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Perfluoroalkyl substances in Mediterranean aquatic environments: Catalonia and Greece

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Summary. Perfluorinated alkyl substances (PFASs) are industrial chemicals that have been widely used for more than 60 years. However, during the last decade, concern about their occurrence in the environment has arisen due to the high resistance of these compounds to degradation, bioaccumulation attached to proteins, and bio-magnification through the food chain. In addition, some PFASs can impair different metabolic functions, thus posing a risk to human health, especially during the early stages of life. Despite recent scientific and regulatory attention, most of the data available thus far on PFASs come from studies of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), although both compounds have largely been replaced by other shorter-but also longer-chain compounds, some of which can be degraded to PFOA and PFOS. PFASs spread in the environment via the aquatic cycle, where they reach drinking water, one of the main routes of human exposure to these contaminants. The Mediterranean region, with its dry summers and periodic floods, is particularly sensitive to water contamination. This article examines current knowledge on the presence of PFASs in the environments of two typical Mediterranean regions, Catalonia and Greece. [Contrib Sci 10:185-192 (2014)]

Introduction

Per- and polyfluorinated substances (PFASs) have been manufactured since the decade of 1950. Due to the strong bonds between carbon and fluorine atoms, these compounds are highly stable. In addition, some of them are both hydrophobic and oleophobic and are therefore used in many industrial

applications, including as stain repellents, textile, paints, waxes, polishes, electronics, adhesives, and in food packaging. For decades, the most commonly produced PFASs were perfluorooctane sulfonate (PFOS) and their salts (Fig. 1), used in components of fire-fighting foam concentrates, and perfluorooctanoic acid (PFOA), used as an emulsifier in industrial applications and in the production of fluoropolymers such as

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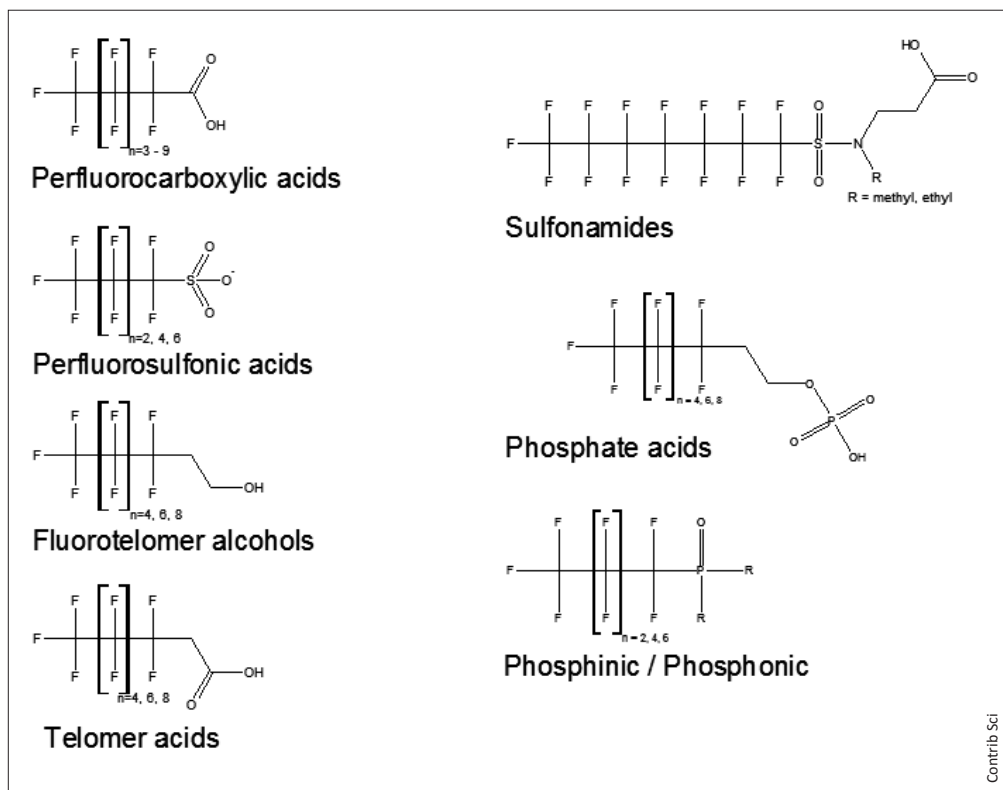


Fig. 1. The structure of the most common PFASs.

polytetrafluoroethylene. PFOS and PFOA, as well as other perfluorocarboxylic acids, are stable degradation products and/or metabolites of neutral PFASs, such as fluorotelomer alcohols, perfluorinated sulfonamides, and perfluorinated sulfonamide ethanols.

