

Presence of Perfluoroalkyl Substances (PFASs) in Spanish Surface Waters

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1 Introduction

Rivers can receive the input of treated or untreated effluents from wastewater treatment plants, urban and industrial discharges and agricultural run-off, becoming an important pathway for the transport and mobilization of pollutants to the oceanic waters. Because of the high water solubilities of perfluoroalkyl substances (PFASs), surface water is a significant medium for their long-range transport and widespread global distribution^{1,2}. PFASs are emerging organic contaminants which present persistence, toxicity, potential for bioaccumulation and remarkable ubiquity in the environment. In fact, perfluorooctane sulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) have been included to Annex B (May 2009) and Annex A (May 2019), respectively, as persistent organic pollutants in the Stockholm Convention, and perfluorohexane sulfonic acid (PFHxS) is presently proposed for listing. PFOS is also listed as substance of priority concern in the European Water Framework Directive³ due to its persistence, toxicity and widespread use and detection in rivers, lakes, transitional and coastal waters.

Under the leadership of the Spanish Ministry for the Ecological Transition and Demographic Challenge, a Spanish monitoring program framed in the Stockholm Convention National Implementation Plan has been developed to evaluate the current status and temporal trends of PFOS in river water⁴. Thus, a study area of high representativeness was selected and evaluated to reflect the ecological status of one of the main European watersheds: the Tagus River watershed in its Spanish section. The monitoring of the presence of emerging pollutants is mandatory to preserve the ecological quality of its different ecosystems. Since PFAS concentrations can also vary spatially in water bodies⁵ several sampling locations were targeted in the present survey along a 300-km tract of the river.

2 Materials and Methods

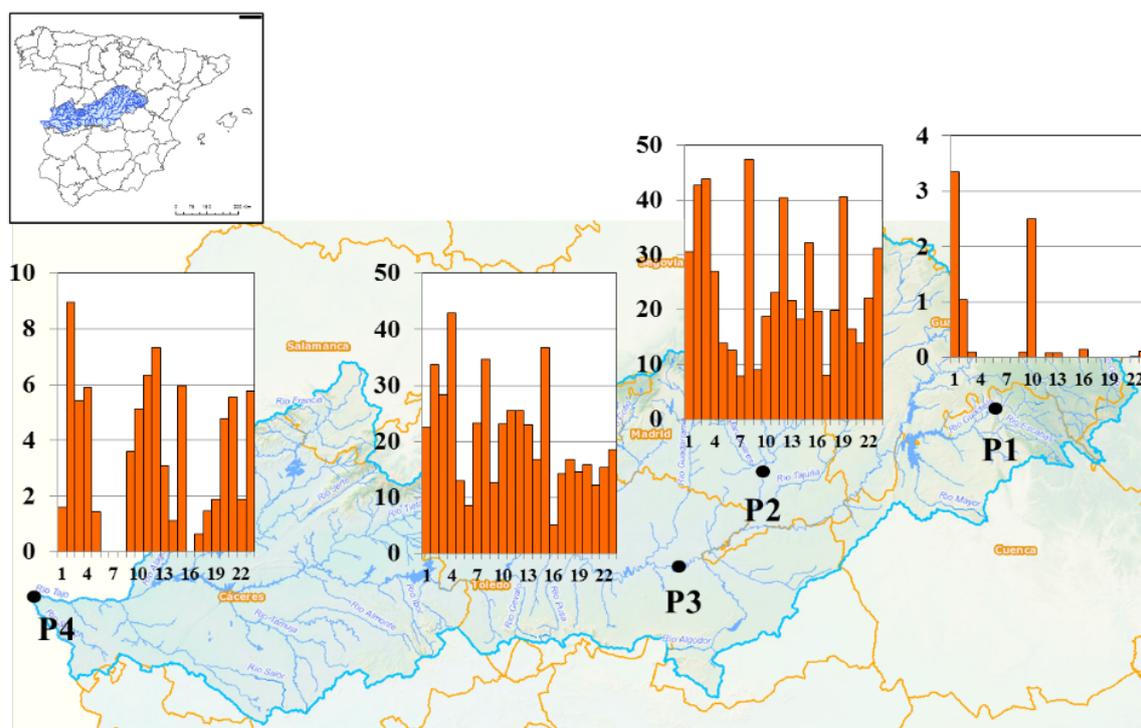
A total of 92 river water samples were collected in 23 different monitoring campaigns performed during five years (from February 2013 to August 2018) to determine the presence of 20 PFASs consisting of 4 perfluoroalkyl sulfonic acids (PFSAs; C4, C6, C8, C10), 13 perfluoroalkyl carboxylates (PFCAs; C4-C14, C16, C18) and 3 perfluoroalkyl sulfonamides (PFOSAs; C8). Four sampling points were selected to represent different typologies of the Tagus River watershed in its Spanish section: P1 is located in a remote area near the source, P2 and P3 are located in urban and industrial areas (P2: metropolitan area of Madrid and P3: metropolitan area of Toledo) and P4 is located in a background reservoir next to the Portuguese border (Figure 1).

