

# PERFLUORINATED ALKYL SUBSTANCES IN WATER, SEDIMENT AND BIOTA FROM THE JUCAR RIVER (VALENCIA, SPAIN)

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## Introduction

Perfluoroalkyl substances (PFASs) are emerging persistent organic pollutants (POPs) consisted of a long perfluorinated chain — carbon-fluorine bonds are very stable— and a polar head —conferring them tensioactive characteristics and unique properties to make materials stain- and stick-resistant. These compounds have been and are widely used in industry to produce oil/water/color repellency and isolation. Some examples of common PFASs-based products are electrical wire insulation, specialist circuit boards, plumbers tape, waterproof membranes for garments (such as Gore-Tex), surgical implants, dental floss, engine protector additives, non-stick coatings, molded parts and coatings for use in a wide range of chemically hostile environments<sup>1,2</sup>.

PFASs are thermal and chemical stable, highly persistent in the environment, bioaccumulable and toxics for human beings and wildlife<sup>3</sup>. Animal studies of the straight-chain perfluoroalkyl sulfonates (PFAS) and perfluoroalkyl carboxylates (PFAC) have shown that these compounds are well absorbed orally, but poorly eliminated; they are not metabolized, and they undergo extensive uptake from enterohepatic circulation. Perfluorooctane sulfonate (PFOS) and its precursor, Perfluorooctyl sulfonyl fluoride (POSF), were already included as Persistent Organic Pollutants by the Stockholm Convention and their use was prohibited since June 2008 by the European Union<sup>1</sup>.

Although levels of PFASs in the environment have not decreased in the last decade, a clear trend shows that short-chain PFASs are replacing longer ones as they are considered less toxic. This change in the PFASs pattern is due to since 2000, the USA has taken various actions to help minimize the potential impact of PFASs, including the publication of New Use Rules on PFAS chemicals<sup>1,2</sup>.

Over the last decade, advances in analytical techniques have resulted in studies describing the occurrence of PFASs in water (including drinking water), sediments, air, organisms, and even in ice caps<sup>4-7</sup>. In fact, PFASs have been detected in human blood samples throughout the world.

Contamination of aquatic ecosystems with PFASs is from point and non-point sources but always related with industrial or urban areas. However, relatively little was known about sources, distribution and fate among matrices including sediment, soil, water, and biota<sup>6,8</sup>. Understanding the levels, distribution and sources of PFASs to the environment is of great significance to ensure that their environmental levels are compatible with good health of ecosystems and humans.

The aim of the present study was to determine the distribution of 21 PFASs in water, sediments and biota samples collected in the Júcar River (East of Spain) to describe the current quality of this Spanish Mediterranean basin in order to understand the possible effects of global change on ecosystem services. This river basin host large cities (Cuenca, Requena, Valencia) and, until recently, has suffer uncontrolled wastewater discharge of both, industrial and human origin.

