Supplementary material

Title

Perfluoroalkyl acids (PFAAs): distribution, trends and aquatic ecological risk assessment in surface water from Tagus River basin (Spain)

Authors

Irene Navarro[a*], Adrián de la Torre[a], Paloma Sanz[a], María de los Ángeles Martínez[a]

[a]Group of Persistent Organic Pollutants. Department of Environment, CIEMAT, Avda. Complutense 40, 28040 Madrid, Spain.

*Corresponding author: Tel: +34 91 346 61 43. Fax: +34 91 346 62 69. E-mail address: i.navarro@ciemat.es (I. Navarro).

Table of contents

S1. Materials and Methods

S1.1. Standards and reagents

EnviCarb cartridges (500 mg, 6 mL) were provided from Sigma-Aldrich (St. Louis, MO, USA) and Oasis WAX cartridges (500 mg, 6 mL) from Waters (Milford, MA, USA).

Other chemicals used as Ammonium acetate, ammonium hydroxide, sodium acetate, acetic acid, methanol, acetonitrile were purchased from Scharlau (Barcelona, Spain).

S1.2. Chemical analysis

Water samples (2 L) filtered by glass fiber filters and spiked with MPFAC-MXA, N-d3-MeFOSA and N-d5-EtFOSA (Wellington Laboratories Inc.,Guelph, Canada) were extracted with Oasis WAX preconditioned with 12 mL of 0.1% ammonium hydroxide in methanol and 12 mL of Milli-Q water. After sample loading, the cartridges were rinsed with 12 mL of 25 mM sodium acetate buffer (pH 4). After drying, the analytes were eluted with 8 mL of 0.1% ammonium hydroxide in methanol and purified with EnviCarb cartridges. The final extracts were concentrated to 140 µL under a gentle nitrogen stream, reconstituted with 240 µL of methanol and 240 µL of 2 mM ammonium acetate in Milli-Q water and spiked with $^{13}C_9$-PFNA solution (Wellington Laboratories Inc.,Guelph, Canada). A 20-µl aliquot of the extract was injected into an ACE C18-PFP (50 x 2.1 mm, 3 µm) analytical column on a Varian HPLC 212 Liquid Chromatograph connected to a Varian 320 MS-TQ mass spectrometer.

S1.3. Calculations and Statistical evaluation

S1.2.1. Calculation of the environmental exposure assessment parameters

The environmental risk in the aquatic ecosystem was conducted following the recommendations of the European Chemicals Bureau at Technical Guidance Document on Risk Assessment (European Commission, 2003) and recommendations of European Chemicals Agency at Guidance on information requirements and chemical safety assessment (ECHA, 2008, 2016a; 2016b).

The predicted environmental concentrations (PEC) in surface water was calculated considering the maximum environmental concentration detected (MEC_{water}), the weight fraction of organic carbon in suspended solids (Foc_{susp}) and the partition coefficient organic carbon-water (K_{oc}) (Di Toro et al., 1991; Von der Ohe et al., 2011; Du et al., 2013).

$$PEC_{water}=\frac{MEC_{water}}{Foc_{susp}\times K_{oc}+1}$$

PEC for the sediment compartment (PEC_{sed}) was derived from the concentration estimated in surface (PEC_{water}), the suspended matter-water partitioning coefficient ($K_{susp\text{-}water}$) and the bulk density of suspended matter (RHO_{susp}).

$$PEC_{sed}=\frac{K_{susp\text{-}water}}{RHO_{susp}}\times PEC_{water}\times 1000$$

The assessment of secondary poisoning via the aquatic food chain ($PEC_{oral,predator\ (Aq)}$) was estimated considering the concentration in water (PEC_{water}), the bioconcentration factor (BCF_{fish}) and biomagnification factor in fish (BMF).

$$PEC_{oral,\ predator\ (Aq)}=PEC_{water}\times BCF_{fish}\times BMF$$

The predicted no effect concentration (PNEC) in water ($PNEC_{water}$), sediment ($PNEC_{sediment}$) and for secondary poisoning of birds and mammals aquatic organisms ($PNEC_{oral}$) was obtained from laboratory toxicity tests (Table S10). In some cases, $PNEC_{sed}$ was derived from $PNEC_{water}$, $K_{susp\text{-}water}$ and RHO_{susp}.

$$PNEC_{sed}=\frac{K_{susp\text{-}water}}{RHO_{susp}}\times PNEC_{water}\times 1000$$

The risk characterization for the surface waters was calculated by dividing the PEC by the PNEC for the single compounds. It is accepted that RCR values higher than 1 represent a significant risk while RCR values lower than 1 are considered negligible risks.

$$RCR=\frac{PEC}{PNEC}$$

Table S1. Concentration of PFAAs (ng/L) in Tagus River in the different sampling points and campaigns.

Location	SC	Sampling Date	Season	FR (m^3/s)	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	ΣPFAAs
P1	1	14/02/2013	Winter	3.3	<0.06	<0.03	1.76	<0.02	1.59	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	3.35
P2	1	10/03/2013	Winter	19	<0.06	<0.03	20.38	<0.02	<0.10	<0.02	<0.05	8.24	0.70	1.25	<0.04	30.57
P3	1	11/03/2013	Winter	56	1.64	1.95	12.34	<0.02	<0.10	<0.02	<0.05	4.97	0.62	0.88	<0.04	22.41
P4	1	28/02/2013	Winter	193	<0.06	<0.03	0.91	<0.02	<0.10	<0.02	<0.05	0.67	<0.02	<0.01	<0.04	1.58
P1	2	23/05/2013	Spring	3.3	<0.06	<0.03	<0.01	<0.02	<0.10	0.09	<0.05	<0.01	<0.02	<0.01	0.95	1.04
P2	2	20/05/2013	Spring	7.7	1.07	9.37	12.26	5.30	<0.10	<0.02	2.44	8.93	1.09	2.22	<0.04	42.68
P3	2	12/05/2013	Spring	26	1.53	6.70	18.21	<0.02	<0.10	<0.02	<0.05	5.77	0.68	0.90	<0.04	33.80
P4	2	30/05/2013	Spring	149	0.37	0.90	1.87	2.69	<0.10	0.60	0.62	1.60	0.30	<0.01	<0.04	8.94
P1	3	29/08/2013	Summer	1.1	<0.06	<0.03	<0.01	<0.02	<0.10	0.09	<0.05	<0.01	<0.02	<0.01	<0.04	0.09
P2	3	27/08/2013	Summer	5.1	2.73	12.37	16.12	<0.02	<0.10	<0.02	1.86	9.37	1.33	<0.01	<0.04	43.78
P3	3	26/08/2013	Summer	17	2.36	5.32	7.50	<0.02	2.41	2.61	1.26	6.53	0.39	<0.01	<0.04	28.39
P4	3	21/08/2013	Summer	156	0.29	0.84	0.97	<0.02	0.31	1.11	0.61	1.27	<0.02	<0.01	<0.04	5.41
P1	4	28/11/2013	Autumn	1.9	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	4	26/11/2013	Autumn	4.2	2.02	5.34	7.77	<0.02	1.71	4.26	1.23	4.17	0.54	<0.01	<0.04	27.05
P3	4	25/11/2013	Autumn	29	1.16	11.46	15.97	<0.02	2.13	<0.02	2.01	5.79	1.61	2.07	0.65	42.85
P4	4	20/11/2013	Autumn	474	<0.06	<0.03	3.08	<0.02	<0.10	1.28	<0.05	1.49	<0.02	0.05	<0.04	5.90
P1	5	13/02/2014	Winter	18.4	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	5	11/02/2014	Winter	61	1.54	5.10	3.76	<0.02	<0.10	<0.02	<0.05	3.52	<0.02	<0.01	<0.04	13.92

P3	5	10/02/2014	Winter	141	<0.06	5.37	4.09	<0.02	<0.10	<0.02	<0.05	3.50	<0.02	<0.01	<0.04	12.96
P4	5	27/02/2014	Winter	757	<0.06	<0.03	1.43	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	1.43
P1	6	22/05/2014	Spring	2.5	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	6	18/05/2014	Spring	4.4	<0.06	<0.03	12.56	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	12.56
P3	6	13/05/2014	Spring	23	<0.06	<0.03	8.60	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	8.60
P4	6	29/05/2014	Spring	147	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P1	7	28/08/2014	Summer	1.3	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	7	27/08/2014	Summer	5.4	<0.06	<0.03	7.88	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	7.88
P3	7	25/08/2014	Summer	20	2.21	7.58	7.05	<0.02	1.04	<0.02	<0.05	5.38	<0.02	<0.01	<0.04	23.25
P4	7	21/08/2014	Summer	194	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P1	8	20/11/2014	Autumn	1.2	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	8	05/11/2014	Autumn	7.7	<0.06	<0.03	34.42	<0.02	<0.10	<0.02	<0.05	11.16	1.71	<0.01	<0.04	47.30
P3	8	06/11/2014	Autumn	35	<0.06	6.64	17.76	<0.02	<0.10	<0.02	<0.05	8.83	1.44	<0.01	<0.04	34.68
P4	8	27/11/2014	Autumn	52	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P1	9	26/02/2015	Winter	3.7	<0.06	<0.03	<0.01	<0.02	<0.10	0.10	<0.05	<0.01	<0.02	<0.01	<0.04	0.10
P2	9	03/02/2015	Winter	28	1.88	<0.03	4.44	<0.02	<0.10	<0.02	<0.05	2.70	<0.02	<0.01	<0.04	9.02
P3	9	05/02/2015	Winter	100	1.87	1.72	5.80	<0.02	<0.10	<0.02	1.05	2.32	<0.02	<0.01	<0.04	12.75
P4	9	12/02/2015	Winter	176	<0.06	<0.03	1.72	<0.02	<0.10	1.12	<0.05	0.39	<0.02	<0.01	0.36	3.60
P1	10	28/05/2015	Spring	0.5	<0.06	<0.03	1.62	<0.02	<0.10	0.88	<0.05	<0.01	<0.02	<0.01	<0.04	2.50
P2	10	10/05/2015	Spring	6.9	<0.06	8.56	4.97	<0.02	<0.10	<0.02	1.58	3.22	0.51	<0.01	<0.04	18.84
P3	10	13/05/2015	Spring	22	<0.06	6.44	5.33	<0.02	2.87	<0.02	2.68	5.22	0.52	<0.01	<0.04	23.07
P4	10	07/05/2015	Spring	31	<0.06	0.94	1.59	<0.02	0.42	1.04	<0.05	1.14	<0.02	<0.01	<0.04	5.13
P1	11	27/08/2015	Summer	1.2	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10