Water samples (2 L) spiked with MPFAC-MXA solution, N-d3-MeFOSA and N-d5-EtFOSA (Wellington Laboratories Inc., Guelph, Canada) were extracted with Oasis WAX (500 mg, 6 mL; Waters, Milford, MA, USA) and purified with EnviCarb (500 mg, 6 mL; Sigma-Aldrich, St. Louis, MO, USA) cartridges. The final extracts were spiked with 13C9-PFNA solution (Wellington Laboratories Inc., Guelph, Canada) and analyzed on a high performance liquid chromatography system (Varian HPLC 212) connected to a triple quadrupole mass spectrometer (Varian 320 MS-TQ).

The identification and quantification were carried out using isotopic dilution method if proper standards were available. Mean recoveries of isotopically labeled surrogate standards ranged between 64% and 88%. Limits of quantification (LOQs), defined as the concentration giving a signal to noise ratio greater than 10 were in the range of 0.01-0.10 ng/L. Blanks were conducted with each sampling site at each sampling campaign and extracted under the same conditions than samples. Blank correction was applied where blank levels were above LOQ. In addition, instrumental blanks (methanol) were run before each sample injection to check the possibility of cross-contamination from HPLC-MS/MS system.

3 Results

PFASs were detected in 76 out of 92 water samples. The mean PFAS levels found in the Tagus River basin were 1.7 ± 1.2 ng/L (mean \pm SD) for PFBS (perfluorobutane sulfonic acid), 4.4 ± 2.9 ng/L for PFHxS, 5.9 ± 5.8 ng/L for PFOS, 1.8 ± 1.2 ng/L for PFPeA (perfluoropentanoic acid), 2.0 ± 2.5 ng/L for PFHxA (perfluorohexanoic acid), 1.3 ± 0.7 ng/L for PFHpA (perfluoroheptanoic acid), 3.6 ± 2.6 ng/L for PFOA, 0.7 ± 0.5 ng/L for PFNA (perfluorononanoic acid), 0.8 ± 0.6 ng/L for PFDA (perfluorodecanoic acid) and 15 ± 13 ng/L for Σ PFASs. In general, positive correlations ($r > 0.408$, $p < 0.05$, Spearman Test), were found among the PFASs studied in water samples, suggesting that they may be from similar sources. PFOS was strongly correlated with PFOA ($r = 0.911$, $p < 0.01$) and significantly with the rest of PFCAs (C4-C10; $r > 0.679$, $p < 0.01$) and PFSAs, (C4 and C6; $r > 0.578$, $p < 0.01$). Similarly, PFOA correlated significantly with the rest of PFCAs (C4-C10; $r > 0.734$, $p < 0.01$) and PFSAs (C4 and C6; $r > 0.636$, $p < 0.01$).



Sampling campaigns					
1=Winter 2012-2013	5=Winter 2013-2014	9=Winter 2014-2015	13=Winter 2015-2016	17=Winter 2016-2017	21=Winter 2017-2018
2=Spring 2013	6=Spring 2014	10=Spring 2015	14=Spring 2016	18=Spring 2017	22=Spring 2018
3=Summer 2013	7=Summer 2014	11=Summer 2015	15=Summer 2016	19=Summer 2017	23=Summer 2018
4=Autumn 2013	8=Autumn 2014	12=Autumn 2015	16=Autumn 2016	20=Autumn 2017	

Figure 1: Geographical distribution of the sampling points along Tagus River watershed and related Σ PFAS concentrations (ng/L) in the different sampling campaigns.

Important differences between sampling points were found. Figure 1 shows that quantification frequency was low at P1 (43%), increased at P4 (83%) and reached maximum values for P2 and P3 (100%). Samples obtained from P2, P3 and P4 sites showed a similar profile composition with a higher contribution of PFOS ($31 \pm 1\%$, mean \pm SD) followed by PFOA ($22 \pm 4\%$), PFHxS ($19 \pm 5\%$), PFHxA ($16 \pm 4\%$), PFPeA ($11 \pm 2\%$), PFBS ($11 \pm 1\%$), PFHpA ($9 \pm 4\%$). This PFAS composition profile clearly differs from that obtained at P1 (PFOS: $30 \pm 4\%$, PFHxA: 46 ± 12 and PFPeA: 24%), mainly due to the low PFAS frequency of detection in this site. Σ PFAS concentrations detected at sampling points located in urban and industrial areas were statistically higher (P2: 24 ± 12 ng/L, mean \pm SD; P3: 21 ± 9.5 ng/L; $p < 0.01$, Kruskal-Wallis Test) than those at background or remote areas (P1: 0.7 ± 1.2 ng/L; P4: 4.1 ± 2.4 ng/L). The levels of the individual compounds detected in P2 and P3 were also statistically higher ($p < 0.01$, Kruskal-Wallis Test) than those in P4, pointing out the cities of Madrid and Toledo as potentially important pollution sources.

