Supporting information

Approaches and Limitations of using Extractable Organofluorine - Combustion Ion Chromatography to Assess PFAS Total in Drinking Water

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Methanol (LC-MS grade), 25% ammonium hydroxide (analytical reagent grade) were purchased from Fisher Scientific (Pittsburgh, PA, USA). Sodium bicarbonate/Sodium carbonate concentrate, for 20x dilution solution, and ammonium acetate (LC-MS grade), sodium trifluoroacetate and perfluorooctanoic acid (PFOA) were bought from Sigma-Aldrich (St Luis, MO, USA). Isotope-labelled TFA ($^{13}C_2$-TFA) was purchased from Toronto Research Chemicals Inc, (Toronto, Canada). Isotope-labelled perfluorobutanoic acid ($^{13}C_3$-PFBA) was purchased from Wellington Laboratories Inc. (Guelph, Canada). Potassium salts of tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) were obtained from Thermo Fischer Scientific (Waltham, MA, USA).

Instrument settings

Table S1. Multiple reaction monitoring and single ion recording settings.

Name	**Precursor/fragment ion (m/z) (quantification)**	**Cone (V)**	**Col (eV)**	**Precursor/fragment ion (m/z) (qualification)**	**Cone (V)**	**Col (eV)**
TFA	112.9/68.96	26	10			
$13C_2$-TFA	114.9/68.96	26	10			
$13C_3$-PFBA	216/172	20	11			
BF_4^-	87	25	NA	86	25	NA
PF_6^-	145	25	NA			

Table S2. SFC-MS/MS source settings.

Source temperature	150°C
Desolvation temperature	450°C
Desolvation gas flow	650 L/h
Cone gas flow	1 L/h
Capillary voltage	2 kV

Table S3. SFC-MS/MS gradient settings.

Time (min)	**Flow rate (mL/min)**	**Mobile phase A** (%)	**Mobile phase B** (%)
0.00	1.3	95	5
6.00	1.3	60	40
7.00	1.3	60	40
7.10	1.3	95	5
8.00	1.3	95	5

Results from TFA screening in Swedish and Norwegian drinking water samples

Table S4. TFA concentrations measured by direct injection in drinking water collected from Norway and Sweden.

Country	Locations	TFA_{direct} (ng L^{-1})	Locations	TFA_{direct} (ng L^{-1})	Country	Locations	TFA_{direct} (ng L^{-1})
Sweden (n=23)	Lidköping	180	Oskarsham	490	Norway (n=9)	Oslo	230
	Malmö	150	Kalmar	470		Bergen	160
	Luleå	210	Karlskrona	530		Alta	100
	Umeå	96	Landskrona	330		Sorland	92
	Sundsvall	250	Halmstad	180		Trondheim	70
	Gävle	390	Jönköping	92		Alesund	150
	Uppsala S	330	Goteborg	250		Klepp	140
	Uppsala C	390	Mölndal	250		Moss	330
	Åkersberga	410	Helsingborg	380		Kristiansand	210
	Stockholm	420	Borås	350			
	Linköping	230	Östersund	150			
	Visby	720					

Extraction recovery test of selected fluorinated compounds in tap water of HLB and WAX SPE cartridges