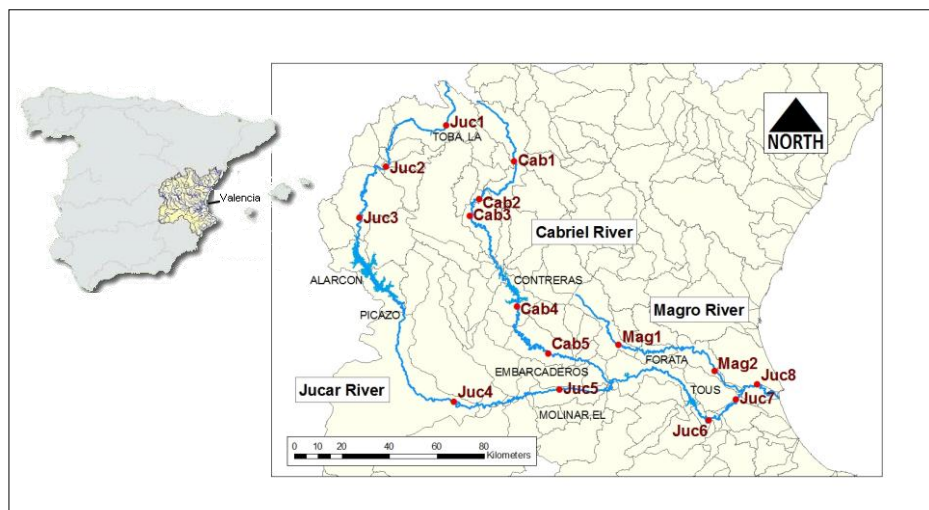
## Materials and methods

Screened PFASs were chosen after a thorough study of the existing literature considering their solubility and their possible presence in the matrices analysed. Twenty-one PFASs were selected including 14 perfluorocarboxylic acids (from 4 to 18 carbons), 6 perfluorosulfonates (from 4 to 10 carbons) and one perfluorosulfonamide.

The Júcar basin was designated as a European Pilot River Basin for the implementation of the WFD and is located in the east of Spain. It has an area of 21,632km<sup>2</sup>, a main stream length of approximately 500 km, and an average precipitation of 510 mm/year. Urban water use is 118.64hm<sup>3</sup>/year for 1,030,979 people, and irrigated

area is 187,855ha, consuming 1,394hm<sup>3</sup>/year. It is a much regulated basin, with a total reservoir capacity of 2,643hm<sup>3</sup>. Main industry located in the basin includes several sectors (automotive, furniture, tiles, etc.).

**Fig.1.** Location of the sampling points at the Jucar River Basin.



Grab water and sediment samples were collected. PFASs were extracted from sediments with acidified methanol by ultrasonication and cleaned up by solid-phase extraction (SPE) and from water by SPE using STRATA X reversed mode cartridges and methanol as eluent<sup>8</sup>. The chromatographic instrument was an HP1200 series LC combined with an Agilent 6410 triple quadrupole (QQQ) mass spectrometer, equipped with an electrospray ionization (ESI) interface working in negative ionization mode.

For fish extraction, the sample was digested using potassium hydroxide in methanol on an orbital shaker at room temperature. Samples were then centrifuged, and supernatants were directly injected into the turbulent flow chromatographic system that uses two columns in tandem for clean-up<sup>9</sup>. The triple quadrupole mass spectrometer Thermo Scientific TSQ Vantage (Thermo Fisher Scientific, San Jose, CA), equipped with a Turbo Ion Spray source was used for analytical purposes.

The recoveries were in the range of 69–110%, 62–103% and 87–110 % for water, sediment and biota with RSDs (%)  $\leq$  20 %. LOQs ranged from 0.01 to 2 ng/L for water, from 0.04 to 8 ng/g for sediments, and from 0.02 to 2.26 pg/ $\mu$ L for biota.

A strict quality control was carried out to check the results. So, every 15 samples analysed a procedural blank and a positive control sample were injected. Each water, sludge and biota samples were analyzed in triplicated and the average concentration is reported. Wherever possible, try to refer to published methods<sup>2</sup>.

## Results and discussion

In terms of detection frequency, most of the PFASs were detected at least once. From the 21 analytes included in this study, 11 were detected in water and sediment and 14 in biota samples. PFOS, perfluoropentonic acid (PFPeA) and the perfluorobutanoic acid (PFBA) were the most frequent, being the sulfonate present in all the biota samples and the acid in all the sediment samples. In fact all samples were contaminated with at least one PFAS.

**Table 1** summarizes the results of the water monitoring. Of the 21 analytes screened, 10 were not detected. Most of the PFASs were found in less of 30% of the samples. However, PFBA, PFPeA and perfluorooctanoic acid (PFOA) showed high frequencies ( $\geq$  50 %). PFBA, perfluorodecanoic acid (PFDA) and PFOS showed concentrations higher than 100 ng/L, as the 644.19 ng/L of PFBA.