As can be seen in Table 1, the levels of PFASs obtained during the winter campaigns (9 ng/L, median for Σ PFASs) seemed to offer lower values compared to spring (14 ng/L), summer (19 ng/L) and autumn (17 ng/L), but this result lacked statistical significance ($p > 0.05$, Kruskal-Wallis Test). Regarding temporal trends, a statistically significant ($r > -0.829$, $p < 0.05$) decrease of some PFASs (PFHxS, PFOS, PFOA, PFDA and PFUDa) was observed from 2013 to 2018.

The annual average environmental quality standards (AA-EQS) for PFOS established in the Directive, 2013/39/EU is 0.65 ng/L for inland surface waters. The annual average PFOS concentrations (9.2, 11, 4.5, 4.8, 3.1 and 2.9 ng/L for 2013, 2014, 2015, 2016, 2017 and 2018, respectively) were above this AA-EQS but below the maximum allowable concentration (MAC-EQS; $36 \mu\text{g/L}$)³. The sampling points where annual average PFOS concentrations more often complied with the AA-EQS were P1 and P4, while in P2 and P3 levels surpassed it more frequently, reaching values up to 20 times over. Additionally, AA-EQS for inland surface waters have been fixed in Italy for other PFASs: PFBA ($7 \mu\text{g/L}$), PFBS and PFPeA ($3 \mu\text{g/L}$), PFHxA ($1 \mu\text{g/L}$) and PFOA ($0.1 \mu\text{g/L}$)⁷. In our study the annual average concentrations for these PFASs (PFBS: 1.0-3.9 ng/L; PFBA: 2.0-4.0 ng/L; PFPeA: 1.0-2.6 ng/L; PFHxA: 1.4-2.7 ng/L; PFOA: 2.2-6.5 ng/L) were below the Italian AA-EQS established.

Table 1: Descriptive statistics (mean \pm SD; (median); min-max) of PFAS water concentration (ng/L) in Tagus River in the different seasons

	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	Σ PFASs
Winter	1.4 \pm 0.5 (1.5) 0.5 - 2.0	3.2 \pm 1.9 (2.8) 0.4 - 5.8	4.4 \pm 4.7 (3.4) 0.6 - 20		1.6 \pm 0.7 (1.7) 0.8 - 3.0	1.5 \pm 1.4 (1.1) 0.07 - 3.4	1.1 \pm 0.3 (1.1) 0.7 - 1.5	2.9 \pm 1.9 (2.4) 0.4 - 8.2	0.5 \pm 0.2 (0.5) 0.3 - 0.7	0.7 \pm 0.4 (0.6) 0.3 - 1.3		10.2 \pm 8.8 (9) 0.07 - 31
Spring	1.5 \pm 1.6 (1.0) 0.3 - 5.2	4.4 \pm 3.1 (3.6) 0.4 - 9.4	5.9 \pm 4.8 (4.6) 0.6 - 18	3.3 \pm 1.8 (2.7) 1.8 - 5.3	1.6 \pm 1.1 (1.4) 0.3 - 3.1	1.3 \pm 1.6 (0.7) 0.02 - 6.2	1.2 \pm 0.8 (1.0) 0.3 - 2.7	2.9 \pm 2.3 (2.3) 0.3 - 8.9	0.5 \pm 0.3 (0.5) 0.3 - 1.1	0.9 \pm 0.6 (0.8) 0.4 - 2.2	0.5 \pm 0.4 (0.3) 0.2 - 1	13.5 \pm 11.6 (14) 0.02 - 43
Summer	2.2 \pm 1.5 (2.1) 0.3 - 5.3	4.7 \pm 3.4 (4.5) 0.8 - 12	5.4 \pm 4 (6.4) 0.6 - 16	3.1 \pm 1.3 (3.1) 2.2 - 4	2.1 \pm 1.4 (2.0) 0.3 - 4.7	3.2 \pm 3.7 (1.5) 0.09 - 13	1.6 \pm 0.7 (1.5) 0.6 - 2.9	4.3 \pm 2.8 (4.5) 0.9 - 9.5	0.9 \pm 0.6 (0.7) 0.4 - 2.1	0.8 \pm 0.8 (0.5) 0.2 - 2.6		18.5 \pm 14.4 (19) 0.09 - 44
Autumn	1.6 \pm 0.8 (1.3) 0.6 - 3	5.4 \pm 2.9 (5.3) 0.6 - 11	8.8 \pm 9.2 (5.1) 0.9 - 34		1.9 \pm 1.3 (2.1) 0.3 - 5	1.9 \pm 1.8 (1.3) 0.07 - 6	1.1 \pm 0.6 (1.0) 0.5 - 2	4.3 \pm 3.1 (3.9) 1.2 - 11	0.8 \pm 0.6 (0.5) 0.2 - 1.7	0.7 \pm 0.6 (0.5) 0.05 - 2.1		19.6 \pm 16.1 (17) 0.07 - 47