P2	11	17/08/2015	Summer	4.6	3.80	<0.03	7.36	<0.02	2.12	<0.02	1.84	6.03	0.79	1.26	<0.04	23.19
P3	11	06/08/2015	Summer	19	3.26	<0.03	7.38	<0.02	2.21	4.11	1.51	6.05	0.48	0.47	<0.04	25.48
P4	11	18/08/2015	Summer	3.5	<0.06	<0.03	2.00	<0.02	0.79	1.35	<0.05	2.01	<0.02	0.19	<0.04	6.33
P1	12	19/11/2015	Autumn	0.8	<0.06	<0.03	<0.01	<0.02	<0.10	0.07	<0.05	<0.01	<0.02	<0.01	<0.04	0.07
P2	12	16/11/2015	Autumn	5.9	3.03	5.46	8.60	4.02	4.64	5.59	1.86	5.57	0.54	1.11	<0.04	40.41
P3	12	22/11/2015	Autumn	29	1.75	5.10	6.51	<0.02	2.24	2.96	1.66	4.31	0.42	0.59	<0.04	25.54
P4	12	25/11/2015	Autumn	122	0.63	0.58	1.48	<0.02	0.34	1.75	0.51	1.26	0.34	0.43	<0.04	7.31
P1	13	25/02/2016	Winter	5.2	<0.06	<0.03	<0.01	<0.02	<0.10	0.07	<0.05	<0.01	<0.02	<0.01	<0.04	0.07
P2	13	02/02/2016	Winter	6.3	<0.06	4.53	5.20	<0.02	1.89	3.12	1.51	3.97	0.42	1.01	<0.04	21.64
P3	13	24/02/2016	Winter	30	<0.06	5.80	5.61	<0.02	1.74	3.44	1.31	4.09	0.35	0.68	<0.04	23.01
P4	13	10/02/2016	Winter	19	<0.06		0.91	1.11	<0.10	0.35	<0.05	0.73	<0.02	<0.01	<0.04	3.10
P1	14	25/04/2016	Spring	4.7	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	14	19/04/2016	Spring	20	<0.06	3.10	2.53	<0.02	3.06	2.36	1.44	4.07	0.75	0.99	<0.04	18.30
P3	14	02/05/2016	Spring	37	<0.06	<0.03	6.87	<0.02	2.69	2.49	1.29	2.55	0.36	0.60	<0.04	16.85
P4	14	04/05/2016	Spring	320	<0.06	<0.03	<0.01	<0.02	<0.10	0.16	0.31	0.34	<0.02	<0.01	0.30	1.11
P1	15	13/09/2016	Summer	1.1	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	15	26/08/2016	Summer	5.0	3.61	7.05	8.21	<0.02	4.69	<0.02	1.68	5.49	0.75	0.76	<0.04	32.25
P3	15	01/08/2016	Summer	20	5.31	5.66	7.09	4.00	4.28	1.53	2.73	5.35	0.44	0.40	<0.04	36.79
P4	15	24/08/2016	Summer	241	<0.06	1.04	1.41	<0.02	1.04	<0.02	0.90	1.57	<0.02	<0.01	<0.04	5.97
P1	16	28/11/2016	Autumn	1.2	<0.06	<0.03	<0.01	<0.02	<0.10	0.14	<0.05	<0.01	<0.02	<0.01	<0.04	0.14
P2	16	18/11/2016	Autumn	6.8	2.80	6.19	4.61	<0.02	1.22	<0.02	<0.05	3.70	0.48	0.72	<0.04	19.71
P3	16	18/11/2016	Autumn	31	<0.06	<0.03	5.07	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	5.07
P4	16	15/11/2016	Autumn	57	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10

P1	17	27/02/2017	Winter	1.8	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	17	16/02/2017	Winter	31	2.04	<0.03	2.50	<0.02	0.85	<0.02	<0.05	2.30	<0.02	0.37	<0.04	8.05
P3	17	27/02/2017	Winter	40	1.54	2.62	3.76	<0.02	0.90	3.07	<0.05	2.12	<0.02	0.30	<0.04	14.30
P4	17	28/02/2017	Winter	92	<0.06	<0.03	0.63	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	0.63
P1	18	30/05/2017	Spring	1.3	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	18	26/05/2017	Spring	6.3	0.84	3.62	4.33	<0.02	1.35	6.21	0.67	1.81	0.33	0.67	<0.04	19.83
P3	18	26/05/2017	Spring	18	5.24	0.38	3.91	1.84	1.13	0.45	0.87	2.30	0.26	0.36	<0.04	16.75
P4	18	08/06/2017	Spring	40	0.29	<0.03	<0.01	<0.02	0.33	0.25	<0.05	0.59	<0.02	<0.01	<0.04	1.46
P1	19	30/08/2017	Summer	0.03	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	19	30/08/2017	Summer	6.8	1.26	3.48	6.37	<0.02	3.63	8.31	2.87	9.51	2.12	2.65	0.39	40.58
P3	19	17/08/2017	Summer	18	2.05	1.33	3.09	2.17	1.79	1.27	<0.05	2.82	<0.02	<0.01	<0.04	14.52
P4	19	28/08/2017	Summer	21	0.29	<0.03	0.56	<0.02	<0.10	0.15	<0.05	0.88	<0.02	<0.01	<0.04	1.87
P1	20	24/11/2017	Autumn	0.03	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	20	24/11/2017	Autumn	4.0	1.14	4.53	4.49	<0.02	2.43	0.77	0.61	2.14	<0.02	0.43	<0.04	16.55
P3	20	23/11/2017	Autumn	27	1.31	3.40	4.11	<0.02	2.32	1.30	0.67	2.40	<0.02	0.41	<0.04	15.91
P4	20	29/11/2017	Autumn	164	0.94	<0.03	0.86	<0.02	0.49	0.57	0.48	1.20	0.25	<0.01	<0.04	4.78
P1	21	13/02/2018	Winter	0.03	<0.06	<0.03	<0.01	<0.02	<0.10	<0.02	<0.05	<0.01	<0.02	<0.01	<0.04	<0.10
P2	21	23/02/2018	Winter	4.9	1.08	2.90	3.37	<0.02	3.04	<0.02	0.88	2.30	<0.02	0.34	<0.04	13.90
P3	21	01/02/2018	Winter	27	0.78	1.73	2.71	<0.02	1.92	1.49	0.71	2.48	<0.02	0.42	<0.04	12.24
P4	21	13/02/2018	Winter	0.01	0.47	0.41	1.38	<0.02	0.98	0.84	<0.05	1.47	<0.02	<0.01	<0.04	5.55
P1	22	04/06/2018	Spring	4.5	<0.06	<0.03	<0.01	<0.02	<0.10	0.02	<0.05	<0.01	<0.02	<0.01	<0.04	0.02
P2	22	24/05/2018	Spring	7.8	0.99	4.86	5.98	<0.02	2.52	1.99	0.59	3.51	0.59	0.83	0.24	22.09
P3	22	03/05/2018	Spring	40	1.78	3.34	3.44	<0.02	1.49	1.73	0.99	2.23	<0.02	0.38	<0.04	15.39

P4	22	08/05/2018	Spring	192	<0.06	<0.03	0.57	<0.02	0.33	0.39	<0.05	0.59	<0.02	<0.01	<0.04	1.88
P1	23	07/08/2018	Summer	2.0	<0.06	<0.03	<0.01	<0.02	<0.10	0.11	<0.05	<0.01	<0.02	<0.01	<0.04	0.11
P2	23	16/08/2018	Summer	3.3	1.21	4.45	4.25	<0.02	2.27	12.77	1.45	3.67	0.58	0.61	<0.04	31.26
P3	23	28/08/2018	Summer	22	1.45	2.81	3.22	<0.02	1.69	4.97	1.48	2.66	<0.02	0.24	<0.04	18.51
P4	23	22/08/2018	Summer	296	0.29	<0.03	0.77	<0.02	0.50	2.63	0.65	0.94	<0.02	<0.01	<0.04	5.78

PFDS, PFDoA, PFTrDA, PFTeDA, PFHxDA, PFODA, FOSA, N-MeFOSA and N-EtFOSA were not detected in any sample.

SC: Sampling Campaign. FR: Flow Rate. < LOQ: below LOQ.

Table S2. Target PFAA compounds selected in the present study.

