ARE LEGACY PFAAS BEING REPLACED IN SPAIN?: OCURRENCE OF GENX AND ADONA IN SPANISH SURFACE WATER.

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Introduction

Perfluoroalkyl acid substances (PFAAs) are synthetic chemicals used in a huge variety of consumer and industrial applications such firefighting foams, surface treatment of textile and food, due to their stain, water, oil and grease repellency[1]. Among them, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) were also classified as persistent organic pollutants[2,3] and several efforts to curb the production and commerce of long-chain perfluoroalkyl acids [F-(CF_2)n-CO_2H, n⩾7] and perfluoroalkane sulfonic acids [F-(CF_2)n-SO_3H, n⩾6] have been conducted in the last decade worldwide. Those restrictions leaded to the production of alternative fluorinated compounds such as hexafluoropropylene oxide (HFPO-DA, GenX; Figure 1) and 2,2,3-trifluoro-3-[1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propoxy]propanoic acid (ADONA)[4] an emulsifier in the manufacture of fluoropolymers, initiating an industrial transition to replace long-chained PFAAs. However, it is still unclear if these replacing compounds are safer than the previous ones. GenX presents higher water solubility than PFOA, therefore, difficult to remove by waste water treatment plants (WWTPs)[5]. Moreover, some studies evidence that GenX has a similar toxicity than PFOA at testes[6] while ADONA may be less acutely toxic than PFOS or PFOA in rats[7]. Limited information about the occurrence in rivers of these substitutes is available. Emerging PFAAs substituting banned compound as PFOA are nowadays being used along Europe, and concerning levels are found in superficial river waters: GenX has been found in facility's wastewater discharge and immediately downstream from fluorochemical production plants in Europe, Asia and North America [8, 9, 10, 11] but ADONA concentrations remained specially low when found[11]. To the best of our knowledge, there is no evidence of the presence of these compounds in Spanish rivers. Therefore, the main objective of this study was to investigate de occurrence of GenX and ADONA in Spanish surface water, in order to assess the level of substitution of PFOA and PFOS by these replacements.

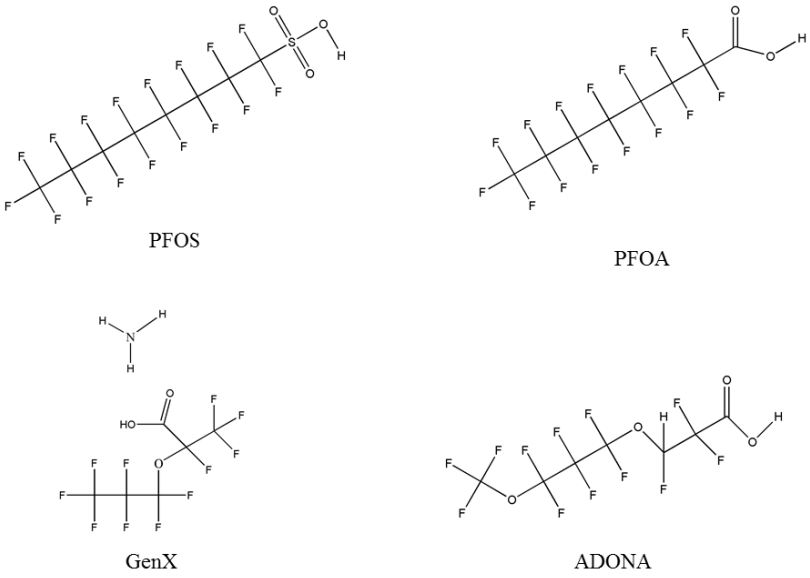

Figure 1. PFOS (CAS nº 1763-23-1), PFOA (CAS nº 335-67-1), GenX (CAS nº 62037-80-3), ADONA (CAS nº 958445-44-8),

Materials and methods

Sampling campaign took place along the Jarama, Manzanares and Henares river basins in Madrid (Spain) during June 2021. Selection of sampling points were conducted considering their proximity to urban and industrial areas (high anthropogenic pressure) and surface water was obtained downstream WWTPs when available (Figure 2). Once in the laboratory 2 L of filtered water samples were spiked with labelled standards (M3 HPFO-DA and

MPFAC-C-ES) and loaded onto an Oasis WAX SPE (6 mL, 500 mg; Waters, Milford, MA, USA) cartridge preconditioned with 12 mL 0.1% NH_4OH in methanol and 12 mL of Milli-Q water. Cartridge was then washed with 12 mL of 25 mM sodium acetate (pH=5) in water and let dry for 1 hour. Next, analytes were eluted from the column using 8 mL of 0.1% NH_4OH in methanol, concentrated to 140 µL under a gentle nitrogen stream and reconstituted with 360 µL methanol and 200 µL of 2 mM ammonium acetate in water containing MPFAC-C-IS as internal standard. Instrumental analysis was carried out on a high-performance liquid chromatography system (Varian HPLC 212) coupled to a triple quadrupole mass spectrometer (Varian 320- MS-TQ) as described by Navarro et al.[12] Aliquots of the sample extracts (20 µL) were injected into a C18 column Polaris 3 C18-A 50 x 2.0 mm (Agilent). The column flow rate was 200 µL/min, and the column temperature was set at 40 ºC. The mobile phases were 2 mM ammonium acetate in water (solvent A) and methanol (solvent B). Data were collected in the multiple-reaction-monitoring (MRM) mode and mass transitions monitored for GenX and ADONA were 329>285, 285>169 and 377>251 and 377>85, respectively.