The extraction recovery of PF_6^- and BF_4^- was evaluated based on spike tests in tap water collected in the laboratory at Örebro University. Triplicate samples (250 mL) were spiked before extraction, and triplicate samples (250 mL) were spiked after extraction, and were extracted together three replicate each of non-spiked tap water and ultrapure water. Samples spiked before and after extraction were amended with 10 ng each of organic compounds (n=71) with 500 ng of the inorganic compounds PF_6^- and BF_4^-. All compounds were spiked with their respective native standard, except TFA where $13C_2$-TFA was used due to the background of native TFA in the tap water. The EOF extraction methods were based on Metzger et al., 2019[1] (HLB) and Kärrman et al., 2021[2] (WAX) with minor modifications. For WAX extraction (Oasis WAX, 6 cc, 150 mg, 30 μm), cartridges were conditioned by sequentially passing through 4 mL 0.1% ammonium hydroxide in methanol, 4 mL methanol and 4 mL ultrapure water. Before loading at 1 mL/min, the pH of samples was adjusted to either 4 (using acetic acid) or 2 (using nitric acids). Following sample loading, the cartridges were washed with 20 mL 0.01% ammonium hydroxide in ultrapure water, 10 mL ultrapure water and 4 mL ammonium acetate (25 mM, pH 4). For the HLB extractions (Oasis HLB, 6 cc, 150 mg, 30 μm), cartridges were conditioned by 4 mL methanol and 4 mL ultrapure water. Samples were adjusted to pH 2 using nitric acid and loaded at 1 mL/min. Following loading of samples, the cartridges were washed with 4 mL of 10 mM nitric acid solution. All cartridges were dried under vacuum for 30 minutes before elution (WAX: 4 mL 0.1% ammonium hydroxide in methanol, HLB: 4 mL of methanol) into 15 mL polypropylene tubes. The eluent was evaporated to 0.5 mL under a stream of nitrogen and transferred to HPLC vials before injection onto a LC-MS/MS (Acquity UPLC, XEVO TQ-S, Waters Corporation, Milford, MA, USA and SFC-MS/MS (Acquity Ultra Performance Convergence Chromatograph and Xevo TQ-S micro, Waters Corporation, Milford, USA) for analytical determination.

Analytical parameters and instrumental settings of perfluoroalkyl acids and precursors, except cationic/zwitterionic PFAS are referred to Larsson et al., 2026[3]. Analysis of basic pharmaceuticals, a pesticide and cationic/ zwitterionic PFAS were performed using an in-house method using SFC-MS/MS in electrospray ionization (ESI) positive mode. In short,

chromatographic separation was conducted using a Torus DEA column (1.7 µm, 3 mm X 100 mm, Waters Corporation Milford, USA) kept at 60 C. Mobile phase consisted of carbon dioxide (A) and 0.1% ammonium hydroxide in methanol (B) using a flow rate of 1.3 mL/min. Make up solvent was methanol at 0.1 mL/min continuously. Automated back pressure regulator was set to 1500 psi. Gradient settings can be found in table S5 and settings related to the mass spectrometer can be found in table S6 and S7. Results from instrumental method performance testing are shown in table S8.

Table S5. Chromatographic gradient settings of SFC-MS/MS ESI positive method. Mobile phase A was carbon dioxide and B 0.1% ammonium hydroxide in methanol.

Time (min)	Flow rate (mL/min)	Mobile phase A (%)	Mobile phase B (%)
0	1.3	93	7
3	1.3	80	20
5	1.3	50	50
6	1.3	50	50
6.01	1.3	93	7
7	1.3	93	7

Table S6. Source settings of SFC-MS/MS ESI positive method.

Source temperature	150°C
Desolvation temperature	450°C
Desolvation gas flow	800 L/h
Cone gas flow	1 L/h
Capillary voltage	3.0 kV

Table S7. Compound specific source settings of SFC-MS/MS ESI positive method.

Name	Precursor/fragment ion (m/z) (quantification)	Cone (V)	Col (eV)	Precursor/fragment ion (m/z) (qualification)	Cone (V)	Col (eV)
AP-FHxSA	485.10/85	30	30	485.10/58	30	40
Diflufenican	395.20/266	25	25	395.20/246	25	32
Citalopram	325.20/262	30	20	325.20/109	30	25
Fluoxetine	310.15/40	20	10	310.15/148	20	8
5:3 FTB	414.10/58	30	35	414.10/104	30	30
Enrofloxacin	360.20/342	30	20	360.20/316	30	20
Seproxetine	296.15/30	20	10	296.15/134	20	6
TAmP-FHXSA	499.10/60	25	35	499.10/73	25	35
Celecoxib	382.10/362	20	29	382.10/282	20	35
CMAmP-6:2 FOSA	571.10/58	30	40	571.10/104	25	30
Ciprofloxacin	332.10/314	25	19	332.10/288	25	20

Table S8. Instrumental method performance testing of ESI positive SFC-MS/MS method for the analysis of pharmaceuticals, cationic/zwitterionic PFAS.