Target compounds	**Name**	**Molecular Formula**
Native compounds		
PFBS	Perfluorobutanesulfonic acid	$CF_3(CF_2)_3SO_3H$
PFHxS	Perfluorohexanesulfonic acid	$CF_3(CF_2)_5SO_3H$
PFOS	Perfluorooctanesulfonic acid	$CF_3(CF_2)_7SO_3H$
PFDS	Perfluorodecanesulfonic acid	$CF_3(CF_2)_9SO_3H$
PFBA	Perfluorobutanoic acid	$CF_3(CF_2)_2COOH$
PFPeA	Perfluoropentanoic acid	$CF_3(CF_2)_3COOH$
PFHxA	Perfluorohexanoic acid	$CF_3(CF_2)_4COOH$
PFHpA	Perfluoroheptanoic acid	$CF_3(CF_2)_5COOH$
PFOA	Perfluorooctanoic acid	$CF_3(CF_2)_6COOH$
PFNA	Perfluorononanoic acid	$CF_3(CF_2)_7COOH$
PFDA	Perfluorodecanoic acid	$CF_3(CF_2)_8COOH$
PFUdA	Perfluoroundecanoic acid	$CF_3(CF_2)_9COOH$
PFDoA	Perfluorododecanoic acid	$CF_3(CF_2)_{10}COOH$
PFTrDA	Perfluorotridecanoic acid	$CF_3(CF_2)_{11}COOH$
PFTeDA	Perfluorotetradecanoic acid	$CF_3(CF_2)_{12}COOH$
PFHxDA	Perfluorohexadecanoic acid	$CF_3(CF_2)_{14}COOH$
PFODA	Perfluorooctadecanoic acid	$CF_3(CF_2)_{16}COOH$
FOSA	Perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NH_2$
N-MeFOSA	*N*-methyl perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NHCH_3$
N-EtFOSA	*N*-ethyl perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NHC_2H_5$
Mass labeled internal standards		
[$^{18}O_2$]-PFHxS	Perfluorohexane [$^{18}O_2$]sulfonic acid	$CF_3(CF_2)_5S^{18}O_2{}^{16}OH$
[$^{13}C_4$]-PFOS	Perfluoro[1,2,3,4-$^{13}C_4$]octanesulfonic acid	$CF_3(CF_2)_3(^{13}CF2)_4SO_3H$
[$^{13}C_4$]-PFBA	Perfluoro[$^{13}C_4$]butanoic acid	$^{13}CF_3(^{13}CF_2)_2{}^{13}COOH$
[$^{13}C_2$]-PFHxA	Perfluoro[1,2-$^{13}C_2$]hexanoic acid	$CF_3(CF_2)_3{}^{13}CF_2{}^{13}COOH$
[$^{13}C_4$]-PFOA	Perfluoro[1,2,3,4-$^{13}C_4$]octanoic acid	$CF_3(CF_2)_3(^{13}CF_2)_3{}^{13}COOH$
[$^{13}C_5$]-PFNA	Perfluoro[1,2,3,4,5-$^{13}C_5$]nonanoic acid	$CF_3(CF_2)_3(^{13}CF_2)_4{}^{13}COOH$
[$^{13}C_9$]-PFNA	Perfluoro[1,2,3,4,5-$^{13}C_9$]nonanoic acid	$^{13}CF_3(^{13}CF_2)_7{}^{13}COOH$
[$^{13}C_2$]-PFDA	Perfluoro[1,2-$^{13}C_2$]decanoic acid	$CF_3(CF_2)_7{}^{13}CF_2{}^{13}COOH$

[$^{13}C_2$]-PFUdA	Perfluoro[1,2-$^{13}C_2$]undecanoic acid	$CF_3(CF_2)_8{}^{13}CF_2{}^{13}COOH$
[$^{13}C_2$]-PFDoA	Perfluoro[1,2-$^{13}C_2$]dodecanoic acid	$CF_3(CF_2)_9{}^{13}CF_2{}^{13}COOH$
N-d3-MeFOSA	*N*-methyl-d3-perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NHCD_3$
N-d5-EtFOSA	*N*-ethyl-d5-perfluorooctanesulfonamide	$CF_3(CF_2)_7SO_2NHC_2D_5$

The components of MPFAC-MXA solution are [$^{18}O_2$]-PFHxS, [$^{13}C_4$]-PFOS, [$^{13}C_4$]-PFBA, [$^{13}C_2$]-PFHxA, [$^{13}C_4$]-PFOA, [$^{13}C_5$]-PFNA, [$^{13}C_2$]-PFDA, [$^{13}C_2$]-PFUdA and [$^{13}C_2$]-PFDoA.

Table S3. Recoveries (%) of isotopically labeled surrogate standards in water samples.

Compound	**Recovery (%; mean ± SD)**
[$^{18}O_2$]-PFHxS	85 ± 11
[$^{13}C_4$]-PFOS	88 ± 13
[$^{13}C_4$]-PFBA	64 ± 2
[$^{13}C_2$]-PFHxA	67 ± 3
[$^{13}C_4$]-PFOA	86 ± 7
[$^{13}C_5$]-PFNA	87 ± 10
[$^{13}C_2$]-PFDA	75 ± 5
[$^{13}C_2$]-PFUdA	81 ± 14
[$^{13}C_2$]-PFDoA	79 ± 2
N-d3-MeFOSA	65 ± 2
N-d5-EtFOSA	66 ± 4

Table S4. Limit of quantification (ng/L) in water samples and PFAA concentrations (ng/L) and frequency of detection (%) in blank samples (n=92).

Compound	LOQ (ng/L)	Mean Blank (ng/L) DF (%)
PFBS	0.06	0.02 ± 0.01 (3%)
PFHxS	0.03	0.01 ± 0.01 (3%)
PFOS	0.01	0.01 ± 0.01 (3%)
PFDS	0.01	N.D.
PFBA	0.02	N.D.
PFPeA	0.10	N.D.
PFHxA	0.02	0.81 ± 0.05 (73%)
PFHpA	0.05	N.D.
PFOA	0.01	N.D.
PFNA	0.02	N.D.
PFDA	0.01	0.04 ± 0.02 (10%)
PFUdA	0.04	0.02 ± 0.01 (8%)
PFDoA	0.01	0.02 ± 0.02 (5%)
PFTrDA	0.01	N.D.
PFTeDA	0.02	N.D.
PFHxDA	0.01	N.D.
PFODA	0.01	N.D.
FOSA	0.01	N.D.
***N*-MeFOSA**	0.01	N.D.
***N*-EtFOSA**	0.01	N.D.

LOQ: Limit of quantification; N.D.: not detected; Mean ± standard deviation; DF: detection frequency in blank samples (n=92)

Table S5. Comparison of PFAA concentrations (ng/L) in surface water from European Rivers.