Because of their widespread use in different industrial and domestic applications, PFASs enter the environment through direct and indirect sources. Direct sources include point source discharges. Indirect sources involve effluents and, because of their incomplete removal from wastewater, emissions at wastewater treatment plants (WWTPs). In general, the concentration of PFOS and PFOA in WWTP effluents is higher than in the influent probably because both are released from their neutral precursors. An important source of PFASs is sewage sludge produced in WWTPs, in which PFASs are present in concentrations ranging from ng/g to $\mu\text{g/g}$. Sewage sludge is used in land restoration and in agricultural lands, thereby releasing PFASs and other contaminants into the environment and serving as a potential indirect source of PFASs in humans, through the consumption of crops, air-borne transport, surface water, and ground water draining from these sites [3,16,21,38]. Moreover, PFASs in sludge-amended soil can be mobilized by rainfall [11], reaching phreatic waters.

For these reasons and given the strong resistance of PFASs to degradation, these compounds are widespread around the world, in water, soils, and, because of their high affinity to low molecular weight proteins, biota [24]. Bioaccumulation results in biomagnification through the food chain, in particular through the aquatic food chain finally arriving to humans by dust inhalation, dietary sources, and drinking water [12,22]. Moreover, PFASs can be transported by long-range environmental transport, reaching areas as remote as the Arctic [19,27,29,36] and the Antarctic [26,31].

Currently, PFASs are considered as emerging organic contaminants. Although most of them have not been regulated, actions aimed at the reduction or elimination of PFOS and PFOA emissions were recently initiated. In 2006, the US Environmental Protection Agency (EPA) and the eight major PFAS-producing companies launched the "PFOA Stewardship Program" to phase out global emissions by 2015 [34]. In 2010, PFOS became controlled across Europe by inclusion under the Persistent Organic Pollutant (POP) Regulation (EC 850/2004), under the Stockholm Convention for the global regulation of production and use [32]. PFASs will also need authorization within the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation [4]. In

2009, the EPA's Office of Water (OW) established Provisional Health Advisories (PHA) maximum concentration values for PFOA and PFOS in drinking water, which are a major sources of human exposure [6,28]. PHA values are 0.4 µg/l for PFOA and 0.2 µg/l for PFOS [33].

To protect the environment against PFASs contamination, their presence in different environmental compartments and their fates and behaviors must be assessed, especially the new congeners that have replaced PFOS and PFOA. In the following, we provide a summary of the recent data on PFASs in two typical Mediterranean environments: Catalonia and Greece. Special attention is paid to emerging short- and longer-chain PFASs and the temporal trends of this group of contaminants.

Waste water treatment plants: the main sources of PFASs in the aquatic environment

Clarke et al. [3] ranked different groups of organic contaminants commonly found in sewage sludge with respect to their potential agricultural significance. PFASs scored highest among the group of 11 compounds, based on their persistence in soil (>6 months), their potential accumulation in the food chain of humans, their potential bioaccumulation, and their potential soil ecotoxicity [3].

In their 2011 study in Catalonia, Llorca et al. [16] investigated the presence of PFASs in sewage sludge from five WWTPs along the Llobregat river. Compounds with carbon chains of ten carbons and longer were detected at lower concentrations (ng/g levels or below). However, the concentrations of perfluorocarboxylic acids ranged from 0.4 to 30.3 ng/g. PFOA, perfluorononanoic acid (PFNA), perfluorodecanoate (PFDA), and perfluorododecanoate (PFDoA) were detected in all the samples at concentrations >1.0 ng/g. PFOA was present in high concentrations, most likely due to the biodegradation of other long-chain congeners currently in use [8,15]. Concentrations of PFOA ranged from 0.3 to 10.7 ng/g, and those of PFOS from 53 to 121 ng/g.