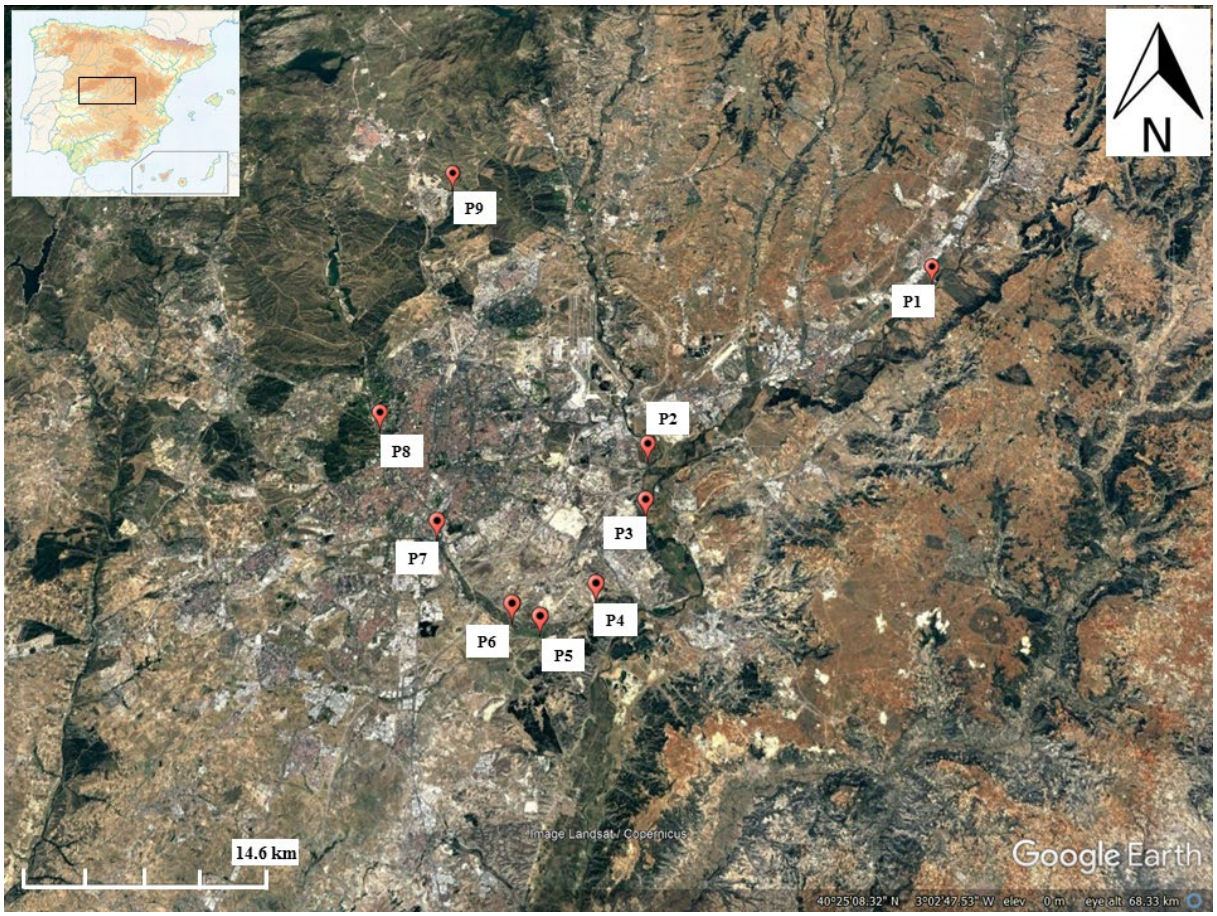

Figure 2. Sampling locations.