River (Location)	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	FOSA	Σ PFAAs	Reference
Tributaries rivers from Lake Maggiore (Italy)	N.A.	N.A.	N.D.-38.5	N.A.	N.A.	N.A.	0.1-2.3	0.6-15.9	0.2-16.2	N.D.-10.8	0.1-38	N.D.-14.1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Loos et al., 2007
European Rivers (Europe)	N.A.	N.A.	N.A.	N.A.	N.A.	<1.4-32	0.20-6.6	<0.65-200	<0.14-1.50	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	McLachlan et al., 2007
Roter Main (Germany)	N.A.	N.A.	0.8-15	N.A.	N.A.	N.A.	N.A.	0.9-14	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Becker et al., 2008
Weißer Main (Germany)	N.A.	N.A.	<0.03-3.5	N.A.	N.A.	N.A.	N.A.	0.8-1.7	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Becker et al., 2008
Trebgast (Germany)	N.A.	N.A.	1.7-3.3	N.A.	N.A.	N.A.	N.A.	1.0-1.3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Becker et al., 2008
Ebro (Spain)	<0.27	0.40-0.43	1.29-2.47	N.A.	N.A.	<0.87	<0.61-0.72	1.9-1.45	0.36-0.44	<0.82	<0.43	<0.34	N.A.	<0.90	N.A.	N.A.	<0.19	N.A.	Ericson et al., 2008
Cortiella (Spain)	<0.27	<0.18	<0.24	N.A.	N.A.	<0.87	<0.61	<0.22	<0.42	<0.82	<0.43	<0.34	N.A.	<0.90	N.A.	N.A.	<0.19	N.A.	Ericson et al., 2008
Francolí (Spain)	<0.27	0.78	5.88	N.A.	N.A.	<0.87	3.38	24.9	0.64	0.49	<0.43	<0.34	N.A.	<0.90	N.A.	N.A.	0.2	N.A.	Ericson et al., 2008
Po (Italy)	N.A.	N.A.	N.D.-25	N.A.	N.A.	N.A.	N.D.-18	1-1270	N.D.-13	N.A.	N.D.-2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Loos et al., 2008
Elbe (Germany)	0.9-3.4	0.3-1.3	0.5-2.9	N.A.	0.9-3.1	1.6-5.0	0.8-2.4	2.8-9.6	0.2-1.1	0.2-0.7	<0.004-0.1	<0.01-0.1	N.A.	N.A.	N.A.	N.A.	0.1-1	7.6-26.4	Ahrens et al., 2009
European Rivers (Europe)	N.A.	N.A.	39	N.A.	N.A.	4	1	12	2	1	<1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Loos et al., 2009
Rhine (Germany-The Netherlands)	0.59-118	<0.51-14.5	1.41-7.34	<1.60-188	<0.66-9.99	0.62-4.48	<0.12-0.97	0.61-4.07	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	4.08-268	Möller et al., 2010
Rhine-Tributaries (Germany -The Netherlands)	0.22-31.1	<0.51-2.93	0.89-10.1	<1.60-115	<0.66-59.3	<0.25-49.9	<0.12-5.78	0.87-42.1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	6.32-309	Möller et al., 2010
Rhine-Meuse Delta (The Netherlands)	7.33-181	<0.51-9.75	1.07-24.8	5.84-335	1.62-69.5	0.86-17.4	<0.12-4.73	1.92-41.4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	20.8-621	Möller et al., 2010
Muga (Spain)	0.67	0.16	1.4	N.A.	N.A.	N.A.	N.A.	6.17	1.25	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	9.62	Sánchez-Ávila et al., 2010
Fluvià (Spain)	0.09	0.09	1.41	N.A.	N.A.	N.A.	N.A.	1.26	0.23	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	3.07	Sánchez Ávila et al., 2010
Ter (Spain)	0.59	0.6	9.56	N.A.	N.A.	N.A.	N.A.	4.83	0.69	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	16.3	Sánchez Ávila et al., 2010
Besòs (Spain)	0.74	<0.03	7.7	N.A.	N.A.	N.A.	N.A.	8.12	<0.06	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	16.6	Sánchez Ávila et al., 2010
Llobregat (Spain)	0.88	0.64	9.13	N.A.	N.A.	N.A.	N.A.	9.63	1.62	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	21.9	Sánchez Ávila et al., 2010
Ebro (Spain)	<0.07	0.12	1.09	N.A.	N.A.	N.A.	N.A.	0.79	0.23	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	2.24	Sánchez Ávila et al., 2010
Orge (France)	4.4	13.6	17.4	N.D.	8.9	11.3	4.5	9.4	1.3	1.1	0.1	0.1	<0.03	<0.05	N.A.	N.A.	N.A.	N.A.	Labadie and Chevreuil, 2011a
Seine (France)	0.6-2.6	3.9-12.0	9.9-39.7	N.D.	2.3-13.7	3.0-16.0	0.5-5.5	1.1-18.0	0.1-1.2	0.1-1.0	<0.06-0.2	<0.09	<0.08	<0.15	N.A.	N.A.	N.A.	N.A.	Labadie and Chevreuil, 2011b
German River (Germany)	N.D.	0.06-5.6	0.04-4.6	2.4-23	0.76-9.4	0.23-13	0.23-24	0.16-6.5	0.03	0.19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.A.	Llorca et al., 2012
Spanish Rivers (Spain)	N.D.	0.06-37	0.04-2709	2.4-125	0.76-13	0.23-31	0.23-27	0.16-68	0.03-52	0.19-213	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.A.	Llorca et al., 2012
Spanish River (Spain)	N.A.	7.3-8.6	2.4-171	0.8-1.3	N.D.	N.D.	0.9-6.2	0.8-11	N.D.	1.2-1.5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Onghena et al., 2012
L’Albufera Natural Park (Spain)	N.D.-5.50	N.A.	0.94-58.1	N.A.	N.D.-5.40	N.D.-6.90	N.D.-18.4	0.99-120.2	0.02-18.5	N.D.-10.0	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.99-120	Picó et al., 2012a
Llobregat (Spain)	0.41-4.10	14.2-33.2	0.01-2710	0.07-111	0.08-2.50	0.63-25.2	0.63-30.9	0.07-146	0.77-52.4	0.07-4.25	0.09	N.D.	0.03-9.75	N.D.	4.25	N.D.	N.D.	21.3-3130	Campo et al., 2015
Rhine (Germany-The Netherlands)	1.4-40.0	0.8-3.6	<0.001-2.7	0.2-2.7	3.4-10.7	1.8-5.4	1.2-2.9	3.5-7.1	0.1-0.6	0.02-0.3	N.A.	N.D.-0.02	N.A.	N.A.	N.A.	N.A.	N.D.-0.1	15.9-111.7	Heydebreck et al., 2015
Elbe (Germany)	0.8-3.6	0.3-1.4	<0.01-10.5	<0.02-1.9	0.4-4.8	1.5-4.1	<0.18-1.8	0.8-3.6	0.3-1.0	<0.43-2.7	N.D.-1.5	N.D.-1.1	N.A.	N.A.	N.A.	N.A.	N.D.-0.3	4.6-27.2	Heydebreck et al., 2015
Elbe (Germany)	0.24-238	<0.03-1.0	0.26-3.0	<0.14-2.5	<0.05-4.4	0.50-5.2	N.A.	0.78-5.1	0.07-0.43	0.05-1.2	<0.02-0.11	N.A.	N.A.	N.A.	N.A.	N.A.	<0.05-0.51	4.1-249	Zhao et al., 2015
Weser (Germany)	0.75-1.85	0.30-1.22	0.13-2.41	0.55-1.67	0.20-0.96	0.75-5.31	N.A.	0.99-3.13	0.04-0.17	0.01-0.10	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<0.05-0.42	3.79-15.57	Zhao et al., 2015
Jucar (Spain)	N.D.	12.07-36.7	0.01-128	5.21-644	0.08-2.82	1.44-18.7	0.64-20.1	0.07-52.2	0.85-19.8	0.09-213	0.04-0.62	N.D.	0.04	0.03-0.04	N.D.	N.D.	N.D.	21.1-1140	Campo et al., 2016
Guadalquivir (Spain)	15.0-228.3	1.5-88.5	0.01-42.6	8.0-742.9	0.1-67.8	N.D.	0.4-87.4	4.1-188.6	6.8-116.1	1.8-13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.A.	Lorenzo et al., 2016
Ebro (Spain)	N.D.	1.1-5.8	0.1-27.0	9.8-251.3	0.1-12.5	9.6-31.4	13.7-17.2	2.0-125.0	4.8-7.9	0.1-6.5	N.D.	N.D.	N.D.	6.3	N.D.	N.D.	N.D.	N.A.	Lorenzo et al., 2016
The Netherlands River water (The Netherlands)	12-27	1.5-2.2	2.7-7.1	4.1-14	<4-9.2	4.0-6.4	1.5-2.2	2.8-12	0.49-1.0	0.23-0.86	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	36-65	Gebbink et al., 2017
Swedish Rivers (Sweden)	0.030-19	0.051-18	0.040-6.9	0.47-3.7	N.D.	0.51-4.2	0.36-1.7	0.21-4.2	0.090-5.8	0.024-4.4	0.018-1.8	0.016-0.82	N.D.	0.093-1.5	N.D.	N.D.	0.032-0.46	N.A.	Nguyen et al., 2017
English Rivers (England)	N.D.-41.4	N.A.	2.41-23.8	N.A.	N.A.	N.A.	N.A.	2.33-24.6	2.75-32.5	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	Wilkinson et al., 2017
Tagus (Spain)	<0.06-5.3	<0.03-12	<0.01-34	<0.02-5.3	<0.10-4.7	<0.02-13	<0.05-2.9	<0.01-11	<0.02-2.1	<0.01-2.6	<0.04-0.4	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01	<0.37-47	The present study

N.A.: not available. N.D.: not detected.

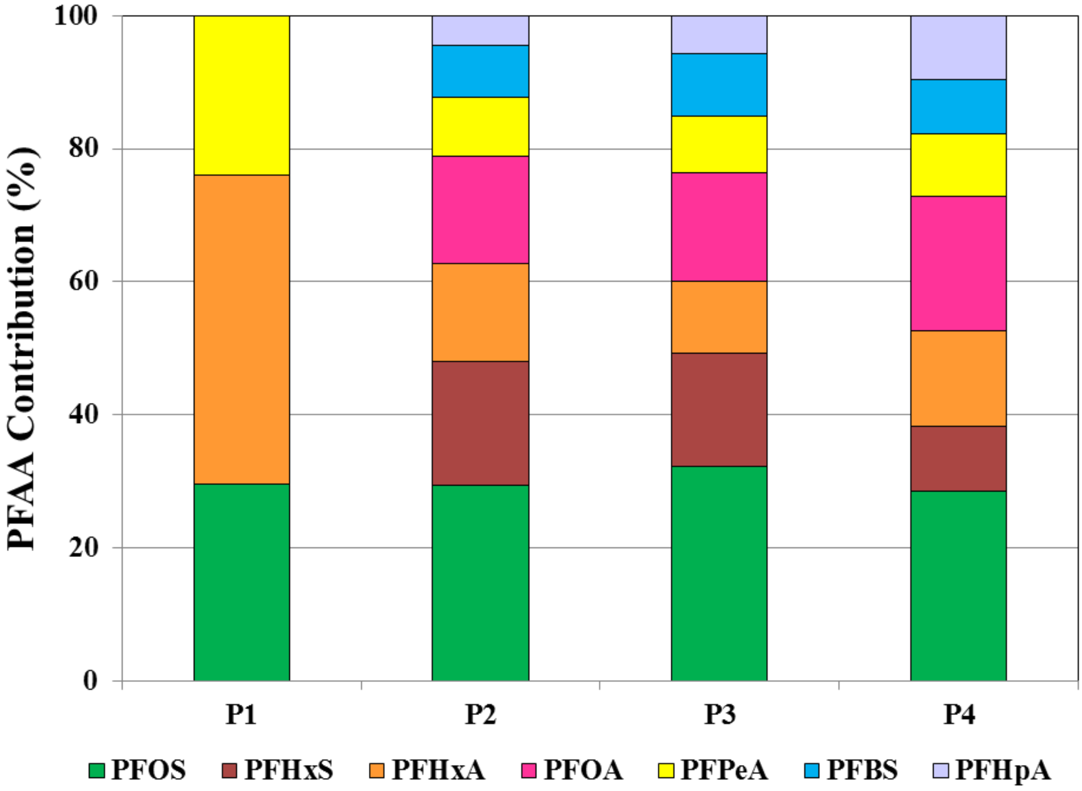

Figure S1. Mean contribution of each compound to the total PFAAs in Tagus River. Only compounds with a detection frequency > 10% and contribution > 5% were represented.

Table S6. Spearman Rho correlation matrix for PFAA concentrations in Tagus River.