**Table 2** shows the concentrations in sediments. Also, in the case of the sediments, 10 compounds were not detected. PFBA, PFPeA, PFOA, perfluorobutane sulfonate (PFBS), PFOS were in more than 50 % of the samples. Concentrations were from 0.05 ng/g d.w. for PFHxs to 29.19 ng/g d.w. for perfluorobutane sulfonate

(PFBS). The partition coefficients of PFASs between sediment and surface water were estimated using the concentration of PFASs in the sediment and in the overlaying water at the same sampling sites always that possible showing an appropriate correlation as previously described<sup>8</sup>.

**Table 1.** Minimum and maximum concentration, mean levels and frequency of PFASs in waters of the Júcar River Basin.

PFASs	Concentration ng/L			Frequency (n)	Frequency (%)
	Min	Max	Mean		
PFBA	5.21	644.19	49.87	9	60
PFPeA	0.08	2.82	0.38	9	60
PFHxA	1.44	18.74	3.82	6	40
PFHpA	0.64	20.14	2.22	6	40
PFOA	0.07	52.15	4.36	8	53
PFNA	0.85	19.8	2.31	4	27
PFDA	0.09	213.01	14.21	3	20
PFUdA	0.62	0.62	0.04	1	7
PFTrDA	0.04	0.04	n.d.*	1	7
PFTeDA	0.03	0.04	0.01	2	13
L-PFHxS	12.07	36.7	3.25	2	13
L-PFOS	0.01	127.98	11.29	6	40

\*n.d. = non-detect

**Table 2.** Minimum and maximum concentration, mean levels and frequency of PFASs in sediments of the Júcar River

PFASs	Concentration ng/g d.w.			Frequency (n)	Frequency (%)
	Min	Max	Mean		
PFBA	2.7	10.67	5.85	15	100
PFPeA	0.4	6.18	0.93	9	60
PFHpA	0.39	1.06	0.14	3	20
PFOA	0.15	6.69	1.32	8	53
i,p-PFNA	1.97	1.97	0.13	1	6.67
PFNA	3.63	3.63	0.24	1	6.67
PFDA	0.37	1.65	0.23	4	26.67
PFTeDA	2.4	4.44	0.46	2	13.33
L-PFBS	2.17	29.18	10.75	14	93.33
L-PFHxS	0.05	0.58	0.06	4	26.67
L-PFOS	0.06	9.83	1.71	10	66.67

**Table 3.** Minimum and maximum concentration, mean levels and frequency of PFASs in biota of the Júcar River

PFASs	Biota Concentration µg/Kg			Frequency (n)	Frequency (%)
	Max	Min	Mean		
PFPeA	10	946	142	13	52
PFHpA	1	111	6	7	28
PFNA	72	72	3	1	4
L-PFBS	0.6	0.6	0.03	1	4
L-PFHxS	0.6	8	1	15	60

**Table 3** outlines the results in biota. PFOA was the prevalent compound, it was found in 56% of the samples and also it was at a higher concentrations ranging from 26 to 151 ng/g wet weight. Other compounds found in the majority of the fish samples were PFOS and PFHxA.

Methodologies used in this research proved to be feasible and efficient ways for systematic PFCs determination in different matrices. All samples with the exception of 3 fish samples had PFCs. Twelve different PFCs were detected in water, 11 in sediment and 5 in biota samples. Perfluoropentanoic acid was the PFCs found at highest concentration in biota (946.44 ng/g ww), perfluorobutane sulfonate in sediment (29.18 ng/g d.w.) and perfluorobutanoic acid in water (644.19) showing the prevalence of short chain PFCs. Despite the fact that production of L-PFOS ceased in 2002, the results of this study indicate that it still exists in the marketplace and is actively used. The calculation of distribution constants (Kd or Koc) in sediment and bioaccumulation factors (BAF) in biota confirms only in part other reported results, probably because there are too many uncontrolled variables in a field study, that can affect in an unexpected way the results

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