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PERFLUOROALKYL ACIDS IN THE SURFACE WATERS OF THE WESTERN MEDITERRANEAN SEA

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Introduction

Perfluoroalkyl acids (PFAAs), namely perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFSAs), have been recognized as ubiquitous environmental contaminants[1]. PFAAs have been emitted to the environment from direct sources (i.e., emissions from manufacture, product use and disposal) but they can also be formed in the environment as degradation products of some per- and polyfluorinated precursors (e.g., fluorotelomer alcohols, polyfluoroalkyl phosphates, polyfluorinated amides/sulfonamides)[2–4]. Known sources of PFAAs to the aquatic environments include effluents from industrial and residential waste water, landfill effluents, contaminated wet atmospheric depositions, and runoff from contaminated soil. Due to the carboxylic/sulfonic acid groups, PFCAs and PFSAs are less volatile and more soluble in water than legacy persistent organic pollutants. As a result, marine waters are their main environmental reservoirs. Transport to the deep waters and burial into sediments were identified as final sinks of the environmental burden of persistent PFAAs[5,6].

Owing to their elevated persistence, many PFAAs were detected also in pristine areas including open oceans[7]. Two main transport pathways were proposed to account for the presence of PFAAs in remote areas: i) long-range atmospheric transport of volatile neutral precursors degraded in remote regions; and ii) direct transport of PFAAs by oceanic currents or by means of sea spray. While the atmospheric inputs are the main drivers of contaminations by PFAAs in inland environments[8], the ocean transport was found to be the dominant pathway in marine environments even in remote areas[9].

The aims of the present study were to: i) assess for the first time PFAA water contamination in open Mediterranean surface water; and ii) to assess spatial and seasonal variability of PFAA levels.

Materials and methods

Samples were collected along two cruises of R/V Urania in the western Mediterranean in spring (24 March–9 April) and autumn (4 November–1 December) 2014. In order to obtain spatially integrated data, several (7–14) surface water grab samples were collected in selected sampling areas (along routes 50–120 km long), pooled to a total volume of 5 L prior to extraction and processed together. A total of 6 aggregated samples were collected during the spring cruise and 9 aggregated samples during the autumn cruise. Water samples were collected into pre-cleaned amber glass bottles using the ship water inlet positioned at 4 m below sea surface.

Immediately after merging the samples from different spot locations, solid phase extraction (SPE) was performed on board. SPE procedure was based on the protocol published in Benskin et al., 2012[10] with some modifications. pH was adjusted to 4 and samples were spiked with ^{13}C-labelled recovery standards prior to extraction. SPE of each individual aggregated sample was conducted through 5 Oasis WAX 150mg cartridges in parallel (i.e., approximately 1 L of sample was passed through individual cartridge) using silicone tubes connecting the sample bottle to the cartridges. Following loading the sample on SPE cartridges, the columns were dried for 15 minutes under vacuum and under controlled atmosphere, packed and stored at –20 °C until the end of the cruise. Samples were then shipped to the laboratory and kept at –20 °C prior to further processing. The wash and elution steps were performed according to Benskin et al., 2012[10]. The eluents were combined and reduced to near dryness using nitrogen. Samples were reconstituted in 0.5 mL of MeOH and completed to the final volume of 1 mL by the addition of HPLC grade water. 200 µL aliquots were then transferred to a microvial insert and analyzed using HPLC-MS/MS. Teflon bottles, Teflon-lined caps, and any suspect fluoropolymer materials were avoided throughout the sample preparation and analysis.

The instrumental analysis was performed according to Sharma et al.,2016[11]. Briefly, samples were analyzed using HPLC-MS/MS (Agilent 1290 HPLC coupled to AB Sciex QTRAP 5500 mass spectrometer). The systems were interfaced with an electrospray ion source operated in negative ionization mode.

Results and discussion

PFAAs in the Western Mediterranean Sea

13 out of the 15 PFAAs screened in this study (C_5–C_{14} PFCAs, C_4, C_6–C_8 and C_{10} PFSAs) were detected at least once in the surface water of the Western Mediterranean (Fig. 1). To the authors' knowledge, this is the first report of open sea water concentrations of PFAAs in the Mediterranean Sea.

[Figure 1]

Figure 1 Map of sampling sites in the Western Mediterranean and individual PFAA concentrations (pg/L) for R/V Urania cruises in spring and autumn 2014. Concentrations were corrected for recoveries on the basis of two labelled recovery standards ($^{13}C_8$-PFOA and $^{13}C_8$-PFOS).

The detection frequencies of PFHxA, PFHxS and PFOS were 100%. PFHpA and PFOA were detected in 93% and 87% of samples, respectively. These compounds were the most abundant among the measured PFAAs and ranged 60–219 pg/L, 11–49 pg/L, 33–75 pg/L, <4.3–167 pg/L and <9.5–118 pg/L, respectively. PFDA was detected in 80% of all samples at concentrations <0.7–26 pg/L. In the spring cruise, PFNA was detected in 100% of the samples at concentrations 24–49 pg/L. PFNA could not be quantified in the autumn cruise due to higher values in blanks as a result of a laboratory contamination.

PFAA spatial and seasonal distribution

The sum of PFAA concentrations (ΣPFAA) varied between 282–671 pg/L. ΣPFAA was found maximum along the northern coast of Sicily in both cruises (671 pg/L in spring and 530 pg/L in autumn). ΣPFAA levels did not vary much across other areas with a uniform distribution throughout the western basin. Limited variability in ΣPFAA between the samples collected in coastal areas and those collected in more open sea areas suggests that besides diffuse coastal sources, inflow from the Atlantic and generally homogeneous pattern of PFAA atmospheric deposition control the PFAA distribution pattern. This is corroborated by the fact that no significant correlation of seawater salinity and seawater temperature with ΣPFAA was found. Sampling locations, however, did not include areas in proximity or within major river estuaries. The signals from riverine inputs are not, therefore, directly observable in the present dataset and the assessment of their influence requires, therefore, an indirect analysis.