	PFBS	**PFHxS**	**PFOS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUdA**	**ΣPFAAs**	**ΣPFSAs**	**ΣPFCAs**	**Flow rate**	**SC^{a}**	**Season**
PFBS	1																
PFHxS	0.408*	1															
PFOS	0.578**	0.784**	1														
PFBA	-0.2	0.886*	0.857*	1													
PFPeA	0.437*	0.529**	0.704**	1.000**	1												
PFHxA	0.345	0.571**	0.681**	0.943**	0.457**	1											
PFHpA	0.634**	0.676**	0.705**	0.6	0.578**	0.659**	1										
PFOA	0.636**	0.786**	0.911**	0.893**	0.753**	0.734**	0.868**	1									
PFNA	0.128	0.495*	0.679**	1.000**	0.574**	0.534*	0.686**	0.779**	1								
PFDA	-0.081	0.567**	0.713**	1.000**	0.456*	0.595**	0.506*	0.777**	0.800**	1							
PFUdA	0.5	0.5	0.8	.	-0.5	-0.3	0.6	0.6	0.5	0.5	1						
ΣPFAAs	0.556**	0.782**	0.837**	0.857*	0.741**	0.898**	0.835**	0.945**	0.748**	0.766**	-0.029	1					
ΣPFSAs	0.616**	0.872**	0.920**	0.821*	0.677**	0.826**	0.739**	0.921**	0.668**	0.686**	-0.087	0.956**	1				
ΣPFCAs	0.458**	0.504**	0.575**	0.857*	0.805**	0.895**	0.796**	0.842**	0.498**	0.626**	-0.086	0.907**	0.830**	1			
Fow rate	-0.338*	-0.301	-0.376**	-0.429	-0.476**	0.181	-0.421*	-0.496**	-0.33	-0.265	-0.543	-0.058	0.2	0.157	1		
SC^{a}	-0.289	-0.348*	-0.381**	-0.559	-0.019	0.104	-0.318	-0.355**	-0.308	-0.402*	-0.829*	-0.135	-0.172	0.045	-0.126	1	
Season	0.125	0.254	0.244	0.524	0.116	0.129	0.055	0.234	0.156	-0.012	0.395	0.249*	0.069	0.098	-0.127	0.073	1

^{a}SC: sampling campaign; * ($p < 0.05$); ** ($p < 0.01$).

Table S7. Estimated mass flow rate (kg/y) of PFAAs in Tagus River watershed.

	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	ΣPFAAs
P1	---	---	---	---	---	0.01 ± 0.005	---	---	---	---	---	0.1 ± 0.1
	---	---	---	---	---	(0.01)	---	---	---	---	---	(0.01)
	---	---	0.03 - 0.2	---	---	0.002 - 0.01	---	---	---	---	---	0.002 - 0.4
P2	0.7 ± 0.8	1.7 ± 2.2	2.5 ± 2.9	---	0.6 ± 0.4	1.0 ± 0.6	0.3 ± 0.2	1.7 ± 1.6	0.2 ± 0.2	0.3 ± 0.2	0.1 ± 0.02	7.0 ± 5.8
	(0.4)	(1.1)	(1.4)	---	(0.4)	(1.0)	(0.3)	(0.9)	(0.1)	(0.2)	(0.1)	(5.1)
	0.1 - 2.9	0.5 - 9.8	0.5 - 12	0.8 - 1.3	0.2 - 1.9	0.1 - 1.8	0.1 - 0.9	0.3 - 6.7	0.1 - 0.5	0.1 - 0.7	0.06 - 0.1	1.4 - 27
P3	2.0 ± 1.3	5.1 ± 5.1	7.8 ± 6.4	---	1.6 ± 0.7	2.0 ± 1.2	1.3 ± 0.8	4.5 ± 3.4	0.6 ± 0.5	0.6 ± 0.5	---	21 ± 13
	(1.5)	(4.2)	(4.7)	---	(1.6)	(2.2)	(1.2)	(3.5)	(0.4)	(0.4)	---	(18)
	0.7 - 5.9	0.2 - 24	1.8 - 22	1.1 - 2.5	0.7 - 3.1	0.3 - 3.8	0.5 - 3.3	1.3 - 16	0.2 - 1.6	0.2 - 1.9	---	5.0 - 57
P4	1.7 ± 1.6	3.9 ± 2.7	8.5 ± 13	---	2.1 ± 2.5	4.9 ± 7.3	3.8 ± 1.9	5.0 ± 5.6	---	---	---	21 ± 23
	(1.6)	(4.1)	(4.8)	---	(1.4)	(2.3)	(3)	(3.6)	---	---	---	(11)
	0.0002 - 4.8	0.9 - 7.9	0.001 - 46	0.7 - 13	0.0004 - 7.9	0.0003 - 25	2.0 - 6.9	0.001 - 22	1.3 - 1.4	0.02 - 1.6	2.0 - 3.0	0.002 - 88
Total	1.4 ± 1.3	3.6 ± 4.2	5.9 ± 8	2.9 ± 4.3	1.3 ± 1.4	2.4 ± 4.5	1.4 ± 1.6	3.6 ± 4	0.5 ± 0.5	0.5 ± 0.5	1 ± 1.2	14 ± 16
	(1.1)	(2.2)	(3.5)	(1.2)	(1.0)	(1.1)	(0.8)	(2.5)	(0.3)	(0.4)	(0.4)	(8.7)
	0.0002 - 5.9	0.22 - 24	0.001 - 46	0.7 - 13	0.0004 - 7.9	0.0003 - 25	0.1 - 6.9	0.001 - 22	0.1 - 1.6	0.02 - 1.9	0.06 - 3.0	0.002 - 88

Mean ± standard deviation, (median), min-max.

Table S8. Comparison of mass flow rates (kg/y) of PFAAs in surface water.

River (Location)	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	Σ PFAAs	Reference
Po (Italy)	---	---	---	---	---	---	---	2600	---	---	---	---	Loos et al., 2008
Elbe (Germany)	---	---	---	---	---	---	---	---	---	---	---	480-540	Ahrens et al., 2009
Danube (Austria)	---	---	186-208	---	---	0-241	84-99	1059-1168	0	0	---	---	Clara et al., 2009
Schwechat (Austria)	---	---	0.16-4.7	---	---	0-0.19	0-0.32	0.04-1.2	0-0.20	0-0.20	---	---	Clara et al., 2009
Liesing (Austria)	---	---	0.29-0.58	---	---	0-0.15	0.04-0.08	0.16-0.34	0.03	0.02	---	---	Clara et al., 2009
Rhine (Germany-The Netherlands)	5100	---	400	10500	300	200	---	200	---	---	---	17000	Möller et al., 2010
Rhine-Meuse Delta (The Netherlands)	90	---	30	50	80	30	---	70	---	---	---	400	Möller et al., 2010
Chao Phraya (Thailand)	---	---	34.1	---	34.4	---	---	104	---	---	---	---	Kunacheva et al., 2011
Seine (France)	---	---	---	---	---	---	---	---	---	---	---	485	Labadie and Chevreuil, 2011b
Hun (China)	---	---	0.57-5.51	---	---	3.01-8.92	0.80-6.12	3.01-15	---	---	---		Sun et al., 2011
L'Albufera Natural Park (Spain)	---	---	---	---	---	---	---	---	---	---	---	5672	Picó et al., 2012a
Hanjiang (China)	---	---	127	---	---	---	---	107	31.4	44.4	19.4	---	Wang et al., 2013
Japanese Rivers (Japan)	---	---	---	---	---	---	---	---	---	---	---	33.5-8700	Takemine et al., 2014
Spanish Rivers (Spain)	0.01-2	0.05-9.4	0.0007-34	0.002-13	0.0003-1.3	0.002-0.8	0.1-26	0.01-21	0.004-0.6	0.003-3.6	0.003	---	Campo et al., 2015
Lambro (Italy)	65	---	46	---	---	---	---	60	---	---	---	---	Castiglioni et al., 2015
Yodo (Japan)	---	---	---	---	---	---	20.6-41.2	48.4-97.0	9.5-19.1	3.7-7.4	2.7-5.3	86.5-173.4	Niisoe et al., 2015
Elbe (Germany)	69 ± 46	19 ± 12	35 ± 14	29 ± 35	31 ± 18	71 ± 37	---	83 ± 36	7.0 ± 3.8	7.7 ± 11	0.7 ± 1.3	335 ± 100	Zhao et al., 2015
Weser (Germany)	---	---	10 ± 7	---	---	---	---	23	---	---	---	102 ± 22	Zhao et al., 2015
Cabriel (Spain)	---	---	---	1.26-1.27	0.02-0.27	0.71-1.63	0.16-0.17	0.01	1.1	---	---	---	Campo et al., 2016
Jucar (Spain)	---	5.09	0.001-17.8	0.97-74.4	0.01-0.18	---	1.82	4	0.22-1.54	0.01-29.6	---	---	Campo et al., 2016
Bothnian Bay Basin (Sweden)	---	---	---	---	---	---	---	---	---	---	---	0.23-42	Nguyen et al., 2017
Bothnian Sea Basin (Sweden)	---	---	---	---	---	---	---	---	---	---	---	6.1-418	Nguyen et al., 2017
Baltic Proper Basin (Sweden)	---	---	---	---	---	---	---	---	---	---	---	0.54-78	Nguyen et al., 2017
Kattegat Basin (Sweden)	---	---	---	---	---	---	---	---	---	---	---	1.5-82	Nguyen et al., 2017
English Rivers (England)	N.D.-0.7	---	0.02-0.8	---	---	---	---	N.D.-0.7	0.02-0.6	---	---	---	Wilkinson et al., 2017
Chinese Rivers (China)	0.73-2400	0.24-21400	2.8-3000	20-5500	4.5-1100	5.8-5900	4.9-1300	20-15500	2.6-710	0.58-330	0.067-150	---	Pan et al., 2018
Tagus (Spain)	0.0002 - 5.9	0.22 - 24	0.001 - 46	0.7 - 13	0.0004 - 7.9	0.0003 - 25	0.1 - 6.9	0.001 - 22	0.1 - 1.6	0.02 - 1.9	0.06 - 3.0	0.002 - 88	The present study

N.D.: not detected.