Results and discussion

Perfluorobutanesulfonic acid (PFBS), sodium perfluoropentanesulfonate (PFPeS), perfluorohexane sulfonate (PFHxS), perfluoroheptanoic acid (PFHpS), PFOS, perfluorononanesulfonic acid (PFNS), perfluorodecanesulfonic acid (PFDS), perfluorododecanesulfonic acid (PFDoS), perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), undecafluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), PFOA, perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTrDA), perfluorotetradecanoic acid (PFTeDA), perfluorohexadecanoic acid (PFHxDA) and perfluorooctadecanoic acid (PFODA) were analysed. However only PFBS, PHFxS, PFOS, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA and ADONA were quantified above method detection limits in the water samples (Table 1). As mentioned before, sampling points were selected presenting elevated anthropogenic pressure and therefore it was not strange to found higher ∑PFAAs concentrations (56.0 ng/L; median for the sum of PFBS, PFHxS, PFOS,

PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA and PFudA) than those reported in our previous study (13 ng/L)[12] for the same area. This result evidenced that the selection of sampling points was adequate to evaluate PFAAs substitution degree. Concerning emerging PFAAs, only ADONA levels (0.44 and 0.04 ng/L) were quantified in 2 out of 9 samples. Even if there are studies evidencing that GenX was not measurably removed by conventional surface water treatment processes (coagulation, flocculation, sedimentation, filtration, disinfection with chlorine)[9] it was not detected in any sample.

Works studying substitution with GenX and ADONA in The Netherlands' locations close to WWTP drainages found HFPO-A concentrations up to 16 times higher than PFOA, and analysis of Chinese rivers aroused concentrations 42 times greater than the ones on The Netherlands and Germany[8,10]. Sun et al (2016) sampled raw water tap at three WWTP in EEUU, and found up to 4500 ng/L of GenX (631 ng/L average), approximately 8 times the average summed PFCA and PFSA concentrations (79 ng/L)[9]. Pan et al (2017) also found GenX up to 2060 ng/L in Xiaoqing River river, but ADONA, was below the detection limit in all samples.[11] On contrary, Kim et al (2021) neither found GenX or ADONA in Nakdong river (South Korea) and suggested that other short-chain PFAAs (e.g., PFBS, PFHxS, and PFHxA) have been preferred replacements for PFOA and PFOS.[13] In the present study, PFBS (4.72 and 9.20 ng/L, 2/9; n/N, Table 1), PFHxS (3.63 ng/L, 7/9; median, n/N) and PFHxA (10.4 ng/L, 9/9) were quantified at similar levels than PFOA (7.78 ng/L, 9/9) or PFOS (10.4 ng/L, 9/9). Therefore, a similar trend could be hypothesized for the area studied in Spain. Moreover, our results also show elevated concentrations for PFPeA (15.7 ng/L; 7/9), that has been proposed as a PFOA substitute. However this result must be viewed with caution regarding its sampling size. Even assuming that replacement of regulated PFAAs by GenX or ADONA is apparently not happening in a notorious way yet, further research is still needed to understand their behavior in the environment.

Acknowledgements

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Table 1. Concentrations of PFAAs found in Jarama, Manzanares and Henares river basins.

Sample	ADONA	GenX	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFDoS	PFBA	PFPeA
P1	0.44	N.D.	N.D.	N.D.	N.D.	N.D.	4.96	N.D.	N.D.	N.D.	N.D.	7.77
P2	N.D.	N.D.	N.D.	N.D.	8.85	N.D.	24.4	N.D.	N.D.	N.D.	N.D.	N.D.
P3	0.04	N.D.	N.D.	N.D.	9.30	N.D.	16.9	N.D.	N.D.	N.D.	N.D.	11.2
P4	N.D.	N.D.	N.D.	N.D.	3.24	N.D.	10.4	N.D.	N.D.	N.D.	N.D.	12.2
P5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	3.53	N.D.	N.D.	N.D.	N.D.	31.4
P6	N.D.	N.D.	N.D.	N.D.	3.16	N.D.	5.99	N.D.	N.D.	N.D.	N.D.	13.8
P7	N.D.	N.D.	4.72	N.D.	2.88	N.D.	6.19	N.D.	N.D.	N.D.	N.D.	9.91
P8	N.D.	N.D.	9.20	N.D.	3.63	N.D.	10.9	N.D.	N.D.	N.D.	N.D.	N.D.
P9	N.D.	N.D.	N.D.	N.D.	29.5	N.D.	50.5	N.D.	N.D.	N.D.	N.D.	23.7

Sample	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	ΣPFAAs[a]
P1	2.37	3.62	3.95	0.97	1.69	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	25.5
P2	5.88	4.56	8.29	2.24	2.25	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	56.5
P3	6.80	3.52	5.32	1.23	1.67	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	56.0
P4	13.3	6.39	7.88	1.97	2.19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	57.5
P5	18.2	6.15	13.5	2.29	2.62	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	77.7
P6	14.4	6.66	7.78	1.46	1.73	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	54.9
P7	10.4	5.47	6.25	1.06	0.89	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	47.8
P8	3.52	4.17	3.00	0.55	1.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	36.3
P9	24.6	9.38	20.73	2.18	1.55	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	162

[a] sum of PFBS, PFHxS, PFOS, PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA and PFUdA