The mean mass flow rate of PFASs were calculated in the Tagus River basin: 1.4 \pm 1.3 kg/y for PFBS, 3.6 \pm 4.2 kg/y for PFHxS, 5.9 \pm 8 kg/y for PFOS, 1.3 \pm 1.4 kg/y for PFPeA, 2.4 \pm 4.5 kg/y for PFHxA, 1.4 \pm 1.6 kg/y for PFHpA, 3.6 \pm 4 kg/y for PFOA, 0.5 \pm 0.5 kg/y for PFNA and PFDA and 14 \pm 16 kg/y for Σ PFASs, being PFOS, PFHxS and PFOA the compounds with higher contribution. The estimated mass flow rates of Σ PFASs were 0.1 \pm 0.1 kg/y at P1, 7.0 \pm 5.8 kg/y at P2, 21 \pm 13 kg/y at P3 and 21 \pm 23 kg/y at P4. As expected, mass flow rates for Σ PFASs at P1 were significantly lower ($p < 0.01$, KruskalWallis Test) than those at the rest of locations. In the case of the urban and industrial areas, P3 showed significantly higher ($p < 0.01$, Kruskal-Wallis Test) values than P2. The mass flow rates of Σ PFASs at P4 (located in a background reservoir next to the Portuguese border) did not show statistically significant differences ($p > 0.05$, Kruskal-Wallis Test) with urban/industrial areas, being the values at P4 comparable to those obtained at P3. Although Σ PFAS concentrations at P4 were significantly lower ($p < 0.01$, Kruskal-Wallis Test) than concentrations at P2 and P3, the flow rates at this point were higher, suggesting a possible dilution effect in the concentrations at P4 and pointing out a possible constant PFAS emission through the basin.

4 Discussion

In general, contamination levels in Tagus river basin were in agreement with others reported for European rivers^{1,8,9,10}. Besides, PFOS was also found the predominant compound in river waters from France⁹, Spain¹¹ or Germany¹². Differences between sampling points were detected, pointing out urban and industrial areas as potentially important pollution sources compared to background or remote areas. These findings were in accordance with a previous study conducted in surface waters in France, in which the most polluted sites were found near urban areas or industrial sites⁶.

Regarding temporal trends, a decrease of some long chain PFASs (PFHxS, PFOS, PFOA, PFDA and PFUdA) was observed. Some studies displayed temporal trends in which shorter chain PFASs tended to increase in river water^{8,10,12}, nevertheless the predominance of PFOS and PFOA has been also reported^{8,9,12}.

The annual average environmental quality standards (AA-EQS) for PFOS established in the Directive, 2013/39/EU is 0.65 ng/L for inland surface waters³. This value was surpassed more frequently in the sampling points related to urban and industrial areas. Surface water concentrations higher than the AA-EQS for PFOS have been also detected in other European rivers^{1,5,8,10}. The EQS should not be exceeded in order to protect human health and the environment. Compared to PFAS mass flows from other rivers, the mass flows from Tagus River were in accordance with values recently found in other European rivers such as Baltic Proper Basin or Kattegat Basin in Sweden¹ and Weser River in Germany⁸. Higher values have also been observed in France⁹, Spain¹¹, Sweden¹ or Germany⁸.

5 Conclusions

The presence of PFASs in surface water has been periodically evaluated through the course of a major European watershed (Tagus River basin in its Spanish section), being PFOS the predominant compound with the highest measured levels. The results point out the necessity for improving the water quality to protect aquatic ecosystems and contribute to the progressive reduction of emissions of hazardous substances to water. The monitoring of PFASs in surface water is mandatory to preserve the ecological quality of the ecosystem. Besides, the reported concentrations are of interest since these surface waters may be treated by water treatment plants to generate tap water, where the presence of PFASs could have human health implications.

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7 References

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