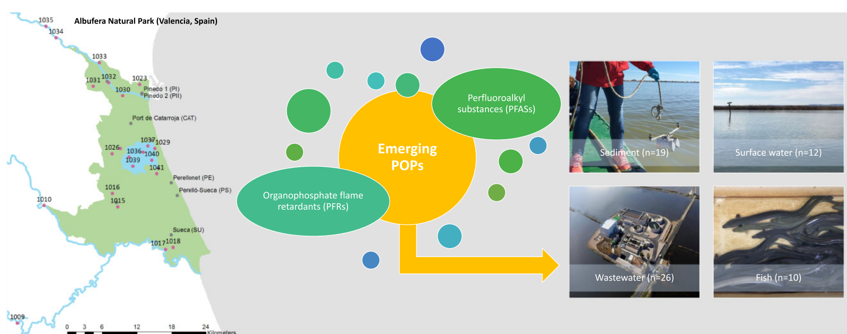
HIGHLIGHTS

- 21 PFASs and 9 PFRs were quantified in sediment, water and fish from a wetland area.
- TCIPP and PFOS were the predominant compounds detected in all the samples.
- Mean levels of PFOS in water and fish were higher than the annual average EQS.
- High levels of PFASs from different sources were observed in wastewater effluents.

GRAPHICAL ABSTRACT



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ABSTRACT

The analysis of perfluoroalkyl substances (PFASs) and organophosphate flame retardants (PFRs) in the different environmental compartments of a characteristic coastal wetland, the Albufera Natural Park (Valencia, Spain), is required for understanding the transport, accumulation and fate of these pollutants in an area under high anthropogenic pressure. Samples included 13 wastewater treatment plant influents, 13 effluents, 12 surface water, 19 sediment samples and 10 fish individuals from the Albufera Natural Park and the surrounding area. Tris(2-chloroisopropyl) phosphate (TCIPP) and perfluorooctane sulfonate (PFOS) were at the highest concentrations in water, 330.2 ng L^{-1} and 47.8 ng L^{-1}, respectively. In fish and sediment PFOS was also the most detected while perfluorooctanoic acid (PFOA) was in all types of water. Higher levels of target compounds (mainly PFASs) in wastewater effluents compared to influent suggested both, formation from precursors during treatment and poor removal efficiency. Mean levels of PFOS in water and fish were higher than the environmental quality standards (EQS) established by the European Union Directive 2013/39/EU. The influence of the metropolitan area of Valencia and its surrounding industrial belt could explain the significantly higher levels reported in the northern part (influenced by the Turia River).

1. Introduction

Organophosphate flame retardants (PFRs) and perfluoroalkyl substances (PFASs) are emerging persistent organic pollutants (POPs)

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widely used in industry as surfactants, plasticizers and anti-foaming agents and as additives in electronics, lubricants, paints, etc. (Wei et al., 2015; Kim et al., 2015). The concern about the occurrence, transport and fate of these compounds in aquatic ecosystems is raising (Lorenzo et al., 2016a; Woudneh et al., 2015; García-López et al., 2009; Barón et al., 2014; Beškoski et al., 2013). PFRs and PFASs are bioaccumulative and could pose adverse effects on humans and wildlife (Farhat et al., 2014; Araki et al., 2014; Bull et al., 2014). As a result, the European Union banned the manufacture and use of the carcinogenic PFR tris(2-chloroethyl)phosphate (TCEP) (European Parliament Regulation, 2008), which has been replaced progressively by tris(1,3-dichloro-2-propyl) phosphate (TDCIPP) (also classified as carcinogen), and tris(2-chloroisopropyl) phosphate (TCIPP) (considered as possible carcinogen) (European Parliament Regulation, 2008; European Parliament Directive, 2014). Concerning PFASs, perfluorooctane sulfonate (PFOS) (included in the list of the Stockholm Convention) and perfluorooctanoic acid (PFOA) are strongly regulated (Environment Canada, 2010; D. European Parliament, 2008; UNEP, 2010; EPA, US Environmental Protection Agency, 2006; 3M, 2000). These emerging POPs were found ubiquitously in the aquatic environment, being present in drinking water (Ericson et al., 2009; Li et al., 2014), wastewater influent and effluent (Kim et al., 2017; Arvaniti et al., 2012), river water (Lorenzo et al., 2016a; Cristale et al., 2013a), fish (Pignotti et al., 2017; Santín et al., 2016), sediment (Cristale et al., 2013a; Campo et al., 2016) and seawater (Ahrens et al., 2010; Wang et al., 2015). Their continuous release to the environment from point and nonpoint sources such as wastewater treatment plants (WWTP) (major point source) or atmospheric deposition (minor diffuse source) was also documented (Ahrens and Bundschuh, 2014; Cristale et al., 2013b).