Table S9. General parameters used in the environmental exposure assessment for the different compartments.

Parameters			
RHO_{water}	Density of the water phase	kg/m^3	1000
RHO_{air}	Density of air	kg/m^3	1.3
RHO_{solid}	Density of the solid phase	kg/m^3	2500
RHO_{susp}	Bulk density of suspended matter	kg/m^3	9250
$Fwater_{susp}$	Fraction water in suspended matter	m^3/m^3	9
$Fair_{susp}$	Fraction air in suspended matter (only relevant for soil)	m^3/m^3	0.2
$Fsolid_{susp}$	Fraction solids in suspended matter	m^3/m^3	0.1
Foc_{susp}	Weight fraction of organic carbon in suspended solids	kg/kg	0.1
R	Gas constant	Pa m^3/ mol k	8.314
TEMP	Temperature at the air-water interface	K	285

Data obtained by ECHA' recommendations (ECHA, 2016a).

Table S10. Specific parameters used in the environmental exposure assessment.

Parameters		**PFBS**	**PFHxS**	**PFOS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUdA**
Log K_{ow}	---	1.82[a]	3.16[a]	4.49[a]	2.14[a]	2.81[a]	3.48[a]	4.14[a]	4.81[a]	5.48[a]	6.15[a]	6.82[a]
K_{oc}	L/kg	85.5[a]	471[a]	2562[a]	21.9[a]	51.3[a]	120[a]	283[a]	655[a]	1538[a]	3610[a]	8474[a]
HENRY	Pa m^3/mol	1.46[a]	40.3[a]	3.19 x 10^{-4}[b]	12.1[a]	63.4[a]	333[a]	1.75 x 10^{3}[a]	2.53[c]	4.84 x 10^{4}[a]	2.30 x 10^{5}[a]	1.34 x 10^{6}[a]
BCF_{fish}	L/kg	3.16[a]	3.16[a]	3.16[a]	3.16[a]	3.16[a]	3.16[a]	3.16[a]	3.16[a]	10[a]	56[a]	56[a]
BMF	---	1	1	2	1	1	1	1	2	10	10	10
$K_{air-water}$	m^3/m^3	6.16 x 10^{-4}	0.02	1.34 x 10^{-7}	5.11 x 10^{-3}	0.03	0.14	0.74	1.10 x 10^{-3}	20.4	97	566
$K_{susp-water}$	m^3/m^3	11.1	20.8	73	9.55	10.3	12.0	16.2	25	51.5	119	334
Kp_{susp}	L/kg	8.55	47.1	256	2.19	5.13	12.0	28.3	65	154	361	847

Log K_{ow}: octanol-water partitioning coefficient; K_{oc}: partition coefficient organic carbon-water; HENRY: Henry's law constant; BCF_{fish}: bioconcentration factor (fish); BMF: biomagnification factor in fish.

$K_{air-water}$: air-water partitioning coefficient; $K_{susp-water}$: suspended matter-water partitioning coefficient; Kp_{susp}: partition coefficient solid-water in suspended matter.

Data obtained by ECHA' recommendations (ECHA, 2016a).

[a] Data obtained by EPISuite 4.1. [b] Brooke et al., 2004. [c] Stemmler and Lammel, 2010.

Table S11. Predicted environmental concentrations in the aquatic environmental ecosystem studied: PEC$_{\text{water}}$ (mg/L), PEC$_{\text{sed}}$ (mg/kg), and PEC$_{\text{oral, predator (Aq)}}$ (mg/kg).

	PFBS	**PFHxS**	**PFOS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUdA**
P1											
PEC$_{\text{water}}$	---	---	6.48 x 10^{-9}	---	---	6.90 x 10^{-8}	---	---	---	---	---
PEC$_{\text{sed}}$	---	---	5.40 x 10^{-8}	---	---	8.98 x 10^{-8}	---	---	---	---	---
PEC$_{\text{oral, predator (Aq)}}$	---	---	4.33 x 10^{-8}	---	---	2.18 x 10^{-7}	---	---	---	---	---
P2											
PEC$_{\text{water}}$	3.98 x 10^{-7}	2.49 x 10^{-7}	1.34 x 10^{-7}	1.66 x 10^{-6}	7.67 x 10^{-7}	9.97 x 10^{-7}	9.91 x 10^{-8}	1.68 x 10^{-7}	1.36 x 10^{-8}	7.18 x 10^{-9}	4.71 x 10^{-10}
PEC$_{\text{sed}}$	4.79 x 10^{-7}	5.60 x 10^{-7}	1.06 x 10^{-6}	1.72 x 10^{-6}	8.53 x 10^{-7}	1.30 x 10^{-6}	1.74 x 10^{-7}	4.60 x 10^{-7}	7.56 x 10^{-8}	9.21 x 10^{-8}	1.70 x 10^{-8}
PEC$_{\text{oral, predator (Aq)}}$	1.26 x 10^{-6}	7.89 x 10^{-7}	8.46 x 10^{-7}	5.26 x 10^{-6}	2.42 x 10^{-6}	3.15 x 10^{-6}	3.13 x 10^{-7}	1.06 x 10^{-6}	1.36 x 10^{-6}	4.04 x 10^{-6}	2.65 x 10^{-7}
P3											
PEC$_{\text{water}}$	5.55 x 10^{-7}	2.29 x 10^{-7}	7.08 x 10^{-8}	1.26 x 10^{-6}	7.02 x 10^{-7}	3.83 x 10^{-7}	9.23 x 10^{-8}	1.33 x 10^{-7}	1.03 x 10^{-8}	5.80 x 10^{-9}	---
PEC$_{\text{sed}}$	6.68 x 10^{-7}	5.14 x 10^{-7}	5.59 x 10^{-7}	1.30 x 10^{-6}	7.80 x 10^{-7}	4.99 x 10^{-7}	1.62 x 10^{-7}	3.64 x 10^{-7}	5.76 x 10^{-8}	7.44 x 10^{-8}	---
PEC$_{\text{oral, predator (Aq)}}$	1.76 x 10^{-6}	7.23 x 10^{-7}	4.48 x 10^{-7}	3.97 x 10^{-6}	2.22 x 10^{-6}	1.21 x 10^{-6}	2.92 x 10^{-7}	8.40 x 10^{-7}	1.03 x 10^{-6}	3.26 x 10^{-6}	---
P4											
PEC$_{\text{water}}$	9.43 x 10^{-8}	2.08 x 10^{-8}	1.20 x 10^{-8}	8.48 x 10^{-7}	1.63 x 10^{-7}	1.99 x 10^{-7}	3.08 x 10^{-8}	3.02 x 10^{-8}	1.94 x 10^{-9}	1.10 x 10^{-9}	4.71 x 10^{-10}
PEC$_{\text{sed}}$	1.13 x 10^{-7}	4.67 x 10^{-8}	9.46 x 10^{-8}	8.75 x 10^{-7}	1.81 x 10^{-7}	2.59 x 10^{-7}	5.39 x 10^{-8}	8.29 x 10^{-8}	1.08 x 10^{-8}	1.42 x 10^{-8}	1.70 x 10^{-8}
PEC$_{\text{oral, predator (Aq)}}$	2.98 x 10^{-7}	6.57 x 10^{-8}	7.57 x 10^{-8}	2.68 x 10^{-6}	5.16 x 10^{-7}	6.30 x 10^{-7}	9.73 x 10^{-8}	1.91 x 10^{-7}	1.94 x 10^{-7}	6.21 x 10^{-7}	2.65 x 10^{-7}
Total (mean)											
PEC$_{\text{water}}$	3.49 x 10^{-7}	1.66 x 10^{-7}	5.59 x 10^{-8}	1.26 x 10^{-6}	5.44 x 10^{-7}	4.12 x 10^{-7}	7.40 x 10^{-8}	1.10 x 10^{-7}	8.61 x 10^{-9}	4.70 x 10^{-9}	4.71 x 10^{-10}
PEC$_{\text{sed}}$	4.20 x 10^{-7}	3.74 x 10^{-7}	4.41 x 10^{-7}	1.30 x 10^{-6}	6.05 x 10^{-7}	5.36 x 10^{-7}	1.30 x 10^{-7}	3.02 x 10^{-7}	4.80 x 10^{-8}	6.02 x 10^{-8}	1.70 x 10^{-8}
PEC$_{\text{oral, predator (Aq)}}$	1.10 x 10^{-6}	5.26 x 10^{-7}	3.53 x 10^{-7}	3.97 x 10^{-6}	1.72 x 10^{-6}	1.30 x 10^{-6}	2.34 x 10^{-7}	6.97 x 10^{-7}	8.16 x 10^{-7}	2.64 x 10^{-6}	2.65 x 10^{-7}

PEC_{water}: Predicted environmental concentration in surface water (mg/L).

PEC_{sed}: Predicted environmental concentration in sediment (mg/kg)

$PEC_{oral,predator\ (Aq)}$: Predicted environmental concentration of contaminant in the food (fish) of fish-eating predators ($mg/kg_{wet\ fish}$).

Table S12. Predicted no effect concentrations in the aquatic environmental ecosystem studied: $PNEC_{water}$ (µg/L), $PNEC_{sed}$ (mg/kg) and $PNEC_{oral}$ (mg/kg).

	$PNEC_{water}$ (µg/L)	**$PNEC_{sed}$** (mg/kg)	**$PNEC_{oral}$** (mg/kg)
PFBS	372[a]	1.164[b]	0.0167[c]
PFHxS	250[d]	1.46[b]	0.0167[c]
PFOS	25[e]	0.067[f]	0.0167[e]
PFBA	110[g]	0.295[b]	0.158[h]
PFPeA	320[d]	0.925[b]	0.158[h]
PFHxA	97[i]	0.328[b]	0.158[h]
PFHpA	20[h]	0.091[b]	0.158[h]
PFOA	20[j]	0.143[b]	0.158[j]
PFNA	100[i]	1.45[b]	0.158[h]
PFDA	10[d]	0.334[b]	0.158[h]
PFUdA	33.84[k]	3.18[b]	0.158[h]

$PNEC_{water}$: Predicted no effect concentration in water (µg/L).