Name	RT (min)	Linear range (ng mL^{-1})	Cal. Points	R^2	S/N at lowest cal. point (n=3)	RSD at QL (n=3)
AP-FHxSA	0.72	0.05 - 100	11	0.9965	17	7%
Diflufenican	0.75	0.05 - 100	11	0.9983	10	7%
Citalopram	1.68	0.05 - 100	11	0.9984	28	9%
Fluoxetine	2.31	0.05 - 100	11	0.9995	321	4%
5:3 FTB	2.92	0.05 - 100	11	0.9997	22	11%
Enrofloxacin	3.00	0.2 - 30	7	0.9988	16	16%
Seproxetine	3.25	0.1 - 100	10	0.9990	32	10%
TAmP-FHXSA	3.18	0.05 - 100	11	0.9998	10	9%
Celecoxib	3.35	0.5 - 100	8	0.9993	21	6%
CMAmP-6:2 FOSA	3.86	0.1 - 10	10	0.9998	13	2%
Ciprofloxacin	4.75	5 - 30	4	0.9999	210	3%

Recovery results - solid phase extraction of fluorinated compounds in EOF-CIC methods

Results from recovery tests are found below. Table S9 contains data on the recovery of BF4 and PF6; table S10 contains information on the recovery of certain basic and neutral fluorinated pharmaceuticals (n=6) together with one neutral pesticide. Included for comparison, table S11 shows the recovery of perfluoroalkyl acids and precursors (n=64).

Table S9. Recovery of PF_6^- and BF_4^- in tap water using WAX and HLB extraction protocols modified for EOF analysis. The recovery is displayed in % (standard deviation within parentheses) at 2000 ng L^{-1} (0.25 L).

Name	HLB-EOF	WAX-EOF (pH 4)	WAX-EOF (pH 2)
BF_4^-	<1%	46 (18.6)	5 (0.4)
PF_6^-	12 (2.8)	76 (6.3)	78 (1.7)

Table S10. Recovery of selected pharmaceuticals in tap water using WAX and HLB extraction protocols modified for EOF analysis. Recovery (shown in % and standard deviation within parentheses) at 40 ng L^{-1} (0.25 L).

Name	HLB-EOF	WAX-EOF (pH 4)	WAX-EOF (pH 2)
Seproxetine	105 (2.1)	88 (3.3)	94 (2.0)
Fluoxetine	103 (2.2)	97 (2.4)	98 (3.8)
Citalopram	106 (6.3)	103 (6.2)	99 (5.8)
Ciprofloxacin	108 (4.0)	24 (1.9)	92 (1.5)
Enrofloxacin	100 (2.4)	52 (3.2)	94 (4.7)
Celecoxib	96 (0.4)	97 (2.4)	95 (3.0)
Diflufenican	60 (1.3)	65 (2.5)	68 (0.5)

Table S11. Recovery of selected per-and polyfluoroalkyl acids and precursors in tap water using WAX and HLB extraction protocols modified for EOF analysis. Recovery is shown in % (standard deviation within parentheses) at 40 ng L^{-1} (0.25 L).