Among the different freshwater aquatic ecosystems, wetlands have been recognized at global scale as a driving force for biodiversity conservation and rural socio-economic improvement (Mitsch and Gosselink, 2000). Wetlands are very sensitive areas severely threatened by water pollution, disturbances on the water regime, clogging of marshes, dune system urbanization, industrial pressures and high population. This is evident by estimated wetland losses in the 20th century reported to be between 64 and 71%, and for some regions, notably Asia, even higher (Davidson, 2014). Emerging POP contamination is one of the factors that adversely affect these fragile aquatic ecosystems including their biota. The PFAS loads in wetlands have already been determined in the Mediterranean area (the Ebro Delta (Pignotti et al., 2017) and the Albufera Natural Park (Picó et al., 2012)), but also in a Hong Kong wetland (Loi et al., 2011), in mangrove sediments from India (Corsolini et al., 2012), European eels from the Loire Estuary in France (Couderc et al., 2015) and surface waters of Xixi wetland in China (Xu et al., 2016), establishing the widespread occurrence of these compounds. Organophosphate flame retardants have been less studied, and their presence in aquatic environments has been determined in mangrove sediments from the Pearl River Estuary, China (Hu et al., 2017), and in a restored wetland and lake from Aarhus, Denmark (Matamoros et al., 2012). Furthermore, to our knowledge there are no reports on the co-occurrence of several classes of emerging POPs that could offer a more complete overview of their occurrence and threat to wetland ecosystems.

The purpose of this study was to establish the patterns and concentrations of emerging POPs (PFRs and PFASs) in sediment, fish and water from a typical Mediterranean wetland, the Albufera Natural Park (Valencia, Spain) with an environmental forensics perspective of chemically fingerprinting environmental samples. To this end, this study was focused on the evaluation of the occurrence and environmental fate of 21 PFASs and 9 PFRs in 67 samples (38 water, 19 sediment and 10 fish). Firstly, the identification of contamination sources included the analysis of samples from the two rivers with the largest contribution to the wetland (Turia and Jucar Rivers), and from some major irrigation channels. Samples of influents and effluents from 10 WWTPs, the effluents of which are discharged into the channels in order to allow crop irrigation and maintenance of the ecological flow of the lake were also analyzed and discussed.

2. Materials and methods

2.1. Chemicals and reagents

A total of 21 PFASs, consisting of 14 perfluorocarboxylates (C_4–C_{14}, C_{16} and C_{18}), 1 unsaturated carboxylic acid (C_{10}) and 6 perfluorosulfonates (C_4, C_6–C_{10}), and 9 PFRs, consisting of 5 non-halogen and 4 halogen containing PFRs, have been monitored. Some characteristics of target compounds, including their acronym, CAS number, empirical formula, Log K_{ow} and solubility in water are provided in Supplementary data (**Table S1**). Mass-labelled compounds with ^{2}H, ^{13}C and ^{18}O were used as internal standards (IS). Stock standard and working solutions were prepared in methanol and stored at 4 °C. Methanol was bought from VWR (Radnor, PA, USA) and formic acid from AMRESCO (Solon, OH, USA), both at the highest purity grade. Ultrapure water was obtained from a Milli-Q SP Reagent Water System (Millipore, Bedford, MA, USA).

2.2. Study area and sample collection

The Albufera Natural Park has an area of 21,120 ha and it is located 10 km to the South of Valencia City. It was declared a Natural Park in 1986, and since 1989 is recognized as “Wetland of International Importance” in the Ramsar Convention on Wetlands (B.O.d. Estado, 1990). The park is also part of the Natura 2000 network, it was named Special Protection Area (SPA) in 1990 (D. European Parliament, 2009), and Site of Community Importance (SCI) in 2006 (D. European Parliament, 1992). It consists of a highly eutrophic coastal lagoon surrounded mainly by rice fields that occupy the primitive marshland. The Turia River, to the north, the Jucar River, to the South, and a network of irrigation channels bring fresh water to the Albufera system. The sea connection of the Albufera is controlled by artificial channels called “golas” (Soria, 2006). Water quality is compromised due to the high density of population around the Albufera Natural Park, the use of agrochemicals in the surrounding fields and the WWTP discharges to alleviate the threat to the park from the general water scarcity of the area (Vazquez-Roig et al., 2011; Vazquez-Roig et al., 2010).

The sampling campaign was carried out during the winter 2016–2017. A geospatial analysis was carried out taken into consideration water sources, land use, human pressure and the influence of the wastewater treatment plants and the Turia and Jucar Rivers (limits of the study area) to divide the area in structural functional sectors. Based on that, a random sampling design was applied in a way that most of the influences and potential source to the area are taken into account. Sixty-seven samples were collected from 22 sampling points and included 12 surface waters, 13 WWTP influents and effluents (from 10 WWTPs) and 19 sediment samples. Ten fish samples, comprising 7 specimens of European eel (*Anguilla anguilla*), 2 flathead grey mullets (*Mugil cephalus*) and one common carp (*Cyprinus carpio*), all of them from the Albufera Natural Park, were obtained from the local Fishermen's Association “El Palmar”. European eels are included in the Red List of the International Union for Conservation of Nature (IUCN) and classified as Critically Endangered. At the Albufera Lake, it lives in mud, crevices, and under stones. This is a very long-lived species with a maximum life span of 85 years. Flathead grey mullet is a diurnal feeder, consuming mainly zooplankton, dead plant matter, and detritus. Common carp is often considered a destructive invasive species, being included in the list of the world's 100 worst invasive species created by the IUCN Invasive Species Specialist Group, due to its predilection for the vegetal substrate of the shallow lagoons, as the Albufera Lake, which serves as food for native species. These fish are also an important part of the human diet. Water samples (2 L) from Turia and Jucar Rivers,