Gómez-Canela et al. [10] studied the occurrence and fate of five PFASs in sewage sludge from 15 WWTPs in Catalonia. Their results were in agreement with those of Llorca et al. [16], as PFASs were detected in all samples, and the concentrations of total PFASs ranged from 0.28 to 5.20 ng/g dry weight (dw), with a prevalence of PFOS.

Because PFASs cannot be completely eliminated during conventional wastewater treatment works, treated effluents are one of the main inputs into natural waters. Sánchez-Avila

et al. [25] studied the content of PFASs in the effluent of a WWTP located on the Llobregat river, in a highly industrialized and populated area. WWTP effluent values were <0.77 ng/l for perfluorobutanoic acid (PFBS), <0.03 ng/l for perfluorohexanesulfonic acid (PFHxS), 14.1 ng/l for PFOS, 61.9 ng/l for PFOA, and <0.06 ng/l for PFNA (Table 1). The levels of these compounds were higher in the effluent water than in the surface water of the river. The PFASs discharged into the river through WWTP effluents arrive to potable water treatment plants and thus to humans through tap water. WWTP processes also redistribute some of the PFASs from influent water to sludge.

In another study, Llorca et al. [17] analyzed the treated effluents of five WWTPs in Spain, including some plants located in Catalonia. The compound profiles were similar for the different WWTPs in Spain, with PFBA, PFOS, and PFOA being the most frequent compounds and those with the highest concentrations. However, these higher concentrations were detected closer to industrialized areas than to densely populated areas. That study also compared the results obtained in Spain with those from a series of WWTPs in Germany. The compound profiles in the two countries differed. While in Germany the more frequent analytes were those with short carbon chains, in Spain eight-carbon-chain compounds were the most frequently detected (PFOA in 63% and PFOS in 46% of analyzed samples). Unlike in German samples, PFNA and PFDA were also detected (with maximum concentrations of 213 ng/l).

Arvaniti et al. [2] developed an analytical method for the determination of 18 PFASs in the dissolved and particulate phases of wastewater (raw and treated) and in dewatered sewage sludge. The 18 PFASs consisted of ten perfluoroalkyl carboxylate acids (C5-C14), five perfluoroalkylsulfonates (C4-C10), and three perfluoroalkylsulfonamides (PFOSA, N-Me-FOSA, N-EtFOSA). The method was applied to influents, effluents, and sludge from two WWTPs in Greece: Plant A in Athens, receiving 80% domestic wastewater and 20% industrial wastewater, and Plant B in Mytilene, Lesbos Island, which receives only domestic wastewater [1]. Two sampling campaigns were performed, in September 2009 and February 2010, at both plants. In the influent wastewater, PFPeA, PFOA, and PFOS were detected in all samples; PFHpA, PFUdA and PFHxS in seven, seven, and six out of 24 samples, respectively; and PFNA and PFHxA in 5 and 4 samples, respectively. PFDA, PFDoA, PFTrDA, PFTeDA, PFHpS, PFDS, and PFOSA were detected sporadically whereas PFBS, N-MeFOSA, and N-EtFOSA were below the detection limit for all wastewater samples analyzed. In the WWTP of Mytilene, PFTrDA had the

Table 1. Levels of PFASs reported in Mediterranean areas of Greece and Spain in comparison to other countries