Name	HLB-EOF	WAX-EOF (pH 4)	WAX-EOF (pH 2)
TFA	<1%	35 (18.5)	7 (0.8)
PFPrA	10 (2.3)	59 (19.7)	72 (5.1)
PFBA	81 (16.5)	99 (1.0)	100 (1.2)
PFPeA	79 (16.2)	95 (0.8)	100 (2.5)
PFHxA	81 (16.0)	96 (0.2)	103 (3.1)
PFHpA	81 (12.1)	96 (0.5)	100 (2.4)
PFOA	78 (10.6)	94 (0.8)	100 (2.5)
PFNA	74 (7.4)	93 (2.1)	99 (5.3)
PFDA	63 (15.7)	95 (1.7)	93 (9.2)
PFUnDA	61 (10.5)	97 (1.4)	88 (0.6)
PFDoDA	64 (9.0)	99 (1.1)	90 (2.3)
PFTrDA	66 (7.9)	99 (2.8)	91 (3.3)
PFDoDS	72 (7.8)	96 (4.1)	90 (2.6)
PFTDA	71 (10.5)	102 (4.0)	93 (2.7)
PFHxDA	71 (26.1)	106 (7.6)	94 (6.1)
PFOcDA	84 (48.4)	136 (27.4)	99 (14.7)
TFMS	2 (0.1)	77 (9.8)	58 (4.3)
PFEtS	35 (4.4)	98 (2.1)	97 (3.3)
PFPrS	101 (7.7)	98 (2.9)	93 (2.7)
PFBS	98 (3.9)	96 (1.6)	101 (2.2)
PFPeS	99 (2.2)	98 (0.1)	98 (1.2)
PFHxS	101 (2.0)	96 (1.9)	98 (5.3)
PFHpS	98 (3.4)	98 (0.8)	100 (4.1)
PFOS	91 (3.9)	96 (3.3)	97 (9.9)
PFNS	76 (11.8)	96 (3.4)	93 (16.7)
PFDS	77 (8.4)	98 (4.1)	92 (1.9)
FBSA	83 (2.7)	94 (1.4)	98 (2.1)
PFHxSA	75 (6.0)	86 (2.3)	94 (2.2)
PFOSA	62 (23.2)	89 (17.2)	87 (18.8)
MeFBSA	34 (10.2)	46 (17.3)	63 (5.5)
MePFHxSA	25 (16.0)	39 (24.0)	42 (5.9)
N-MeFOSA	14 (5.1)	20 (8.6)	42 (1.5)
N-EtFOSA	13 (5.7)	19 (9.0)	43 (0.8)
N-MeFOSE	44 (2.4)	63 (7.2)	68 (3.2)
N-EtFOSE	50 (3.4)	63 (6.6)	72 (3.9)
N-MeFOSAA	78 (5.7)	91 (1.9)	90 (1.4)
N-EtFOSAA	84 (5.4)	93 (0.6)	91 (2.6)
4:2 FTSA	98 (2.4)	91 (2.8)	101 (2.5)
6:2 FTSA	99 (1.5)	92 (1.8)	104 (2.0)
8:2 FTSA	91 (3.1)	92 (4.8)	97 (8.8)
3:3 FTCA	69 (8.7)	84 (0.3)	95 (1.5)
7:3 FTCA	26 (14.2)	27 (4.9)	54 (7.6)
5:3 FTCA	35 (9.7)	42 (2.4)	69 (3.5)

6:2 FTUCA	31 (12.9)	63 (2.1)	78 (3.2)
8:2 FTUCA	27 (16.8)	35 (1.3)	58 (7.9)
10:2 FTUCA	23 (11.5)	42 (1.3)	56 (1.0)
8:2 PFESA	65 (23.8)	94 (6.4)	96 (34.1)
6:2 PFESA	87 (7.3)	96 (2.3)	81 (25.5)
3.6-OPFHpA	73 (19.2)	98 (0.9)	100 (3.1)
PFEESA	100 (2.5)	97 (0.8)	101 (1.9)
HFPO-DA	80 (13.4)	99 (2.1)	106 (3.5)
PF4OPeA	75 (16.8)	99 (2.1)	98 (3.6)
ADONA	76 (10.2)	96 (1.0)	98 (2.0)
NTF2	4 (5.1)	98 (2.5)	93 (4.0)
PFHxPA	81 (2.8)	81 (2.3)	92 (5.5)
PFDPA	82 (5.1)	93 (2.0)	89 (5.4)
PFOPA	62 (4.3)	73 (0.7)	84 (3.6)
6_6_PFPiA	75 (8.4)	96 (2.6)	92 (1.7)
6_8_PFPiA	69 (18.5)	95 (5.1)	92 (3.3)
8_8_PFPiA	73 (40.6)	119 (17.7)	92 (7.7)
5:3 FTB	104 (4.3)	106 (5.6)	98 (1.3)
AP-FHxSA	105 (4.4)	97 (1.5)	97 (3.5)
TAmP-FHXSA	104 (5.1)	101 (3.4)	99 (2.4)
CMAmP-6:2 FOSA	102 (1.2)	103 (2.5)	84 (0.4)