ΣPFAA levels were similar between the spring and autumn cruises. Generally higher levels (factor of 2) were found in autumn for two compounds routinely detected in both cruises: PFHxA and PFOS while PFPA concentrations tended to be lower in autumn. The general surface water circulation pattern and more intense atmospheric depositions and riverine inflow could have resulted in higher concentrations of PFAAs during colder and wetter periods. Considering the small observed differences and the uncertainties behind the analytical method, these conditions appear not to determine sensible changes in the marine water contamination levels.

PFAA sources in the Western Mediterranean Sea

The contribution of atmospheric deposition, riverine and coastal inputs and the advective inflow from the Atlantic to the PFAA loading into Western Mediterranean basin can be estimated using the data on PFAA occurrence and measured water/rain fluxes (Table 1).

Table 1 Estimation of PFAA annual inputs to the Western Mediterranean Sea (in t/year).

[Table 1]

Data on PFAA deposition levels in Europe are very scarce. One study from Northern Germany identified PFOA and PFBA as the main PFAA contaminants in rainwater[12]. PFAA pattern observed in the aforementioned study was different from the relative profile observed in water in the present study which points out to low influence of atmospheric inputs, as can be seen from the estimation provided in Table 1.

In terms of riverine inputs, the largest effluent to the Western Mediterranean is the Rhône river in France. This river drains some of the most populated and industrialized areas of Europe and represents major sources of PFAAs to marine waters[14–16]. Available data of PFAA discharge from the Ebro river (Spain)[17] were also taken into consideration. These were more than one order of magnitude lower compared to the Rhône (Table 1). Other rivers flowing into the Western Mediterranean basin are the Tiber, Jucar, Cheliff, Moulouya, Mejerdah and Tafna. Although PFAA concentrations in those rivers are not available, it is likely that their overall contribution will be less significant compared to the inputs from the Rhône and Ebro. The Western Mediterranean surface waters are not likely to be affected by riverine inputs to the eastern basin because those are conveyed to sub-surficial water masses in the deep water formations areas and enter the western basin through the Levantine Intermediate Water, a current streaming between 100 and 600 m depth through the Sicily Channel and leaving the western basin from the deeper part of the Strait of Gibraltar.

PFAA inputs delivered to the Mediterranean from the Atlantic inflow were calculated using PFAA data from the recent literature on Atlantic water concentrations in proximity of the Gibraltar multiplied by the annual water inflow from the Atlantic to the western Mediterranean basin[13,18,19]. Overall, direct releases from rivers and coastal sources, as well as the advective inflow from the Atlantic, are likely the controlling factors over the occurrence and distribution of PFAAs in the Western Mediterranean. Nevertheless, more data on PFAA levels in the atmospheric deposition are needed to conclusively determine the dominant PFAA sources to the area.

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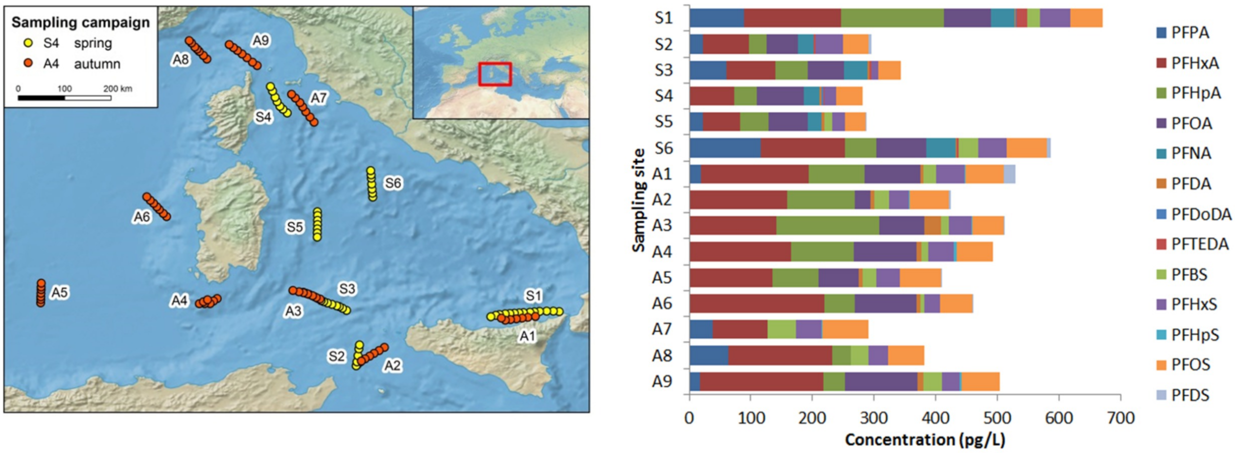

Figure 1

Table 1

Source	PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFDoDA	PFTEDA	PFBS	PFHxS	PFHpS	PFOS	PFDS	Refs.
Atm. deposition	n.a.	0.17	0.14	0.82	0.29	0.32	0.13	1.76	0.17	0.09	0.06	0.48	n.a.	12,13
Rhône river	n.a.	0.69-4.04	n.a.	3.93-5.49	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.74	n.a.	14–16
Ebro river	0.02	0.03	0.04	0.14	0.01	0.01	n.a.	0.01	n.a.	0.01	n.a.	0.04	n.a.	17
Atlantic inflow	0.62	0.82-1.40	0.15-1.03	1.68-2.40	0.80	0.51-0.72	n.a.	n.a.	0.33-0.39	0.31-0.37	0.47	1.26-1.54	n.a.	13,18,19