No of PFAS	Origin	Matrices	Results	Ref.	
18 Compounds	Catalonia WWTPs from Catalonia, Spain (2010)	Sewage sludge (n=5)	PFBA = <MLOD-22.6 ng/g dw PFPeA = <MLOQ-17.2 ng/g dw PFHxA = <MLOD-4.8 ng/g dw PFHpA = <MLOQ-4.5 ng/g dw PFOA = 7.0-30.3 ng/g dw	PFOS = 53-121.1 ng/g dw PFDS = <MLOD-7.5 ng/g dw FOSA = <MLOD-10.7 ng/g dw PFODA = <MLOD-0.9 ng/g dw PFBS = <MLOD-7.6 ng/g dw	[3]
14 Compounds	Ebro River (Garcia and Mora) Francoll River Cortella River (Spain)	Surface river water	PFHpA = MLOQ – 3.38 ng/L PFHxS = MLOQ – 0.78 ng/L	PFDA = MLOQ – 0.82 ng/L PFOA = MLOQ – 24.9 ng/L PFNA = MLOQ – 0.64 ng/L	[19]
10 Compounds	L'Albufera de Valencia, Spain	Sediment	PFPeA = < MLOD – 0.02 ng/g PFHxA = < MLOQ – 0.10 ng/g PFHpA = < MLOQ – 0.95 ng/g PFOA = 0.03 – 10.9 ng/g	PFOS = 0.10 – 4.80 ng/g PFDA = < MLOD – 1.25 ng/g PFDS = < MLOD – 2.00 ng/g	[28]
Greece					
18 Compounds	2 WWTPs from Greece (2009-2010)	Influents	PFPeA = <1.7-106 ng/L PFHxA = <0.4-3.6 ng/L PFHpA = <0.6-8.6 ng/L PFOA = <0.7-20.7 ng/L PFNA = <0.8-3.4 ng/L	PFHxS = <0.2-20.7 ng/L PFHpS = <0.1-19.6 ng/L PFOS = <1.0-26.3 ng/L PFDS = <0.5-107.4 ng/L PFOSA = <0.1-14.0 ng/L	[27]
Other countries					
6 Compounds	Conasauga River, Altamaha River and streams and ponds of Dalton (Georgia, USA)	Surface river	PFOA = 2.6 – 1280 ng/L PFNA = 0.6 – 456 ng/L	PFUDA = 0.1 – 117 ng/L FOSA = 10.7 – 420 ng/L	[34]
PFOS	Rivers: Tone, Arakawa, Tama (Tokyo, Japan)	Surface river water	PFOS = 0.5 – 58 ng/L		[35]
7 Compounds	Rivers from Northern of China	Surface river water	PFOS = < MLOD – 31 ng/L PFOA = 0.43 – 82 ng/L PFHpA = < MLOD – 35 ng/L	PFDoA = < MLOD – 0.29 ng/L PFHxS = < MLOD – 5.8 ng/L	[36]
19 Compounds	WWTPs from Hong Kong ● Plant (A) and (B): secondary treatment by activated sludge method ● Plant (C): chemically enhanced primary treatment	Sludge	PFBA = 3.1-111.4 ng/g PFPeA = 0.5-10.1 ng/g PFHxA = 0.3-27.8 ng/g PFHpA = 0.4-4 ng/g PFOA = 1.3-15.7 ng/g	PFTeA = 0.2-46 ng/g PFBS = 0.6-6.4 ng/g PFHpS = 106.6 ng/g (one sample) PFOS = 3.1-7304.9 ng/g	[37]
17 Compounds	WWTPs from Zürich, Switzerland (2008)	Digested sewage sludge	∑PFCAs = 16.9-21.6 ng/g dw (PFOA = 5.0-9.1 ng/g dw) (PFOA>PFDoA >PFHxA>PFNA>PFHpA) PFOS = 117-670 ng/g dw	6:2 FTUCA = 2.1-3.4 ng/g dw 8:2 FTUCA = 5.4-14.8 ng/g dw FOSA = 2-5 ng/g dw	[38]

highest mean and maximum concentrations: 75.7 and 453.0 ng/l respectively. The mean concentrations of PFPeA in the influents of the Athens and Mytilene WWTPs were 26.7 and 24.8 ng/l respectively. The mean concentrations of PFOA and PFOS in the influents did not exceed 16.5 and 13.4 ng/l (in Plant A), respectively, with lower levels (<4.2 ng/l) of both compounds in Plant B. The average daily loads of PFASs were as high as 18,960 mg/day for PFPeA in the WWTP of Athens and 1022 mg/day for PFTrDA in the WWTP of Mytilene. Normalization of the daily loads in the WWTP of Mytilene to the number of served inhabitants yielded 0.02 ± 0.06 mg PFHxA and 14.2 ± 34.7 mg PFTrDA per day and per 1000 habitants.