$PNEC_{sed}$: Predicted no effect concentration in sediment (mg/kg).

$PNEC_{oral}$: Predicted no effect concentration for secondary poisoning of birds and mammals (mg/kg).

[a] Negrão et al., 2016. [b] Value calculated from $PNEC_{water}$. [c] Value based on PFOS data. [d] Von der Trenk et al., 2018. [e] Brooke et al., 2004. [f] Møskeland, 2010. [g] Gredelj et al., 2018. [h] Value based on PFOA data. [i] Hoke et al., 2012. [j] Environment Canada, 2012. [k] Picó, 2012b.

Table S13. The risk characterization ratios estimated for freshwater (RCR$_{water}$) and sediment (RCR$_{sed}$) organisms and for fish-eating predators (RCR$_{oral,fish}$) in the different sampling points.

	PFHxS	**PFOS**	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUdA**
P1										
RCR$_{water}$	---	2.74×10^{-7}	---	---	7.12×10^{-7}	---	---	---	---	---
RCR$_{sed}$	---	8.07×10^{-7}	---	---	2.74×10^{-7}	---	---	---	---	---
RCR$_{oral, fish}$	---	2.59×10^{-6}	---	---	1.38×10^{-6}	---	---	---	---	---
P2										
RCR$_{water}$	9.98×10^{-7}	5.35×10^{-6}	1.51×10^{-5}	2.40×10^{-6}	1.03×10^{-5}	4.96×10^{-6}	8.39×10^{-6}	1.36×10^{-7}	7.18×10^{-7}	1.39×10^{-8}
RCR$_{sed}$	3.84×10^{-7}	1.58×10^{-5}	5.82×10^{-6}	9.22×10^{-7}	3.95×10^{-6}	1.91×10^{-6}	3.23×10^{-6}	5.22×10^{-8}	2.76×10^{-7}	5.36×10^{-9}
RCR$_{oral, fish}$	4.72×10^{-5}	5.07×10^{-5}	3.33×10^{-5}	1.53×10^{-5}	2.00×10^{-5}	1.98×10^{-6}	6.72×10^{-6}	8.59×10^{-6}	2.56×10^{-5}	1.68×10^{-6}
P3										
RCR$_{water}$	9.15×10^{-7}	2.83×10^{-6}	1.14×10^{-5}	2.19×10^{-6}	3.95×10^{-6}	4.61×10^{-6}	6.64×10^{-6}	1.03×10^{-7}	5.80×10^{-7}	---
RCR$_{sed}$	3.52×10^{-7}	8.35×10^{-6}	4.39×10^{-6}	8.43×10^{-7}	1.52×10^{-6}	1.77×10^{-6}	2.55×10^{-6}	3.98×10^{-8}	2.23×10^{-7}	---
RCR$_{oral, fish}$	4.33×10^{-5}	2.68×10^{-5}	2.51×10^{-5}	1.40×10^{-5}	7.67×10^{-6}	1.85×10^{-6}	5.31×10^{-6}	6.54×10^{-6}	2.06×10^{-5}	---
P4										
RCR$_{water}$	8.32×10^{-8}	4.79×10^{-7}	7.71×10^{-6}	5.10×10^{-7}	2.06×10^{-6}	1.54×10^{-6}	1.51×10^{-6}	1.94×10^{-8}	1.10×10^{-7}	1.39×10^{-8}
RCR$_{sed}$	3.20×10^{-8}	1.41×10^{-6}	2.96×10^{-6}	1.96×10^{-7}	7.91×10^{-7}	5.92×10^{-7}	5.81×10^{-7}	7.45×10^{-9}	4.25×10^{-8}	5.36×10^{-9}
RCR$_{oral, fish}$	3.94×10^{-6}	4.53×10^{-6}	1.70×10^{-5}	3.27×10^{-6}	3.99×10^{-6}	6.16×10^{-7}	1.21×10^{-6}	1.23×10^{-6}	3.93×10^{-6}	1.68×10^{-6}
Total (mean)										
RCR$_{water}$	6.65×10^{-7}	2.23×10^{-6}	1.14×10^{-5}	1.70×10^{-6}	4.25×10^{-6}	3.70×10^{-6}	5.51×10^{-6}	8.61×10^{-8}	4.70×10^{-7}	1.39×10^{-8}
RCR$_{sed}$	2.56×10^{-7}	6.58×10^{-6}	4.39×10^{-6}	6.54×10^{-7}	1.63×10^{-6}	1.42×10^{-6}	2.12×10^{-6}	3.31×10^{-8}	1.81×10^{-7}	5.36×10^{-9}
RCR$_{oral, fish}$	3.15×10^{-5}	2.12×10^{-5}	2.51×10^{-5}	1.09×10^{-5}	8.25×10^{-6}	1.48×10^{-6}	4.41×10^{-6}	5.45×10^{-6}	1.67×10^{-5}	1.68×10^{-6}

References

Ahrens, L., Felizeter, S., Sturm, R., Xie, Z., Ebinghaus, R., 2009. Polyfluorinated compounds in waste water treatment plant effluents and surface waters along the River Elbe, Germany. Mar. Pollut. Bull. 58, 1326-1333. https://doi.org/10.1016/j.marpolbul.2009.04.028.

Becker, A.M., Gerstmann, S., Frank, H., 2008. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere 72, 115-121. https://doi.org/10.1016/j.chemosphere.2008.01.009.

Brooke, D., Footitt, A., Nwaogu TA., 2004. Environmental risk evaluation report: Perfluorooctanesulphonate (pfos).

Campo, J., Pérez, F., Masiá, A., Picó, Y., Farré, M., Barceló, D., 2015. Perfluoroalkyl substance contamination of the Llobregat River ecosystem (Mediterranean area, NE Spain). Sci. Total Environ. 503-504, 48-57. http://dx.doi.org/10.1016/j.scitotenv.2014.05.094.

Campo, J., Lorenzo, M., Pérez, F., Picó, Y., Farré, M., Barceló, D., 2016. Analysis of the presence of perfluoroalkyl substances in water, sediment and biota of the Jucar River (E Spain). Sources, partitioning and relationships with water physical characteristics. Environ. Res. 147, 503-512. http://dx.doi.org/10.1016/j.envres.2016.03.010.

Castiglioni, S., Valsecchi, S., Polesello, S., Rusconi, M., Melis, M., Palmiotto, M., Manenti, A., Davoli, E., Zuccato, E., 2015. Sources and fate of perfluorinated compounds in the aqueous environment and in drinking water of a highly urbanized and industrialized area in Italy. J. Hazard. Mater. 282, 51-60. http://dx.doi.org/10.1016/j.jhazmat.2014.06.007.

Clara, M., Gans, O., Weiss, S., Sanz-Escribano, D., Scharf, S., Scheffknecht, C., 2009. Perfluorinated alkylated substances in the aquatic environment: An Austrian case study. Water Res. 43, 4760-4768. https://doi.org/10.1016/j.watres.2009.08.004.

Di Toro, D.M., Zarba, C.S., Hansen, D.J., Berry, W.J., Swartz, R.C., Cowan, C.E., Pavlou, S.P., Allen, H.E., Thomas, N.A., Paquin, P.R., 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. Environ. Toxicol. Chem. 10, 1541-1583. https://doi.org/10.1002/etc.5620101203.

Du, X., Li X., Luo, T., Matsuur, N., Kadokami, K., Chen, J., 2013. Occurrence and aquatic ecological risk assessment of typical organic pollutants in water of Yangtze River estuary. Procedia Enviro. Sci. 18, 882 - 889. https://doi.org/10.1016/j.proenv.2013.04.119.

ECHA, 2008. Guidance on Information Requirements and Chemical Safety Assessment. Chapter R.10: Characterisation of Dose [concentration]-response for Environment.

ECHA, 2016a. Guidance on Information Requirements and Chemical Safety Assessment. Chapter 16. Environmental exposure assessment, Version 3.0.

ECHA, 2016b. Guidance on Information Requirements and Chemical Safety Assessment. Part E: Risk Characterisation, Version 3.0.

Environment Canada, 2012. Screening Assessment Report Perfluorooctanoic Acid, its Salts, and its Precursors. Available at: https://www.ec.gc.ca/ese-ees/370AB133-3972-454F-A03A-F18890B58277/PFOA_EN.pdf.

Ericson, I., Nadal, M., van Bavel, B., Lindström, G., Domingo, J.L., 2008. Levels of perfluorochemicals in water samples from Catalonia, Spain: is drinking water a significant contribution to human exposure?. Environ. Sci. Pollut. Res 15, 614-619. https://doi.org/10.1007/s11356-008-0040-1.

European Commission, 2003. Technical Guidance Document on Risk Assessment. Part II. Available at: https://echa.europa.eu/documents/10162/16960216/tgdpart2_2ed_en.pdf.

Gebbink, W.A., van Asseldonk, L., van Leeuwen, S.P.J., 2017. Presence of emerging per- and polyfluoroalkyl substances (PFASs) in river and drinking water near a fluorochemical production plant in the Netherlands. Environ. Sci. Technol. 51, 11057-11065. https://doi.org/10.1021/acs.est.7b02488.