Example chromatogram of TFA and $^{13}C_2$-TFA in samples and procedural blank

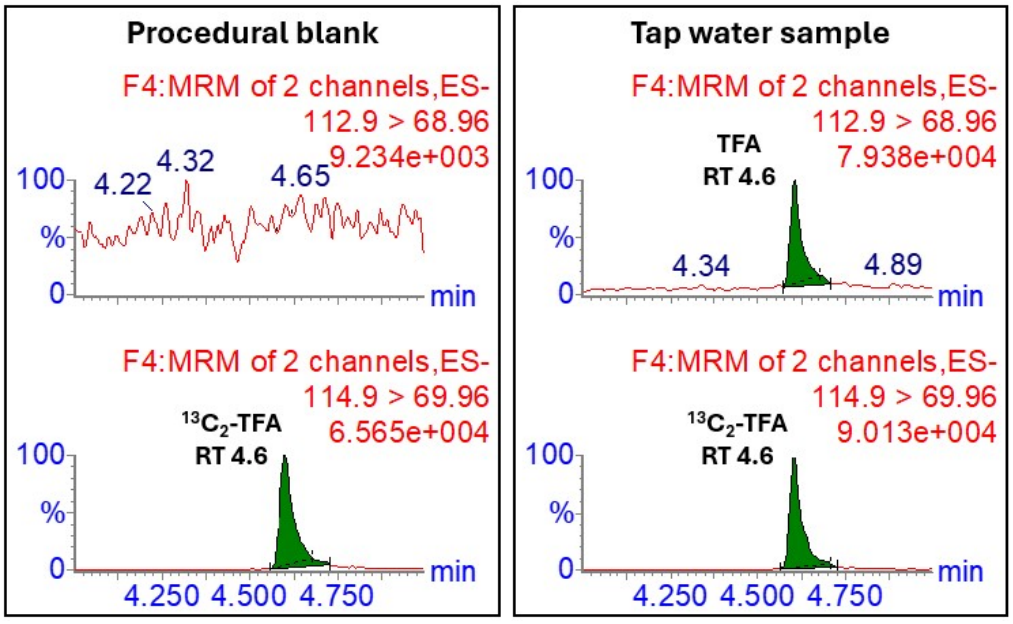

Figure S1. SFC-MS/MS chromatogram of TFA and mass labelled internal standard ($^{13}C_2$-TFA) of typical tap water sample (Frankfurt) together with typical procedural blank.

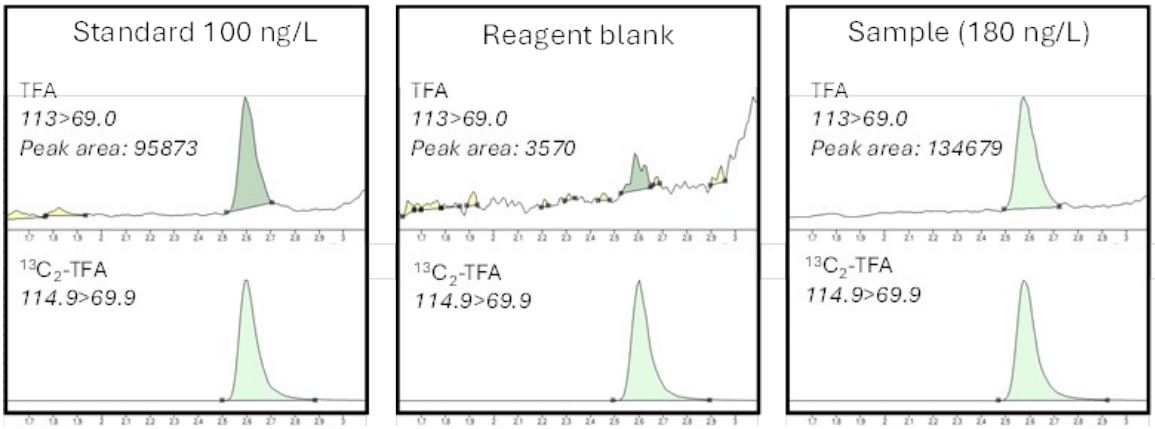

Figure S2. Mixed mode LC-MS-MS chromatograms of TFA and mass labelled internal standard ($^{13}C_2$-TFA) of standard. reagent blank and a sample (Lidköping).

References

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