In treated wastewater, PFPeA was the dominating compound and it was found in all samples. The highest mean and maximum concentrations were measured in Plant A, 76.0 and 209.4 ng/l, respectively. Maximum PFOA and PFOS concentrations were 34.0 and 21.0 ng/l (both in Athens) respectively. The levels of all other PFASs were <62.4 ng/l (PFTeDA, in the Athens WWTP). The concentrations of PFPeA detected in the Greek WWTPs were higher than those in Spain (Table 1). An analysis of the distribution of PFASs between particulate and dissolved phases showed that eight out of 15 detected PFASs were mainly in the dissolved phases of the influent and effluent wastewater [1] whereas PFDoA, PFTeDA, PFHpS, PFDS, and PFOSA were detected only in the particulate phase and PFPeA and PFTrDA mainly in the particulate phase. As in previous studies, mean negative removal efficiencies were calculated for PFPeA and PFOA, while no clear trends were determined for PFOS, PFHxA, PFHpA, and PFUdA [1].

The PFASs concentrations in the sludge from the Greek WWTPs are reported in Table 1. In dewatered sludge samples, PFOS was the dominant analyte from both WWTPs. The highest mean and maximum concentrations were 6.7 ng/g dry weight (PFOS in Athens) and 45.2 ng/g dry weight (PFPeA in Athens), respectively. PFOA concentrations in sewage sludge did not exceed 19.4 ng/g dw (Athens WWTP). Generally, PFASs concentrations in the dewatered sludge were slightly higher in Plant A than in Plant B [1]. Table 1 summarizes different works reporting concentrations in sewage sludge and environmental matrices from Catalonia and Greece, in comparison to other countries.

Occurrence of PFASs in surface water

The first work to report concentrations of PFASs in Catalan rivers (the Ebro River at Garcia and Mora, and the Francolí and Cortiella rivers) was carried out in 2008 by Ericson et al.

[6]. PFHpA, PFHxS, PFOA, PFNA, PFOS, PFOSA, and PFDA were the predominant compounds detected in an area near Tarragona. At these locations, the concentrations were 0.19–25 ng/l (including PFOA and PFOS). In 2010, Sánchez-Ávila et al. [25] reported the presence of five PFASs (PFBS, PFHxS, PFOS, PFOA, PFNA) in different Catalan rivers (Muga, Fluvià, Ter, Besòs, Llobregat, and Ebro). In that study, the concentrations discharged into the rivers by WWTPs and the spatial distributions of these compounds were also assessed. The concentrations of selected PFASs in the river water at the sampling sites were in the range of 2.24–21.9 ng/l, with rivers identified as the major route of transport of these compounds into the sea. In agreement with previous work, PFOS and PFOA were the predominant compounds, with maximum concentrations of ~9 ng/l in the Llobregat and Ter rivers in areas with high industrial and urban pressures. The concentrations reported in that study were comparable to those measured in the waters of other rivers in other industrialized areas in Europe. Nevertheless, the compound profiles were quite different from those of other European countries such as Germany, where in surface water PFOA is generally found at higher concentrations than PFOS [28].

However, the study of Sánchez-Avila et al. [25] examined only a limited number of compounds. Picó et al. [23] reported the spatial distributions of PFASs in water and sediments from the L'Albufera Natural Park (Valencia, Spain), which has a characteristic Mediterranean climate. The most frequent compounds were PFOS and PFOA, with concentrations of 0.94–58.1 ng/l and 0.99–120 ng/l, respectively. However, in sediments, the concentrations of PFOS were higher than those of PFOA, which could be attributed to differences in their physicochemical properties.

The presence of these compounds showed an important spatial distribution and they were widespread along all sampling sites, in agreement with data reported for other European rivers. However, Mediterranean rivers are strongly affected by climate episodes, such as first-flush, which can re-suspend contaminants contained in the sediments. As expected, higher concentrations were found near the mouths of the rivers accessed by heavily populated and industrialized areas. PFHpA had the highest concentration, 30 ng/l. Recent concentration patterns have shown that, in general, the more frequent compounds, and those at higher concentrations, are short-chain PFASs. This is consistent with the replacement of the more persistent long-chain PFASs by new, short-chain ones. In a recent study, Llorca et al. [17] compared the presence of 21 PFASs in water along the entire water cycle, both in Spain and in Germany. An analysis of the 24 surface

water samples from different Spanish rivers showed that PFBA (70% of the samples), PFOA (63%), and PFOS (46%) were the most frequent compounds, followed by PFPeA, PFHxA, and PFHpA. Just one of the 24 Spanish surface waters samples was free of all the studied compounds. Another sample had an extremely high concentration of PFOS (2709 ng/l). However, this concentration level is still 10 times lower than the proposed maximum allowable concentration for PFOS and its derivative salts in inland surfaces (32,000 ng/l), established in 2012 by the European Commission [37].