Gredelj, A., Barausse, A., Grechi, L., Palmeri, L., 2018. Deriving predicted no-effect concentrations (PNECs) for emerging contaminants in the river Po, Italy, using three approaches: Assessment factor, species sensitivity distribution and AQUATOX ecosystem modelling. Environ. Inter., 119, 66-78. https://doi.org/10.1016/j.envint.2018.06.017.

Heydebreck,F., Tang, J., Xie, Z., Ebinghaus, R., 2015. Alternative and legacy perfluoroalkyl substances: differences between European and Chinese River/Estuary Systems. Environ. Sci. Technol. 49, 8386-8395. https://doi.org/10.1021/acs.est.5b01648.

Hoke, R.A., Bouchelle, L.D., Ferrell, B.D., Buck, R.C., 2012. Comparative acute freshwater hazard assessment and preliminary PNEC development for eight fluorinated acids. Chemosphere 87, 725-733. https://doi.org/10.1016/j.chemosphere.2011.12.066.

Kunacheva, C., Tanaka, S., Fujii, S., Boontanon, S.K., Musirat, C., Wongwattana, T., 2011. Determination of perfluorinated compounds (PFCs) in solid and liquid phase river water samples in Chao Phraya River, Thailand. Water Sci. Technol. 64.3, 684-692. https://doi.org/10.2166/wst.2011.686.

Labadie, P., Chevreuil, M., 2011a. Partitioning behaviour of perfluorinated alkyl contaminants between water, sediment and fish in the Orge River (nearby Paris, France). Environ. Pollut. 159, 391-397. https://doi.org/10.1016/j.envpol.2010.10.039.

Labadie and Chevreuil, 2011b. Biogeochemical dynamics of perfluorinated alkyl acids and sulfonates in the River Seine (Paris, France) under contrasting hydrological conditions. Environ. Pollut. 159, 3634-3639. https://doi.org/10.1016/j.envpol.2011.07.028.

Llorca M., Farré, M., Picó, Y., Müller, J., Knepper, T.P., Barceló, D., 2012. Analysis of perfluoroalkyl substances in waters from Germany and Spain. Sci. Total Environ. 431, 139-150. https://doi.org/10.1016/j.scitotenv.2012.05.011.

Loos, R., Wollgast, J., Huber, T., Hanke, G., 2007. Polar herbicides, pharmaceutical products, perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), and nonylphenol and its carboxylates and ethoxylates in surface and tap waters around Lake Maggiore in Northern Italy. Anal. Bioanal. Chem. 387, 1469-1478. https://doi.org/10.1007/s00216-006-1036-7.

Loos, R., Locoro, G., Huber, T., Wollgast, J., Christoph, E.H., de Jager, A., Gawlik, B.M., Hanke, G., Umlauf, G., Zaldívar, J., 2008. Analysis of perfluorooctanoate (PFOA) and other perfluorinated compounds (PFCs) in the River Po watershed in N-Italy. Chemosphere 71, 306-313. https://doi.org/10.1016/j.chemosphere.2007.09.022.

Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide survey of polar organic persistent pollutants in European river waters. Environ. Pollut. 157, 561-568. https://doi.org/10.1016/j.envpol.2008.09.020.

Lorenzo, M., Campo, J., Farré, M., Pérez, F., Picó, Y., Barceló, D., 2016. Perfluoroalkyl substances in the Ebro and Guadalquivir river basins (Spain). Sci. Total Environ. 540, 191-199. http://dx.doi.org/10.1016/j.scitotenv.2015.07.045.

McLachlan, M.S., Holmstrom, K.E., Reth, M., Berger, U., 2007. Riverine discharge of perfluorinated carboxylates from the European continent. Environ. Sci. Technol. 41, 7260-7265. https://doi.org/10.1021/es071471p.

Möller, A., Ahrens, L., Surm, R., Westerveld, J., van der Wielen, F., Ebinghaus, R., de Voogt, P., 2010. Distribution and sources of polyfluoroalkyl substances (PFAS) in the River Rhine watershed. Environ. Pollut. 158, 3243-3250. https://doi.org/10.1016/j.envpol.2010.07.019.

Møskeland, T., 2010. Environmental screening of selected ”new” brominated flame retardants and selected polyfluorinated compounds 2009. TA-2625/2010. Available at: http://www.miljodirektoratet.no/old/klif/publikasjoner/2625/ta2625.pdf

Negrão, R., Marinov, D., Loos, R., Napierska, D., Chirico, N., Lettieri, T., 2016. Monitoring-based Exercise: Second review of the priority substances list under the Water Framework Directive. JRC Science for Policy Report.

Nguyen, M.A., Wiberg, K., Ribeli, E., Josefsson, S., Futter, M., Gustavsson, J., Ahrens, L., 2017. Spatial distribution and source tracing of per- and polyfluoroalkyl substances (PFASs) in surface water in Northern Europe. Environ. Pollut. 220, 1438-1446. http://dx.doi.org/10.1016/j.envpol.2016.10.089.

Niisoe, T., Senevirathna, S.T.M.L.D., Harada, K.H., Fujii, Y., Hitomi, T., Kobayashi, H., Yan, J., Zhao, C., Oshima, M., Koizumi, A., 2015. Perfluorinated carboxylic acids discharged from the Yodo River Basin, Japan. Chemosphere 138, 81-88. http://dx.doi.org/10.1016/j.chemosphere.2015.05.060.

Onghena, M., Moliner-Martinez, Y., Picó, Y., Campíns-Falcó, P., Barceló, D., 2012. Analysis of 18 perfluorinated compounds in river waters: Comparison of high performance liquid chromatography-tandem mass spectrometry, ultra-high-performance liquid chromatography-tandem mass spectrometry and capillary liquid chromatography-mass spectrometry. J. Chromatogr. A 1244, 88-97. https://doi.org/10.1016/j.chroma.2012.04.056.

Pan, Y., Zhang, H., Cui, Q., Sheng, N., Yeung, L.W.Y., Sun, Y., Guo, Y., Dai, J., 2018. Worldwide distribution of novel perfluoroether carboxylic and sulfonic acids in surface water. Environ. Sci. Technol. 52, 7621-7629. https://doi.org/10.1021/acs.est.8b00829.

Picó, Y., Blasco, C., Farré, M., Barceló, D., 2012a. Occurrence of perfluorinated compounds in water and sediment of L'Albufera Natural Park (València, Spain). Environ. Sci. Pollut. Res. 19, 946-957. https://doi.org/10.1007/s11356-011-0560-y.

Picó, 2012b. Occurrence of priority and emerging pollutants in watercourses and prediction of future trends in terms of presence and ecotoxicological effects. Report corresponding to the deliverable 4.1 of the Work Package 4: QUALITY (Consolider-Ingenio 2010 CSD2009-00065). Available at: https://www.idaea.csic.es/scarceconsolider/images/deliverable_4.1.pdf

Sánchez-Avila, J., Meyer, J., Lacorte, S., 2010. Spatial distribution and sources of perfluorochemicals in the NW Mediterranean coastal waters (Catalonia, Spain). Environ. Pollut. 158, 2833-2840. https://doi.org/10.1016/j.envpol.2010.06.022.

Stemmler, I., Lammel, G., 2010. Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. Atmos. Chem. Phys. 10, 9965-9980. https://doi.org/10.5194/acp-10-9965-2010.

Sun, H., Li, F., Zhang, T., Zhang, X., He, N., Zhao, L., Song, Q., Sun, L., Sun, T., 2011. Perfluorinated compounds in surface waters and WWTPs in Shenyang, China: Mass flows and source analysis. Water Res. 45, 2011, 4483-4490. https://doi.org/10.1016/j.watres.2011.05.036.

Takemine, S., Matsumura, C., Yamamoto, K., Suzuki, M., Tsurukawa, M., Imaishi, H., Nakano, T., Kondo, A., 2014. Discharge of perfluorinated compounds from rivers and their influence on the coastal seas of Hyogo prefecture, Japan. Environ. Pollut. 184, 397-404. http://dx.doi.org/10.1016/j.envpol.2013.09.016.

Von der Ohe, P.C., Dulio, V., Slobodnik, J., De Deckere, E., Kühne, R., Ebert, R., Ginebreda, A., De Cooman, W., Schüürmann, G., Brack, W., 2011. A new risk assessment approach for the prioritization of 500 classical and emerging organic microcontaminants as potential river basin specific pollutants under the European Water Framework Directive. Sci. Total Environ. 409, 2064-2077. https://doi.org/10.1016/j.scitotenv.2011.01.054.

Von der Trenck, K.T., Konietzka, R., Biegel‐Engler, A., Brodsky, J., Hädicke, A., Quadflieg, A., Stockerl, R., Stahl, T., 2018. Significance thresholds for the assessment of contaminated groundwater: perfluorinated and polyfluorinated chemicals. Environ. Sci. Eur. 30:19. https://doi.org/10.1186/s12302-018-0142-4.

Wang, B., Cao, M., Zhu, H., Chen, J., Wang, L., Liu, G., Gu, X., Lu, X., 2013. Distribution of perfluorinated compounds in surface water from Hanjiang River in Wuhan, China. Chemosphere 93, 468-473. http://dx.doi.org/10.1016/j.chemosphere.2013.06.014.

Wilkinson, J.L., Hooda, P.S., Swinden, J., Barker, J., Barton, S., 2017. Spatial distribution of organic contaminants in three rivers of Southern England bound to suspended particulate material and dissolved in water. Sci. Total Environ. 593-594, 487-497. http://dx.doi.org/10.1016/j.scitotenv.2017.03.167.

Zhao, Z., Xie, Z., Tang, J., Sturm, R., Chen, Y., Zhang, G., Ebinghaus, R., 2015. Seasonal variations and spatial distributions of perfluoroalkyl substances in the rivers Elbe and lower Weser and the North Sea. Chemosphere 129, 118-125. http://dx.doi.org/10.1016/j.chemosphere.2014.03.050.