Note that shorter-carbon-chain compounds, including PFBA, PFHxA, and PFHpA, were found in all samples from both countries, based on the replacement of PFOS and PFOA. However, PFOS and PFOA were still found in surface waters from Germany and Spain, the consequence of their long-term stability and poor degradability. Nonetheless, short-chain PFASs were the prevalent compounds in German samples whereas PFOS and PFOA were the most frequent analytes found in Spain. PFOS was detected in 46% and PFOA in 63% of the surface waters samples from Spain. These results are in agreement with studies showing that shorter-chain PFASs are predominant in urban and industrial areas, and longer chain PFASs in the fine-grained sediments from major depositional basins [20]. The progressive increase in contamination by short-chain PFASs has also become apparent.

In a recent study, Flores et al. [7] evaluated the occurrence of PFOS and PFOA in river waters from Catalonia and the removal of both contaminants by advanced water treatments in drinking water production. Despite focusing only on these two compounds, their results confirmed the presence of the more persistent PFASs. Although the use and production of these two compounds has almost ceased completely, due to their high resistance to degradation and as end products of other PFASs still in use, PFOS and PFOA continue to be detected at high concentrations in surface waters and sediments. Consistent with their physicochemical characteristics, PFOA is mainly found in water, and PFOS in sediments.

Sediments. Very few studies have assessed the content of PFAS in the sediments of Catalan rivers. In the study of Picó et al. [23], the presence of PFASs was investigated at different sites in L'Albufera de Valencia. Concentrations ranged from the mass limit of detection (MLOD) to 10.9 ng/g. Again, the prevalent compounds were PFOA and PFOS. In that study, the distribution of PFASs between water and sediments was demonstrated. In the Cantabrian Sea samples analyzed by

Gómez et al. [9], the concentrations in sediment river samples were below the MLOD in most cases.

River and coastal biota. Data on the occurrence of PFASs in biota from Catalan rivers are lacking. However, within the project Consolider-SCARCE, the concentrations of these compounds in fish from different Spanish rivers, including the Ebro River, were determined. The more recalcitrant compounds (PFOS and PFOA) were detected at higher median concentrations, 22.6 and 23.6 ng/kg wet weight (ww) for PFOA and PFOS, respectively. PFOS was present in almost all the samples (89%). In some extreme cases, PFOS was present in concentrations as high as 530 ng/g ww in fish species at the top of the aquatic trophic chain, such as wels catfish (*Silurus glanis*). These results indicate biomagnification through the aquatic food chain. Moreover, despite legislation limiting their use and production in the EU, eight-carbon-chain compounds are still prevalent in the environment. The results were in agreement with those of Domingo et al. [5], who measured the concentrations of 13 PFASs in fish and shellfish collected at Catalan coastal areas near the Ebro Delta. The highest mean concentration (2.70 ng/g ww) was that of PFOS, which was detected in all species except mussels. High concentrations of PFOA (mean, 0.074 ng/g ww) were detected in prawn and hake (0.098 and 0.091 ng/g ww, respectively).

The above-described method of Thomaidis et al. (unpublished results) for the determination of 18 PFASs (ten carboxylic acid, five sulfonates, and three sulfonamides, as already described) was applied to determine the levels of these compounds in sea bass and sea bream samples from aquaculture facilities from various sites in the Greek marine environment. PFHpA, PFOA, PFUnA, PFTTrDA, PFOS, N-EtFOSA were the most frequently detected compounds, although their levels never exceeded 2 ng/g wet weight (PFOA and N-EtFOSA).

Conclusions

This review highlights the widespread occurrence of PFASs in the Mediterranean aquatic environment. The effluents of WWTPs are the main diffuse sources of PFASs in the aquatic environment of Greece and Catalonia. Short-chain PFASs have a wider distribution and are present at generally higher levels, consistent with the gradual replacement of long-chain PFASs by (mainly) PFPeA. Studies on the occurrence of PFASs in sediments and biota, as well as in drinking water and foodstuff, are scarce but urgently needed. ■

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Competing interests. None declared.

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